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Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels

Rotterdam, the Netherlands
October 3-7, 1994

Volume 1

Edited by Harry N. Giles
Office of Technical Management
Deputy Assistant Secretary for Strategic Petroleum Reserve
Assistant Secretary for Fossil Energy

U.S. Department of Energy

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Previous Conferences

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2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, USA, July 29-August 1, 1986. Proceedings published by the Southwest Research Institute, Leo L. Stavinoha, editor; San Antonio, Texas, USA, October 1986.

3rd International Conference on Stability and Handling of Liquid Fuels, London, England, September 13-16, 1988. Proceedings published by the Institute of Petroleum (London), R. W. Hiley, R. E. Penfold, and J. F. Pedley, editors; London, England, November 1988.

4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, USA, November 19-22, 1991. Proceedings published by the U. S. Department of Energy, Harry N. Giles, editor; Washington, DC, USA, 1992.

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Preface

Two measures of the success of an international conference are the number of attendees and the number of countries that they represent. Based on these criteria, the 5th International Conference on Stability and Handling of Liquid Fuels was very successful, with 203 attendees from 28 countries. This is the largest number of countries ever represented at these conferences. These figures are highly gratifying to me, in my role as conference chairman. Because of the continuing recession that began before the 1991 conference, many companies and organizations have curtailed or eliminated attendance at international conferences. These cutbacks have especially affected attendance at specialized conferences such as this.

From the papers presented at this conference, jet fuels and other middle distillates continue to be the subject of considerable study. The microbial aspect of petroleum degradation is another subject that still attracts much attention. The use of computer-based expert systems for monitoring storage stability and predicting when products should be used or replaced is on the increase. The causes of fuel degradation apparently are better understood, and less attention was devoted to this topic than in previous years. Interest continues in quality of refined products stored in strategic stockpiles. Test rigs and simulators are now widely used in evaluating stability. New methods for measurement of deposits formed during degradation have been developed and older methods revised. The effects of metals and heterocompounds on gasoline storage stability also continue to be studied.

A broad topic coming to the forefront is that of environmentally-friendly or *green fuels*. Within the United States, legislative initiatives and an enlightened environmental awareness have resulted in stricter practices at fuel handling and storage facilities. The Clean Air Act Amendments of 1990 are requiring refiners to reformulate their fuels or turn to alternate compositions. For marketing in certain ozone nonattainment areas, gasoline must contain at least 2 percent oxygen, and less benzene and other aromatics than previously allowed. By the year 2000, the entire U.S. gasoline pool may be reformulated. Diesel fuel must have an ultra-low sulfur content, and it is possible that even home heating oil may eventually have to conform to this new standard. Product imports must also meet current environmental and statutory requirements. This is compelling offshore refineries to upgrade their processes to produce cleaner fuels for the U.S. market. Because reformulated fuels have only recently appeared in the marketplace, little is known how many of them will withstand the rigors of handling and storage, or succumb to microbial attack. In Europe as well, changes are taking place in the composition of fuels in response to a growing environmental awareness. Many countries are beginning to adopt more stringent policies regarding fuel composition. The world crude oil stream is getting heavier and higher in sulfur, which is complicating the need to produce cleaner fuels. More severe processing is necessary, therefore, to obtain specification products. Moreover, there is a greater tendency to upgrade the bottom of the barrel to provide more transportation fuels in response to rapid growth in demand. These trends are exacerbating problems with product quality and stability.

We are witnessing one of the most dramatic changes in the composition of fuels in more than 50 years. Consequently, the timing of the 5th conference probably could not have been better. Several papers were presented that discussed various aspects of the new fuels that are appearing. I expect the stability and handling of these "future fuels" will be a major theme of the 6th conference. Whatever their composition, we will continue to face the same problems identified by the National Petroleum Council more than 50 years ago, namely: instability, incompatibility, and contamination.

I thank the following who provided generous support for this conference: U.S. Al-Ghamdi; Chevron; Biodeterioration Control Associates; Ethyl; Fuel Quality Services, Inc.; Fina Nederland; KLM, Royal Dutch Airlines; Nalco/Exxon Energy Chemicals, L.P.; Octel America; Paktank International BV; and Rohm and Haas. The Dutch Ministry of Economic Affairs was the conference host and provided invaluable support to the organizers. I am also grateful to the many people that helped me in organizing this conference. I am especially indebted to Mrs. Shirley Bradicich and Mrs. Jan Tucker of the Coordinating Research Council who so admirably handled many arrangements and administrative details. Finally, I thank everyone that attended the conference. Their interest and support ultimately make these conferences successful.

Harry N. Giles
Conference Chairman

5th International Conference
on Stability and Handling of Liquid Fuels
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OPENING ADDRESS

Mr. Drs. C. W. M. Dessens, Director-General of Energy

Ministry of Economic Affairs, P.O. Box 20101, 2500 EC The Hague, The Netherlands

Ladies and gentlemen, it is my pleasure and honour to welcome all of you in Rotterdam, the Netherlands. I am delighted that your Association has chosen Rotterdam to be the host city for the 5th International Conference on Stability and Handling of Liquid Fuels. It gives you the opportunity to discover the beauty and the importance of a country which is in many ways the gateway to Europe. Geographically a gateway, as the country near the sea, and Rotterdam as the largest sea port of the world. And Schiphol (Amsterdam Airport) as one of the largest airports of Europe. Also economically a gateway because a large part of the traded goods to and from Europe pass through the Netherlands. And last but not least Rotterdam is the 'oil gateway' to Europe. The oil flow through the port of Rotterdam is impressive.

The Netherlands are exporting about three quarters of the amount of oil (products) we are importing. I would like to give you some figures. In 1993 the Netherlands imported 55 million tonnes crude oil and about 32 million tonnes oil products. In that same year we exported 0.8 million tonnes crude and 54 million tonnes oil products. Another 11 million tonnes left the country by bunkering of sea going vessels. To sum up: this means that in 1993 an amount of 86 million tonnes of crude oil and oil products entered this country and an amount of 66 million tonnes left this country. Of course mainly through the port of Rotterdam. As an oil gateway we are not just passing through the oil. The Netherlands are an important refining centre, with 5 refineries producing about 65 million tonnes in 1993. These refineries are highly efficient and are producing under stringent environmental regulations, because we think that high economic standards should be combined with high environmental standards. Together with this enormous crude oil and oil product flow there are large oil storage facilities in Rotterdam and some other parts of the Netherlands (Amsterdam, Flushing). An oil trading centre needs oil storage facilities as a central element of all activities.

There are various companies operating within this business and you have the opportunity to visit a storage location in one of your technical tours. The total storage capacity in the Netherlands is about 31 million cubic metres. Crude oil and oil products are not only stored for Dutch oil companies, but also for foreign companies. And of course the Netherlands National Petroleum Stockpiling Agency uses these facilities to a great extent.

Oil storage has various aspects. I would like to mention five different aspects. The first aspect is the strategic stockpiling. Although the world has dramatically changed within the last 25 years and the working of the oil market has significantly improved, strategic stockpiling will remain an essential element in the energy policy of oil consuming countries. Most of these countries are united in the International Energy Agency (IEA). One of the main tasks of the IEA is to guarantee a coordinated response during an oil supply crisis. In this response the IEA member countries have a shared responsibility. In the end all member countries are willing to share the total amount of oil available to the IEA. Nevertheless, it is obvious that it is in the interest of all nations -both consuming and producing oil- to avoid a supply disruption. The second aspect is a pure economic one: storage is business. The oil industry needs the so called 'working stocks'. This means storage of crude oil to ensure that the refinery can continue the producing process. Storage of product can be important for anticipating seasonal demand changes and other marketing reasons. It is interesting to see that also companies from producing countries -for example Aramco- use the storage facilities in Rotterdam. We regard this integration of producer and consumer markets as valuable. It also stresses the importance of Rotterdam as the 'oil centre' of Europe. The third important aspect of oil storage I would like to touch upon is the environmental impact. As in so many economic activities the impact of the activity on the environment should be minimised. Oil storage in itself is a 'clean' process, with very small effect on the environment. But even there progress is possible. To give you two examples: better storage facilities to protect the environment and the stored products, and advanced techniques to reduce evaporation to prevent spillage. Also the safety aspect should be mentioned. Together with environment, safety is an aspect that cannot and should not be ignored. The storage facilities in the Netherlands belong to the best of the world. The fifth and last aspect that I would like to mention is probably the most important. It is about quality. Looking at the program of this conference I can see that a lot of attention will be paid to the quality of the stored product. The main issue is how to avoid degradation of the stored product. There are of course different techniques to stop or at least slow down this process. And as I am told a lot of progress will still be possible in the future.

Ladies and gentlemen, I am impressed by the amount of different topics and issues you will discuss in the coming days. There are so many different topics and various aspects about the stability and handling of liquid fuels I never knew about. There will be sessions about jet fuel. Attention will be paid to the microbiological aspects of storage. Also there will be a presentation on the long-term and strategic storage and product quality control by predictive systems and methods. Of course there will be attention paid to a lot of other topics. The fact that I did not mention these does not mean that they are not important. It is just that the program is so various.

The Ministry of Economic Affairs is honoured to host this conference and to welcome so many people from so many different countries all together. I am confident that it will be an inspiring conference. I hope that you will enjoy the technical tours and for those of you who have some time left that you enjoy the tourist program. It is a honour to declare the 5th International Conference on Stability and Handling of Liquid Fuels to be opened.

5th International Conference
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COMMERCIAL JET FUEL QUALITY CONTROL

Kurt H. Strauss[A]

Abstract

The paper discusses the purpose of jet fuel quality control between the refinery and the aircraft. It describes fixed equipment, including various types of filters, and the usefulness and limitations of this equipment. Test equipment is reviewed as are various surveillance procedures. These include the Air Transport Association specification ATA 103, the FAA Advisory Circular 150/5230-4, the International Air Transport Association Guidance Material for Fuel Quality Control and Fuelling Service and the Guidelines for Quality Control at Jointly Operated Fuel Systems. Some past and current quality control problems are briefly mentioned.

INTRODUCTION

The history of jet fuel quality control dates back to the introduction of commercial turbine powered aircraft, when it was discovered that both the procedures and equipment commonly used for aviation gasoline were inadequate for the new fuel type. Initially new procedures concentrated on viscosity and density differences to develop longer settling rates in tankage and new types of filters which would remove water as well as particulates. A landmark was set in the early 1960's when an international airlines-fuel supplier conference decided on a maximum free water limit of 30 ppm into aircraft. Over time more subtle, one might almost say insidious, contaminants and problems were identified and have had to be guarded against. One concern carried over from aviation gasoline and very much alive today is the possible contamination with other petroleum products.

The paper describes current equipment used to control the quality of jet fuel between the refinery and the aircraft. It presents summaries of major procedures inside and outside the USA and points out differences, imposed to some extent by differences in airport fuel custody. Although important, only limited reference is made to construction standards which are a separate major subject.

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QUALITY CONTROL EQUIPMENT

DESCRIPTIONS

Fixed equipment

Fixed equipment includes filter-separators, clay filters, other types of filters, monitors or fuses, floating suctions, internal floating roofs and internal coatings.

Filter-separators can be considered the key equipment in jet fuel quality control. They are designed to remove free or suspended water and particulates to lower levels than other equipment. In fact, other filtration equipment is normally used to reduce the work load on filter-separators or to remove materials which might keep filter-separators from doing their job. Filter-separators incorporate two stages of filtration with the first stage called the coalescer stage and the second stage the separator stage. The filtration media in the first stage are layered such that extremely small water droplets are coalesced by a densely packed medium (coated fiberglass) and emerge on the outside of the elements as droplets which are mostly large enough to settle by gravity ahead of the second stage. In order to coalesce the droplets the filtration media are packed tight enough to also collect very fine particulates, therefore the term "filter-coalescer" for this stage. Layers ahead of the coalescing layers selectively remove particulates to keep the coalescing medium from early plugging by solids. The water droplets which are too small to settle are carried by the fuel against the second stage, the separator stage. These hydrophobic elements, usually made of teflon-coated mesh, repel the fine droplets and keep them out of the filter-separator's discharge, thereby allowing these units to furnish clean, dry fuel.

The elements in each stage have a flow rating per unit length, depending on qualification results. The desired flow rating for the entire filter-separator then dictates the total length of elements installed. Element installation may be either vertical or horizontal. The sump between the two stages collects the separated water which is removed either manually or automatically. Element replacement is based on pressure drop, operating time, the cleanliness of the filtered fuel or evidence of surfactant disarming by evaluating daily sump samples. Elements are replaced whenever the maximum allowable limit is reached for one of these parameters. Industry and government specifications, listed in Table 1, govern the performance of these units. Only filter-separators qualified against an agreed-upon specification should be used in jet fuel systems.

Field clay filters have only one purpose, to remove low concentrations of polar materials ("surfactants"). These surfactants which are soluble in both fuel and water can coat the glass fibers and destroy the water-attracting nature of the surfaces in the coalescers and separators, thereby keeping them from coalescing and removing water droplets and effectively disarming the filter-separators. In addition to water, disarmed filter-coalescers will also pass fine solids which would normally be removed. Clay filter elements are filled with calcined Attapulgus clay which attracts and adsorbs polar materials. Refinery or bulk clay filters serve the same purpose, but because of their large volume and low velocities, have much more removal capacity than the smaller field clay units. Clay field units contain stacks of individual elements, the number of elements depending upon the rated flow of the housing. However, unlike filter-separators, clay filters are not governed by industry performance specifications and their ratings are based on hydraulic pressure drop considerations. Clay filters are always placed ahead of filter-separators to protect the filter-separators and to avoid the possibility of clay fines in the filtered fuel.

Another filter type, also known as a prefilter, primarily removes solid particulates ahead of filter-separators or clay units. Their relatively inexpensive paper elements makes them an advantageous way of extending the life of the more expensive filter-separator elements. In addition, haypacks or excelsior filters, ahead of clay filters, can remove large quantities of water which might cause the clay to revert to mud under such wet conditions.

Monitors or fuses are another category of water removal devices. Unlike filter-separators which are designed to continue to operate with fairly high concentrations of water, monitors are designed to shut off fuel flow in the presence of water. Usually this is achieved by a layer of treated paper fibers which swell in the presence of water and block fuel flow. Monitors are used in several configurations. They are available in separate housings to take the place of filter-separators. They can be mounted inside filter-separators in place of the second stage separator elements or they can be a third stage following the normal two stages in a filter-separator. When used as separate units, monitors are changed when reaching a maximum pressure drop or when they have shut off fuel flow. Table 1 lists applicable specifications for these devices.

Other items, which are more in the category of construction materials, contribute to quality control. One widely used piece of equipment, the floating suction, is installed in airport storage tanks. This device is a pipe which pivots at the bottom end, the outlet, so that the top end, supported by floats, can move up and down with the fuel level and take suction near the top fuel surface. Floating suctions reduce the required settling time and assure that fuel is not removed from the bottom of the tank where contamination tends to concentrate. Internal floating roofs with a fixed cover over the tank keep dust out of the fuel and also reduce vapor emissions. Lastly, internally coating the entire airport fuel system with paints such as epoxy enamels has eliminates the generation of rust in these systems. However, eliminating corrosion by the use of copper or copper-containing alloys is not permitted because copper in extremely low concentrations acts as a catalyst which reduces the fuel's resistance to high temperatures in jet engines. Zinc ("galvanizing") is not permitted as an internal surface coating because it prevents rusting by acting as a sacrificial material which ends up in the fuel as insoluble solids. Stainless steel or aluminum are sometimes used as tanks for aircraft fuelers, but care must be taken to avoid salt water contact with the aluminum.

Test Equipment Peculiar to Quality Control

A variety of test equipment is used routinely in jet fuel quality control. Some of it is standardized by ASTM or other authorities, some is not, but all of it is described in ASTM Manual 5,[B],[1]. Some equipment detects water in various forms, some identifies or quantifies solids, some does both. Table 2 lists these tests which are in routine field use and gives references to sources for more information.

For water detection the least refined tests are the white bucket test and water finding paste. In the former a white porcelain-coated or stainless steel bucket is employed to sample a transport compartment or tank water drain to find free water which is concentrated by swirling the bucket contents slowly. Suspended water can be detected by trying to read the small lettering on a coin through some 20 cm of fuel. Dyed fuel such as aviation gasoline or darker colored products such as diesel fuel can be identified by their appearance. Water finding paste turns a bright reddish color when it contacts a water layer in the bottom of a tank or compartment. The paste is normally applied to gaging tape or a gaging stick. The

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[B] Superscript numbers refer to references at end of paper.

length of changed color is a direct measure of the depth of water. However, water finding paste does not react to water suspended in droplet form.

A more sensitive water test is the visual appearance or "clear and bright" test. A sample of product is collected in a clear, one liter bottle and is held against the light. A haze caused by free, undissolved water down to concentrations of 50 ppm can be detected by an experienced operator. Swirling the bottle slowly will concentrate larger water droplets and solid contaminants in the center of the bottle's bottom. A chart with different width black lines is now available as an adjunct to ASTM D 4176 to qualitatively rate the concentration of suspended water.

Several tests identify a suspended water concentration of 30 ppm or greater. As mentioned in the Introduction, such a maximum level is generally acceptable during aircraft loading. Three different tests depend on the color change of a filter or of a powder added to the product. In the Shell Detector test 5 ml of product are drawn into a syringe through a plastic monitor holding a chemically treated filter; 30 ppm or more of water will turn the yellow filter a bright blue-green. This test is now also available with a 10 ml syringe, placing the color change at the 15 ppm free water level. In the Velcon Hydrokit (formerly Exxon Hydrokit) fuel is drawn into a sealed test tube containing a powder. A color change in the powder from a light to a stronger pink again indicates the failing water level of 30 ppm. The Metrocator test rates water content by comparing the concentration of black spots on a special paper in the bottle cap after the sample has been shaken inside the bottle. This test is stated to identify 10 ppm of water or greater.

The most sensitive water test, the AquaGlo, quantitatively measures the fluorescence level of a specially treated filter pad after a 500 ml sample has been pushed through the pad under line pressure. This test will identify free water concentration down to a few ppm.

Depending upon particle size and concentration, different tests for solids are appropriate. For large particles, 1 mm or larger, the white bucket or clear and bright tests are satisfactory. For particulates in the micron sizes, a more elaborate test is needed. In the membrane filtration test 4 L or more of product are filtered through an extremely fine membrane (normally 0.8 μm pore size) under line pressure. The mass of solid particulates can be determined by weighing the filtrate in a laboratory or the filter color can be rated by comparison to a standard chart. Membrane color tends to be most useful for detecting abrupt changes in color and tracking the trend of filter effluent quality over a long period of time. There is no direct relationship between membrane color and weight.

The condition of coalescer elements is rated with a more elaborate technique by removing one filter-coalescer element from the housing and testing its coalescing quality by flowing fuel and water through it in a special single element test rig. Failure of this element to coalesce water is cause for removal of all first stage elements in the parent unit. The second stage teflon-coated elements can be tested by simply flowing water over them and assuring that the water does not wet the elements. Clay filter condition can be checked by MSEP testing or installing a sidestream sensor containing clay in parallel with the clay vessel. Periodically the sensor element is removed and tested for its remaining surfactant absorbency. This information can be used to change clay elements when necessary. Water swells monitor elements and causes an increase in differential pressure and then fuel flow shut-off. Therefore, these elements cannot be performance tested before change out.

LOCATIONS

Fixed Equipment

Filter-separators are normally installed at the end of a terminal fuel system, ahead of the delivery system to the airport. The same installation applies to refinery storage when fuel is delivered from a refinery directly to an airport. Filter-separators are also placed at the airport entrance into the fuel system, out of the fuel storage into airport fuelers or into an underground hydrant system and at the end of the delivery system, immediately ahead of the aircraft. Additional units may be present at the airport or the terminal, but between the refinery and the aircraft jet fuel passes through at least four filter-separators in series.

The installation of other filtration equipment depends heavily on operating experience in a particular system. In the USA clay filter are commonly installed in terminals receiving jet fuel from multi-product pipelines and, to a lesser extent, in terminals supplied by marine transport. Clay filters are seldom installed in airport fuel systems because of the preceding cleanup system in the supplying terminals. Again depending on experience, paper filters may be used in terminals, less frequently at airports. As stated earlier, paper filters are simply a cost reduction item when filter-separator life is too short because of high solids content of the fuel. Outside the USA clay filters are less common, probably because of the lack of major multi-product pipelines, the increased use of coated tankers with compartments segregated to jet fuel and the widespread use of conductivity additive which is removed by clay.

On airports, floating suctions are mandatory for fuel tanks as are internal epoxy coatings for systems built of mild steel. Some companies prefer stainless steel tanks for airport fueler compartments, others do not. Off airports, transport trucks supplying airports do not carry product filters and normally have uncoated interiors. The smaller pipelines from terminals to airports are normally internally coated. The large multi-product lines are not coated and depend on the presence of corrosion inhibitors in other products for rust protection.

Test Equipment

Test equipment location depends upon the specific requirements of quality control procedures discussed in the next section.

QUALITY CONTROL PROCEDURES

GENERAL

For a long time quality control was the responsibility of the fuel supplier who had custody of the fuel up to the aircraft. In some cases certain cleanliness requirements were specified in individual airline contracts, often the result of some specific operating problem. However, quality procedures or cleanliness limits have not been included into commercial industry-wide fuel specifications, in part because differences in fuel custody make a universal approach almost impossible. In addition, as will be seen, detailed procedures can differ significantly because of differing handling experience. However, in more recent times a consolidation of commercial airport procedures has taken place and will be discussed here. All procedures assume that all fuel leaving a refinery fully complies with industry fuel specifications. All control procedures start after that approval in the refinery.

WITHIN THE USA

The responsibility for fuel quality control at airports is one major difference between the USA and the rest of the world because in the USA fuel custody changes at the airport boundary, whereas outside the USA custody remains with the fuel supplier up to the aircraft fuel inlet. In the USA, therefore, airlines handle the fuel on airports, outside the USA the fuel suppliers do. Third party fuel handling agencies, where used, reflect this difference as they are responsible to the airlines in the USA but to fuel suppliers outside the USA.

ATA 103

Under the aegis of the Air Transport Association, US airlines have developed ATA Specification 103, Standards for Jet Fuel Quality Control at Airports[2]. This specification is applied wherever ATA member airlines jointly own or operate the airport fuel system or are supplied by independent airport dealers at smaller airports. Otherwise the specification is not binding on such dealers or other fuel handlers at small airports.

ATA 103 requirements are summarized in Figure 1 which lists the tests and other inspections by location and frequency. (The actual document is some 50 pages long and describes other required inspections and construction details.) Note the emphasis on filter-separator performance which, at a minimum, is checked monthly by membrane and free water tests. However, free water tests are made at least once a day at the fueling vehicle and are also done during every aircraft fueling. Filter-separator and storage tank sumps are drained manually every day to prevent a possible buildup of microbial growth. The manual drain is necessary because automatic drains may not be actuated over a long period of time in a relatively dry system. An important part of the process is the maintenance of written records of tests and inspections, including the storage of membrane filters for visual inspection.

Other Quality Control Procedures

The Federal Aviation Administration has issued an Advisory Circular AC 150/5230-4[3] which lists most of the requirements of ATA 103. However, it is advisory, is specifically aimed at airline operations and does not address smaller airports which do not have airline operations. It also does not contain maximum allowable limits for various quality control parameters such as solids or water content.

The API has issued Bulletin No. 1500 entitled "Storage and Handling of Aviation Fuels at Airports"[4]. This bulletin stresses design considerations and lists recommended inspections but does not contain maximum or minimum limits for fuel quality.

API bulletin No. 1542 [5] contains recommendations for airport equipment marking for fuel identification. Such standard markings are particularly important for airports carrying more than one fuel grade.

The US Air Force has issued a Military Standard, MIL-STD-1548B[6], covering the minimum performance and quality requirements for the delivery and service of fuels and oils under US Government procurement contracts at commercial airports. This document parallels the ATA 103 procedures. In addition the standard covers the addition of and testing for antiicing and conductivity improver additives required in military fuels. (The procedures used by the military in its own systems are not covered by this standard.)

Another area of quality control is the prevention of mixing other petroleum products and jet fuel in transportation systems. Where feasible, marine compartments and transport vehicles are maintained in jet fuel so that mixing does not take place. However, in some situations various products may precede jet fuel. There are no industry standards for such fuel handling. Instead, each individual hauler has to have specific procedures which must be followed for non-segregated operation. These procedures can include draining, flushing, compartment cleaning as well as prohibitions against following certain products such as black fuel oils or lubricating oils.

In one major situation product segregation is impossible. Large multi-product pipelines carry the majority of refined products in the USA from the refinery to distribution terminals. Here quality control depends on large tender sizes, turbulent line flow, product sequencing and careful cutting to minimize product contamination on one hand and product loss due to intermixing on the other. There is no segregation by supplier and each product type meets a common specification. Normally, when product is to be removed into a terminal, withdrawal starts after the leading interface passes and is completed before the trailing interface appears. However, at the end of the pipeline all product must be removed and there product cuts are made to protect the higher quality product. For example, some higher octane gasoline is cut into the lower octane product to protect the octane rating. Similarly, some diesel is cut into the low octane gasoline to protect diesel flash point. In each case the most sensitive property must be protected. The importance of large tenders to minimize product degradation is clear. However, some product loss and interface mixing is unavoidable and disposing of the off-specification product becomes part of the pipeline operating cost.

OUTSIDE THE USA

Joint Operated Systems Guide Lines

As pointed out earlier, fuel handling on airports outside the USA is the responsibility of the fuel suppliers or their agents. Eleven major oil companies have therefore agreed on a system of quality control whenever an airport fuel system contains fuel by more than one supplier. Most of the time such a system is operated by one company under the supervision of a local fuel committee. The Guide Lines are summarized in Figures 2 and 3. One major difference with ATA 103 is the required fuel recertification when fuel is delivered by a non-segregated system. Other differences are relatively minor.

The same group also issues fuel specification guidelines to apply to the same airports. These guidelines are distinct from the quality control guidelines and are a combination of the most stringent requirements of ASTM D 1655, DERD 2494 and the IATA Fuel Guidelines. By combining the requirements of the three major specifications, these guidelines assure the acceptability of jet fuel in most parts of the world.

Other Procedures

In airports not jointly operated, the local fuel supplier must have his own quality control manual which normally becomes part of the fueling contract. Such procedures usually contain the procedures in ATA 103 or the Joint Systems Guidelines as a minimum.

To assist in airline supervision of international airports, IATA has issued fuel quality control and fuelling service guidance material[7]. Unlike ATA 103 this document does not contain acceptable quality control limits, but instead furnishes an airline representative a set of forms to be used when inspecting an airport fuel system.

SUMMARY

The preceding review makes clear the importance of fuel quality control in the commercial aviation system. Effective quality control depends heavily on redundant equipment and testing because otherwise the failure of a single system could have catastrophic consequences. Particularly today, operating economics play a critical part in all operations, but cost cutting in quality control can be a dangerous exercise.

The review also illustrates that there is no single road to heaven in jet fuel quality control and a useful and practical system should be based heavily on operating experience.

Acknowledgements

The assistance of Mr. Rick Waite of Velcon Filters Inc. in furnishing some materials for this paper and its presentation is gratefully acknowledged.

Table 1

Equipment Specifications

Filter-separators		
	Commercial	API 1581[8]
		Group 1 = base fuel only
		Group 2 = base fuel + additives
		Class A = at terminals
		Class B = at airport storage
		Class C = at fueling vehicle
	Military	
	Element performance	MIL-F-8901[9]
	Element design and dimensions	MIL-F-52308[10]
	Housing design (600 gpm unit)	MIL-F-27630[11]
Monitors or fuses	**Commercial**	IP Specification[12]
	Military	MIL-M-81380C[13]
Other filter types		no industry or military specifications

Table 2

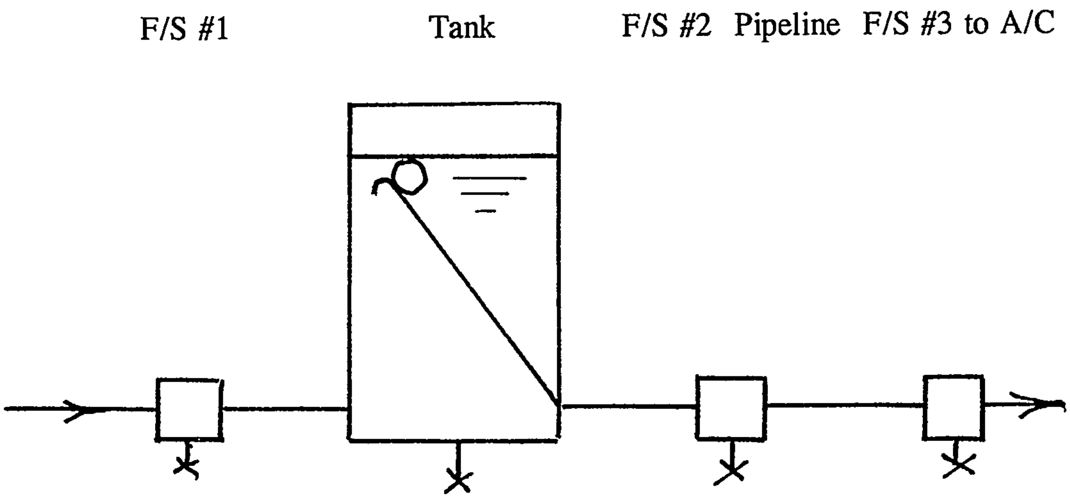
Quality Control Test Equipment

Name	ASTM Standard No.	Manual 5, Page No.
White bucket test	-	7
Water detection paste	-	54
Clear and Bright test	D 4176	7
Shell Detector test	-	47
Velcon Hydrokit	-	48*
Metrocator kit for Undissolved Water	-	50
Aqua-Glo Water Detection Kit	D 3240	52
Membrane filtration test	D 2276	39
Single element coalescer test	-	66
Side-stream clay sensor	D 5000	-

*Listed under Exxon Hydrokit

Figure 1

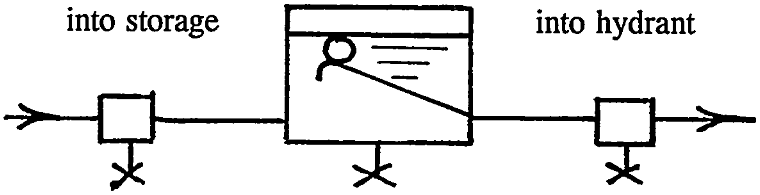
Airport Jet Fuel Quality Control - per ATA 103



Requirements				
Density	Each receipt	-	-	-
Clear & bright	Each receipt	-	-	-
White bucket	Each receipt	-	-	-
sumps	Daily	Daily	Daily	Daily
Press. drop	Each receipt, daily	-	Daily	Daily
Membrane test	P/L receipt	-	Monthly	Monthly
color	3 max/3 gal	-	2 max/3 gal	2 max/3 gal
Free water	P/L receipt	-	Monthly	Monthly
	30 ppm max	-	15 ppm max	15 ppm max
Replace elements	Yearly	-	Yearly	Yearly
Inspect inside	Yearly	Yearly	Yearly	Yearly
Clean	--------------------------as required--------------------------			

Figure 2

Jointly Operated Airport Depots (Storage) - Quality Control

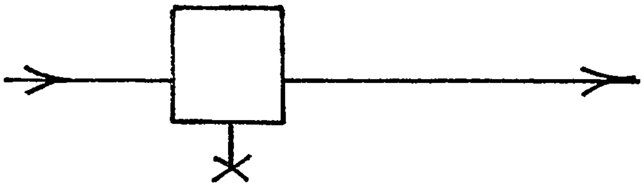


Requirements	Filter-separator into storage	Tank	Filter-separator into hydrant
Each receipt			
Dedicated supply	-	Control check	-
Non-segregated supply	-	Recertification	-
Periodic test	-	6 months	-
Settling time			
Vertical tank	-	2 hours	-
Horizontal tank	-	1 hour	-
Drain water	Daily	Daily	Daily
Pressure drop	Daily	-	Daily
Water check-sump (Chemical test)	Daily	prior to release	Daily
Conductivity	-	Monthly	-
Membrane test			
Sample size	5 L	-	5 L
Colorometric	Monthly	-	Monthly
Gravimetric	3 months	-	3 months
Inspect internally	Yearly	Yearly	Yearly
Element changes	max press. drop	-	max press. drop
	or 24 months	-	or 24 months
Extend with single element test	to 3 years	-	to 3 years
F/S specification, API 1581	Gp II, Class B	-	Gp II, Class B
Clean	-	Every 3 years	-

Figure 3

Jointly Operated into Plane Service - Quality Control

-------Refueller or Hydrant Vehicle-----



	Filter-separator	Hose end
Drain water	Daily	-
Visual test	After start of every pumping After every pumping	-
Chemical water test	After start of every pumping After every pumping	-
Sample retention	24 hours	-
Pressure drop	Daily	-
Membrane test		
Sample size	-	5 L
Colorometric	-	Monthly - 2 max
Gravimetric	-	3 months - 0.2 mg/L max
Inspect internally	Yearly	-
Element changes	Max press. drop or 24 months	-
Extend with single element test	to 3 years	
F/S specification, API 1581	Group II, Class C	-

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THE TRANSITION OF NEW TECHNOLOGY TO SOLVE TODAY'S PROBLEMS

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Extensive research has been conducted in the development of methods to predict the degradation of F-44 in storage. The Low Pressure Reactor (LPR) has greatly enhanced the stability prediction capabilities necessary to make informed decisions concerning aviation fuel in storage. This technique has in the past been primarily used for research purposes. The Naval Air Warfare Center, Aircraft Division, Trenton, NJ, has used this technique successfully to assist the Defense Fuel Supply Center, Cameron Station, Alexandria, VA, in stability assessments of F-44. The High Performance Liquid Chromatography/Electrochemical Detector(HPLC/EC) antioxidant determination technique has also aided in making stability predictions by establishing the amount of inhibitor currently in the product. This paper will address two case studies in which the above new technology was used to insure the rapid detection and diagnosis of today's field and logistic problems.

INTRODUCTION

Due to its unique requirement to store aviation fuel at strategic locations throughout the world, the United States military must be assured the product stored will not significantly degrade prior to usage.

Since 1976, the MIL-T-5624 specification has required the addition of phenolic type antioxidants into fuel to inhibit hydrocarbons from reacting with dissolved oxygen during storage. The antioxidant is added at the refinery prior to exposure to air at a concentration between 17.2 ppm (minimum) and 24 ppm (maximum). Until recently, the refiner added the antioxidant at an acceptable concentration and it was never subsequently measured in the distribution system. A study conducted by the National Institute for Petroleum Energy and Research (NIPER) for the Naval Air Warfare Center, Aircraft Division, Trenton (NAWCADTRN) reported that the degradation process for aviation fuel containing antioxidants and/or any naturally occurring inhibitors begins with the presence of an initial induction period where the formation of significant peroxides is prevented. The induction period is followed by a period of rapid depletion of antioxidant and an increase in peroxide content. The final period is characterized by decreasing peroxide content, darkening in color, and increasing sediment formation. This study also observed that although antioxidant additives will increase the induction period, the free radical chain oxidation mechanism occurring in a reactive fuel will only be delayed.[1] Since the observance of this phenomenon, it has been thought that if the antioxidant concentration is monitored for product in storage, this may provide added information to the stability of the product.

A F-44 Refinery Sampling Survey[2] conducted by the NAWCADTRN indicated that the composition of F-44 has moved from a straight-run distillate to a blend of various process streams which can include significant hydroprocessed material. Since hydroprocessing removes the naturally occurring inhibitors and creates branched chain compounds which have been proven to be extremely susceptible to oxidation, it has become increasingly important to assess a fuel while in storage. In addition, due to the increase hydroprocessing, it is now more than ever necessary for the U.S. military to inject an acceptable concentration of an approved antioxidant to inhibit the free radical initiation of hydrocarbons.

BACKGROUND

From 1982 to 1993 the U.S. Navy conducted an extensive program that addressed many aspects of storage stability. The Program's goal was to develop a reliable, accelerated method for predicting the long-term storage stability of military aviation turbine fuel reserves that could also be used to determine antioxidant effectiveness. The two major test procedures developed in this program were the Low Pressure Reactor (LPR) for predicting the storage stability of fuel and the High Performance Liquid Chromatography/Electrochemical Detector (HPLC/ECD) method for determining antioxidant concentration.

The LPR was developed after considerable research and verification work as a predictive test method to be used for the determination of the stability of aviation fuel.[3] Prior to the LPR, the only test available to measure fuel for their long term oxidative stability was a Go-No-Go test developed by the Coordinating Research Council (CRC).[4] This test was a cumbersome bottle storage test that took three weeks to complete. The LPR improved upon the CRC test and is capable of predicting a fuel's behavior in storage in only 24 to 96 hours of testing.

The HPLC/ECD method for the determination of phenolic antioxidant was developed by Hayes and Hillman[5] and later modified by Vogh.[6] The method was further modified by NAWCADTRN[7] to detect the antioxidants in F-44 regardless of refinery processing technique used. This method consists of an HPLC system coupled with an electrochemical detector. At the current level of antioxidant addition, 17 to 24 mg/L other analytical methods with commonly used detectors did not provide sufficient resolution for identifying antioxidant type or concentration. The addition of the ECD allowed for the identification of the major components contained in all five antioxidants currently approved for use in F-44.

This paper will discuss two case studies in which the LPR and HLPC/ECD test methods were used in the assessment of the stability of F-44 fuel after procurement. The two test methods described and utilized in this study are not included in the MIL-T-5624 specification for procurement and until recently both were used primarily in research studies. However, when used in conjunction with one another a reasonably accurate prediction may be made of a fuel's degradation tendency.

EXPERIMENTAL

The LPR, developed by the Naval Research Laboratory, is a simplified version of the reactor bomb used in the procedure of ASTM D525 (Oxidation Stability of Gasoline, Induction Period Method). After significant evaluation and testing, optimum test conditions of 35 psig air overpressure and 100°C were selected. Testing is conducted for 24 hours with the option to extend to 96 hours if necessary. The 100°C stress temperature has been validated to be predictive of long term storage at ambient conditions.[8] The use of air overpressure prevents oxygen depletion at this elevated temperature and test duration. The Navy has established that the 24 hour/100°C stress test simulates at least six months of ambient storage[3]. Each fuel sample is tested for peroxide concentration (ASTM

D3703), particulates (ASTM D2276) and antioxidant concentration (HPLC/ECD). Additional tests for color (ASTM D156), total acid number (ASTM D3242) and existent gum (ASTM D371) are performed when necessary.

RESULTS AND DISCUSSION

Case #1 F-44 in Long Term Strategic Storage

The U.S. military stores large quantities of product for emergency readiness in strategic reserves throughout the world. As the product ages, rotation of stock may be necessary to ensure the quality of the product. This study addresses 1.5 million barrels of F-44 that has been in storage since 1988.

The fuel, stored in three separate tanks, is required to be tested for limited properties every six months. Although a thorough review uncovered many missing data points in the periodic testing, the results for particulates, existent gums, peroxides and color all met specification. These tests only provide a picture of the current stability of the F-44 and do not allow any prediction of its future stability. It is well documented, however, that a F-44 exhibits stable characteristics until the antioxidant additive is depleted and then can peroxidize at an alarming rate causing rapid degradation.

Due to the quantity and age of the fuel, it was decided to utilize the LPR and HPLC/ECD techniques to evaluate the potential for the fuel to become unstable in the future. In September 1993, "as received" testing was performed on samples from all three F-44 storage tanks. This data included peroxide concentration, existent gum, total acid number, color, and antioxidant concentration. As shown in Table 1, the results for each tank sample were within MIL-T-5624 specification. The antioxidant concentration was below the minimum concentration required at procurement for two of the tanks but was still sufficient to provide adequate protection to the fuel. Since several shipments of fuel were commingled into these tanks, the exact antioxidant was difficult to determine. Therefore, the antioxidant concentrations reported in Table 1 are a measurement of the major antioxidant components detected in each tank. This isn't an exact determination of the antioxidant in the fuel but it is sufficient to evaluate the amount of antioxidant protection available.

The results of the LPR accelerated storage stability testing, Table 2, show after 96 hours of testing the peroxide and existent gum concentrations were within specification for all three tanks. Although the antioxidant concentration was reduced during the LPR testing, it still was 8 ppm or greater for the two tanks measured.

Based on the results of the LPR accelerated testing, it was determined that the F-44 could continue to remain in extended storage. This decision allowed the significant costs involved in the rotation of the F-44 stock from the three tanks to be avoided. Additionally, it was recommended that the fuel be tested using the LPR accelerated storage stability test protocol every 18 to 24 months to continue to ensure adequate future stability.

CASE #2 Abnormally Dark F-44

In February 1992, a complaint was received that a F-44 issued for aircraft use aboard U.S. Navy ships had developed an abnormally dark color. This fuel also formed a dark stain on the filter pads of the shipboard Contaminated Fuel Detector (CFD) that the Navy uses to measure the particulate concentration of its F-44. The dark stain on the pads caused the CFD to give false high particulate readings which significantly effected flight operations. Subsequent complaints were received about abnormally dark F-44 at other locations.

In response to this operational problem, samples of the F-44 in question were evaluated. Specification testing was performed and found that the fuel met all specification properties except for JFTOT thermal stability (ASTM D3241) which failed at both 260°C and 245°C. Color, only a report value, was measured at less than -16, which is significantly below typical values. From this testing and follow-up conversations with the field, contamination was determined not to be the cause of the problem. Instead it was hypothesized that the F-44 had degraded and additional storage was not advisable. To confirm this theory, non-specification LPR and HPLC/ECD testing was conducted. As shown in Table 3, both peroxide and particulate concentration increased over the 96 hour LPR accelerated storage stability test. The fuel, as received, had a low concentration of antioxidant (8 ppm) that was totally depleted after only 24 hours of testing.

The source of the problem F-44 was tracked to a single refinery. Results from the Navy's F-44 Refinery Sampling Program revealed that this refinery produced F-44 from a combination of product streams, some of which consisted of severely processed and/or thermally cracked stock material. In addition, the Navy's Refinery Sampling Program had shown that the F-44 produced by this refinery had significantly higher nitrogen concentrations (30-40 ppm) than any other F-44 (0-10 ppm nitrogen) currently being produced. The F-44 from the initial field complaint was determined to have a nitrogen concentration of 90 ppm.

In order to evaluate the rapid degradation theory, the procurement specification test results were obtained for the batch identified to have caused the initial problem. At procurement the F-44 batch under investigation had a saybolt color of +25 and easily passed the JFTOT thermal stability test at 275°C (1 Visual, 0 delta P). Similar comparisons were made with other F-44 batches from this refinery that had also degraded in the field. In each case, the when the F-44 left the refinery, it was of significantly better quality than when it was measured three to six months later in the field.

After discussions with the refiner could not positively identify the cause of the problem or guarantee the problem would not reoccur, it was decided that LPR accelerated stability testing would be performed on each batch of F-44 produced by the refinery until a satisfactory resolution was obtained. While the LPR test would not solve the problem, it would at least alert the Navy of potential problems and allow them to utilize their stocks accordingly. Additional LPR testing was also performed at six month intervals on F-44 produced by the same refinery but already distributed to other locations. Table 4 shows representative LPR data from this refinery testing. As shown in figures 1 and 2, the 96 hour LPR testing of this sample differs significantly from those determined from the F-44 under investigation. The increase of peroxide concentration and particulates is much lower. Although the refinery will not acknowledge any difference in their production, the results of the LPR testing clearly shows that a more stable product was produced. As expected, the "good stability" F-44 as determined by the LPR did not cause any operational problems in the field.

Although, the LPR and HPLC/ECD did not determine the cause of the instability (those results and testing are beyond the scope of this paper), each played a significant role in ensuring that the problems encountered in the field would not be repeated.

CONCLUSION

As research & development budgets continue to shrink and cost savings become the top priority by which programs are evaluated, it is essential that technology developed in these programs be successfully transitioned into the field. Although the LPR and HPLC/ECD may never become formal

ASTM Society approved test methods or parts of a procurement specification, they do represent two significant tools that improve the U.S. military's ability to evaluate its aviation fuel after procurement. These tools have not only saved the U.S. Navy millions of dollars in the two cases documented in this paper, but more importantly, provide additional assurance that the quality of the product will be acceptable whenever it might be needed.

(The views expressed in this article are those of the author and do not reflect the official policy or position of the Department of Defense or the U.S. Government.)

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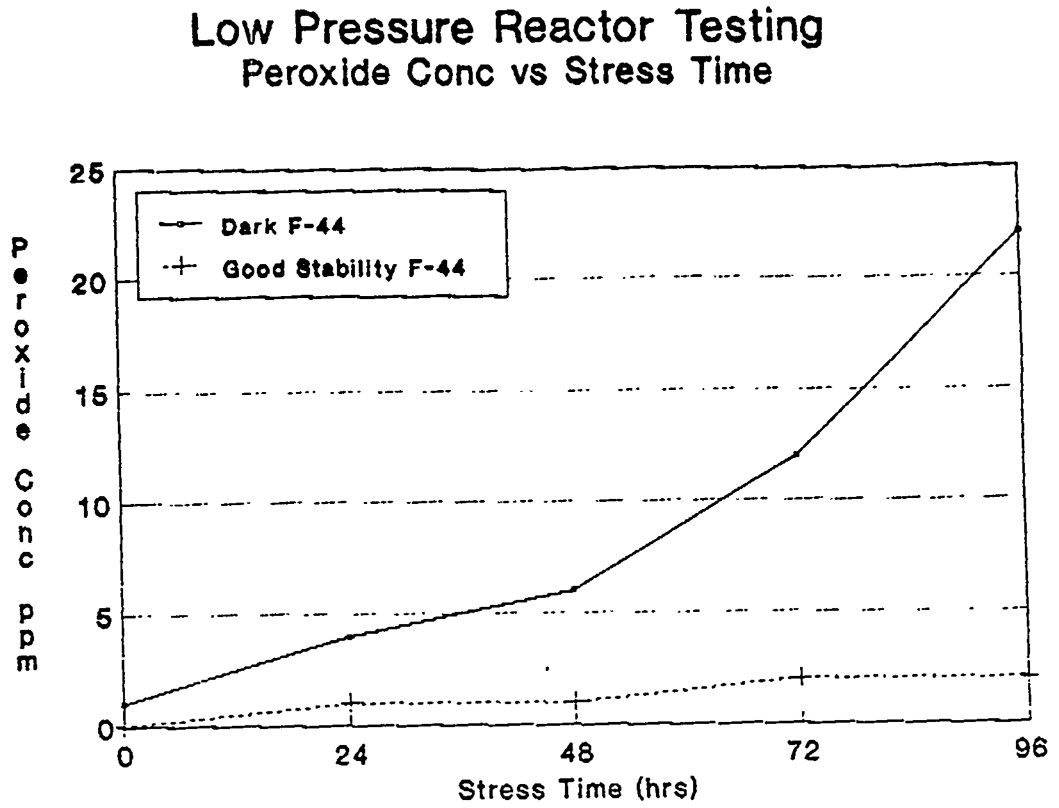

Figure 1

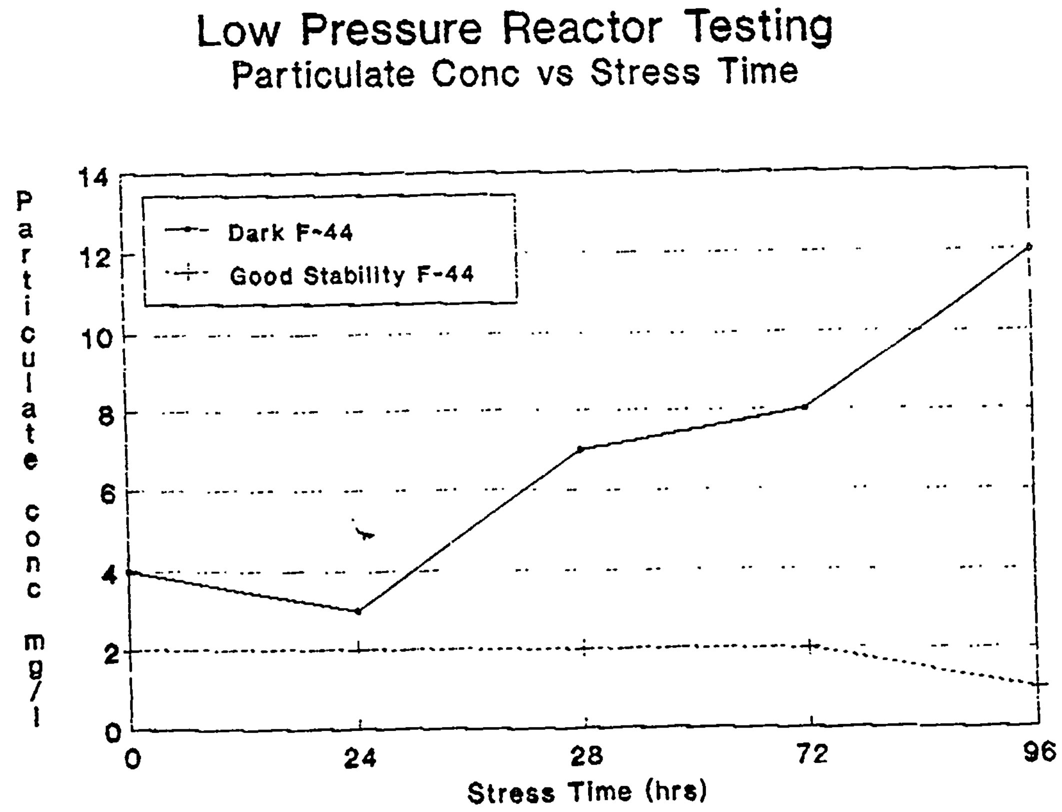

Figure 2

Table 1

TANK SAMPLES "AS RECEIVED"

Tank #	Peroxides (ppm)	Existent Gums (mg/100ml)	Total Acid # (mg KOH/g)	Saybolt Color	Antioxidant Concentration (ppm)*
716	0	0.4	0.004	17	20.1
726	0	0.0	0.006	14	13.9
736	0	0.2	0.004	15	14.2

* Combination of a mixture of Antioxidants

Table 2

LPR ACCELERATED STORAGE STABILITY TEST DAT

TANK # 716					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	1	1	1	1
Existent Gum (mg/100ml)	0.40	0.20	0.60	0.60	0.40
Antioxidant Conc. (ppm)*	20.1	18.6	16.1	13.5	11.2

TANK # 726					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	0	1	2	2
Existent Gum (mg/100ml)	0.00	0.20	0.40	0.00	0.40
Antioxidant Conc. (ppm)*	13.9	12.8	11.6	9.8	7.9

TANK # 736					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	0	1	1	2
Existent Gum (mg/100ml)	0.20	0.40	0.40	0.00	0.40
Antioxidant Conc. (ppm)*	14.2	nm	nm	nm	nm

*Combination of a mixture of Antioxidants
nm - not measured

Table 3

LPR ACCELERATED STORAGE STABILITY TEST DAT

Abnormally Dark F-44					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	1	4	6	12	22
Particulates (mg/l)	4.0	3.0	7.0	8.0	12.0
Antioxidant Conc. (ppm)*	8.2	0.0	0.0	0.0	0.0

*Conc of 2,6-di-tert-butylphenol

Table 4

LPR ACCELERATED STORAGE STABILITY TEST DAT

Good Stability F-44					
LPR Test Time (hr)	0	24	48	72	96
Peroxide No. (ppm)	0	1	1	2	2
Particulates (mg/l)	2.0	2.0	2.0	2.0	1.0
Antioxidant Conc. (ppm)*	14.3	5.2	5.0	4.6	4.7

*Conc of 2,6-di-tert-butylphenol

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ANALYTIC TESTS AND THEIR RELATION TO JET FUEL THERMAL STABILITY

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The evaluation of jet fuel thermal stability (TS) by simple analytic procedures has long been a goal of fuels chemists. The reason is obvious: if the analytic chemist can determine which types of material cause his test to respond, the refiners will know which materials to remove to improve stability. Complicating this quest is the lack of an acceptable quantitative TS test with which to compare any analytic procedures. To circumvent this problem, we recently compiled the results of TS tests for 12 fuels using six separate test procedures. The results covering a range of flow and temperature conditions show that TS is not as dependent on test conditions as previously thought. Also, comparing the results from these tests with several analytic procedures shows that either a measure of the number of phenols or the total polar sulfur present in jet fuels is strongly indicative of the TS. The phenols have been measured using a cyclic voltammetry technique and the polar material by gas chromatography (atomic emission detection) following a solid phase extraction on silica gel. The polar material has been identified as mainly phenols (by mass spectrometry identification). Measures of the total acid number or peroxide concentration have little correlation with TS.

INTRODUCTION

The issue of jet fuel thermal stability (TS) has been the subject of numerous studies and reviews[1,2] during the last 30 plus years. Since 1973, the standard for evaluating jet fuel TS has been the jet fuel thermal oxidative tester (JFTOT) and American Society of Testing and Materials (ASTM) D-3241. While this test may be adequate for determining a go/no-go fuel rating, its usefulness is limited in fuels stability research because:

- the JFTOT is based on a high (260C) operating temperature, and
- the measurement of fuel quality is based on a qualitative visual measurement.

As a result of the JFTOT's limitations several "advances" in evaluating fuel TS have been suggested and implemented in laboratory situations during the last decade. These tests include the hot liquid process simulator (HLPS), JFTOT breakpoint, gravimetric JFTOT[3], quartz crystal microbalance[4,5] (QCM), and a variety of single-tube heat exchangers[6-10] The range of temperatures has been expanded to cover temperatures from 140C to 335C and a range of flow conditions is covered by these new tests. Despite the variety of conditions, they all have one basic item in common with the JFTOT – each laboratory test attempts to determine fuel stability under accelerated test conditions. The accelerated conditions used by the TS tests are limited versus what occurs on an aircraft.

In addition to the development of new TS tests, analytic tests have been designed in an attempt to facilitate understanding of the deposition process and to assist in the evaluation of input parameters (i. e. A-factors and activation energies) for modeling and effectively predicting fuel TS[11]. This has long been a quest of fuel chemists for two major reasons. The first reason is the possible ease of operation of a quantitative analytic procedure. This may result in more rapid sample measurement, more reproducible results, and/or less waste product and simpler apparatuses. The second, and more interesting, reason is that once an analytic test is developed and chemists determine the precise nature of the compounds that yield a given response in a particular test, refiners/suppliers will know how to improve fuels. Complicating the quest for a good analytic test has been the lack of an acceptable quantitative fuel stability standard.

In this paper, we discuss the quantitative TS results from five separate tests covering a range of temperatures from 140C to 335C under both flowing and static conditions. We use the results of these tests for 12 different fuels to develop an "average" TS scale. This scale can then be used to compare several different analytic test procedures. Helping researchers to understand which test prcedures should be weighted heavily and which should not. Comparisons among the different tests allow significant insight into some of the major causes of jet fuel instability and detail a simple method of improving fuel stability.

The analytic tests discussed here have been designed to study oxygen-containing fractions of fuel components. We have chosen these tests (versus other available tests such as alkene or mercaptan sulfur because (a) oxygen-containing compounds are known to concentrate in the deposits, (b) the autoxidation reactions are known to stimulate deposit formation, and (c) many antioxidant molecules are known to be phenolic and antioxidant molecules have been predicted to be deposit precursors[2].

FUELS AND EXPERIMENTS

The U.S. Air Force acquired and distributed a series of jet fuels for test and additive evaluation. These fuels were assigned a four-digit number by the Fuels Branch, Fuels and Lubrication Division of Wright Laboratories (POSF). These fuels are listed in Table 1.

Two modified procedures for the JFTOT have been used to provide two quantitative measures of fuel TS under flowing conditions[12].The first, HLPS, uses stainless-steel tubes and a 335C operating temperature. The total carbon on the tube, measured by carbon burn off, is used as a quantitative measure of TS. The second measure assesses the maximum operating temperature at which the fuel fails ASTM D-3241. This is reported as the JFTOT breakpoint temperature.

Two static tests were also used to evaluate fuel TS. The isothermal corrosion oxidation test (ICOT) heats fuel (185C) under reflux with bubbling air for 5 hours. The quartz crystal microbalance (QCM) is a closed system heated to 140C. In the ICOT[13], the fuel stability is evaluated by gravimetric measure of the filterable deposits formed. In the QCM, the mass of deposits collected on the surface of the quartz crystal is determined by the shift in crystal frequency. The total mass measured at 8 and 15 hours is used in this study[5,14].

The last TS test for each of these fuels is the micro carbon residue test (MCRT). In the MCRT, the fuel is distilled in air at 250C. The resulting deposits remaining in the distillation flask are reported as a measure of fuel TS[13].

The fuels were analyzed for total acid number (TAN) (ASTM D-3242). The total phenol and total peroxide numbers were determined using cyclic voltammetry[15]. The absorbance of a 10-μl fuel sample extracted into basic water (pH=13) was measured using a UV/VIS spectrometer[16]. The absorbance near 300 nm is proportional to the concentration of phenols in the fuel[17]. The total polar carbon, sulfur, and oxygen were determined using solid phase extraction[18,19] on a silica gel and subsequent extraction of the polar material from the gel into methanol. The quantity of material was determined by gas chromatography with atomic emission detection (GC-AED)[20]. Identification of these materials was made by gas chromatography with mass spectrometry (GC-MS) detection.

RESULTS

The results of the six TS tests for each of the 12 fuels are shown in Table 2. The results of the seven analytic test measurements for each of the 12 fuels are shown in Table 3. The total carbon and oxygen areas reported do not include DIEGME (a fuel system icing inhibitor) that is present in some of the fuels. A complete list of the identified compounds and their relative occurrence in the 12 base fuels is given in Table 4.

DISCUSSION

Before proceeding with a discussion of analytic tests, we must first evaluate the TS tests to determine if there is a meaningful and quantifiable TS scale. To evaluate such a scale (if one exists) requires us to compare each available TS test, which we believe in some way measures TS, to this "real" TS scale. The differences between "reality" and the individual tests should be quantifiable and small.

The comparison among different TS tests is complicated by the fact that no two tests are necessarily measuring the same thing. Often a least square fit between one of the tests, JFTOT breakpoint, is used as a measure of the "goodness" of a particular test. These kinds of least square analysis may be valid, but there is no guarantee that the relation between temperature (C) and deposits (mg/l) or some other types of inappropriate comparisons should yield a straight line. Normalization of the test results before comparison does not remove the assumption of linearity between tests. Such a non-linearity was observed by Kauffman[15] even while the relative ranking of the jet fuels was maintained.

A more important criterion for test evaluation is that the tests show the same or a similar ranking of the fuels. The ability to rank fuels similarly relies on the assumption that the individual TS tests exhibit monotonic behavior, even if not linear. That is, one test might discriminate well among fuels that are very thermally stable, while another is better at discriminating between fuels that are not particularly good. A least squares comparison of these two tests would be poor, yet all fuels could be ranked identically. The assumption of monoticity is significantly weaker than linearity and should yield a more robust analysis. Therefore, to evaluate the TS of a jet fuel, we have changed the absolute measurements in Table 2 to reflect the ranking of the fuels (see Table 5). The fuels are listed in order from best to worst average ranking (see Equations 1,2, and 3).

Several items are apparent from Table 5:

- JPTS (2976) is the most stable fuel in each TS tests.
- The second best fuel is POSF-2747.
- All of the tests measure POSF-2985 as one of the two worst fuels.
- While there is general agreement concerning the ranking of the jet fuels, none of the tests are in perfect agreement with the average ranking.
- Interestingly, none of the tests is in agreement with any other test.

The first three statements show that despite the diversity of test conditions, good fuels and bad fuels can be identified by any of the TS tests. That is, while there may not be an absolutely correct TS test, there is at least good general agreement by all tests concerning what constitutes a good or a bad fuel.

The last two statements, however, are the most important to the evaluation of analytic tests. No pair of tests agree completely with each other, and no individual test agrees with the average. Not even the rankings for QCM at 8 and 15 hours are identical. If we are to attempt to develop an analytic test to evaluate TS, we have to understand that an exact match to all tests is not possible. In fact, the goal of any analytic test should not be to match any particular TS test, but rather to be within the noise level of the TS tests. To define the noise of the TS tests, we need to know how far from "reality," or at least from some definable goal, the ranking is. Since the "real" ranking is not a known, we proceed on the assumption that the average of these tests is a good estimate of reality. The difference between the measured ranking and the average ranking (for a given TS test) is defined in Equations 1 and 2. The difference measurement (D_j) for each of the six TS tests is shown in the last row of Table 5.

$$D_j = \sum_{i \text{ fuels}} \frac{|R_{ij} - R_{iave}|}{12} \qquad 1)$$

where R_{ij} is the integer rank of the i^{th} fuel in the j^{th} test when compared to the other 11 fuels (Table 5), R_{iave} is the integer rank associated with r_{iave} (the average ranking in Table 5), and

$$r_{iave} = \sum_{j\ tests} \frac{R_{ij}}{6} \qquad 2)$$

To recap, each combination of fuel i and test j has a rank R_{ij} (an integer between 1 and 12). The average of the R_{ij} averaged over tests j is the average ranking of the fuel I and is called r_{iave}. The average ranking of a fuel r_{iave} can also be considered a TS test and can be ranked just as the other TS tests. The rank of the average ranking is called R_{iave}. The average difference for a test (D_j) is the average of R_{ij} - R_{iave} averaged over the i fuels.

The value D_j is a measure of how far out of place (versus the rank of the average, R_{ij}) on average the jth test ranks all fuels. Clearly the MCRT is the furthest from average and the QCM (8 hrs) test is the closest. The average D (Equation 3) for the six TS tests is 1.11. This is a measure of how close the set of TS tests comes to measuring the "real" thermal stability scale (remember "reality" is assumed to be represented by the average). An analytic test need not be any better than this (D_j =1.16) to be as good as a TS test at predicting thermal stability.

$$D = \sum_{j\ tests} \frac{D_i}{6} \qquad 3)$$

We are now in a position to quantify one of our original observations – that there is general agreement among the TS tests. First, let us consider the meaning of D_j. Starting with the correct order for a fuel (1,2,...12), the smallest change is the switching of two neighboring fuels (2,1,3,4,...12). This is a single permutation. Any ordering can be described as a number of permutations from the correct ordering. Each permutation of neighboring values will increase or decrease D_j by 0.17.

If the order of the fuels for a given test were ranked in a completely inverted order (12,11,10 ... 1), D_j would be 6. The same value (6) comes from a "six-step rotation" (7,8,...12,1,2,...6). We believe this to be a maximum but have not proved it (there are 12! possible arrangements, so the maximum can be found in principle). If one fuel is completely misplaced (12,1,2,3,4...), D_j is 1.83. If the fuels are pairwise misplaced (2,1,4,3,6,5...), D_j is 1. A random test (totally uncorrelated to TS) would be expected to have D_j equal to 3.83 (measure by 25 randomly generated test results for a confidence interval of ± 0.17). The average D for the six tests is 1.16 (seven permutations out of order). Even the MCRT, a distillation test, has a D_j of only 1.67 (ten permutations out of order). If we were to drop the MCRT from consideration as a valid TS test, D would decrease to 1.0.

Now that we have both a working TS scale, the "rank of the average scale (R_{iave})," and an idea of the precision with which the TS tests can reproduce that scale, we can consider the analytic tests and evaluate their ability to predict TS. Again, rather than assume some linear behavior for the analytic tests to reproduce a given TS test, we will rely on the weaker assumption of monotonic behavior. Table 6 shows the ranking of the fuels by analytic test. The fuels are listed in order of average ranking as in Table 5 and ranked by increasing measure of the analytic test. The difference (D_j) between the ranking of the fuels by analytic test versus the average stability scale (R_{iave}) is also shown.

Some observations from Table 6 are as folows:

- TAN and Peroxide number are only slightly better than random guesses for TS.
- One test (UV/VIS) is as close as the TS tests are to the average TS scale.
- Two other tests (Phenols and Sulfur) are as close as the worst TS test (MCRT).
- Similarly to the TS test, the analytic tests (neglecting TAN and Peroxides) can pick both the very good and the very bad fuels.

CORRELATIONS

A simple first guess is that each of the analytic tests is somehow related to thermal stability. A least squares linear fit between the rank (R_{ij}) for the analytic tests and the average rank of the fuel in thermal stability tests (r_{iave}) shows that the average thermal stability test can be predicted from the given set of analytic tests. The correlation coefficient (r^2) is 0.94, and the sum of the squares of the residuals is 6.5. The rank of the prediction of the linear regression shows a difference (D_j) of 0.67. This is well within the range of differences that individual TS tests achieve. The regression parameters are given in Equation 4.

$$r_{iave} = 0.28*\text{Peroxide} + 1.28*\text{Carbon} + 0.31*\text{TAN} + 0.27*\text{UV/Vis} - 1.94*\text{Oxygen} + 1.11*\text{Phenols} - 0.07*\text{Sulfur} \quad 4)$$

A quick look at the values of the coefficients shows that the absolute value of the coefficients of sulfur, UV/VIS, and peroxides are all 0.3 or less. The correlation is still 0.90 when peroxides and UV/VIS have been removed from the basis set of analytic data, and D_j is an identical 0.67. For comparison, we note that individual TS tests generally have r^2 of 0.7 to 0.9 for correlation with the r_{iave}. The individual analytic test r^2 values are shown on the diagonal of Table 7.

Using the total polar materials (carbon, sulfur, and oxygen) and the phenol number only yields a correlation r^2 of 0.84 and D_j of 1.0. The regression parameters for this fit are given in Equation 5.

$$r_{iave} = 0.19 \text{ Sulfur} + 0.94 \text{ Carbon} - 1.35 \text{ Oxygen} + 1.09 \text{ Phenols} + 0.87 \qquad 5)$$

At the opposite side is the question of how simple can we go and still achieve a reasonable TS prediction. As shown in Table 6 and again on the diagonal of Table 7, only one analytic test is a reasonable predictor of thermal stability (UV/VIS). However, if two tests are combined, several combinations are good predictors of TS. Table 7 shows the two-parameter correlations to r_{iave}. The values in the lower triangle of the table are the r^2 for the correlation of r_{iave} with the least squares fit linear combination of two analytic tests (from the row and column headings). The diagonal contains the one parameter r^2. The upper triangle area shows the D_j for the two-parameter test. This table shows again the importance of the sulfur and phenol compounds which have the largest two-parameter correlation (0.80), and a D_j of only 1.33, one permutation higher than the average thermal stability test. For oxygen and UV/VIS, r^2 is 0.80 and D_j is 1.16, emphasizing the need to eliminate phenols (measured by the UV/VIS) and polar oxygen.

APPLICATIONS

Two major applications of the above ranking scheme are immediately available. First, once a sufficient number of fuels have been tested (with both TS and analytic tests) analytic tests alone may be used to evaluate jet fuel TS. A passing test would indicate average TS performance at or above a pre-selected fuel. At a minimum, as suggested by Kauffman[15], only those fuels that pass the analytic tests would be tested in thermal stability tests.

The second application is in making fuels better. As indicated previously, once the source of response to the given analytic is determined it should follow that the removal of that species would improve the fuel. Our strongest correlation is with the UV/VIS test that we believe measures the concentration of base extractable phenols. The second best correlation is with the phenols measured by cyclic voltammetry. The correlation of jet fuel TS with cyclic voltammetry tests has been discussed previously[15].The third strong correlation is with the polar sulfur compounds. The necessity of oxidizable sulfur compounds[21] and the importance of polar sulfur compounds[1] to the formation of deposits has also been discussed previously. These compounds were removed from the fuel by silica gel solid phase extraction. An analysis of the compounds that were removed from all the fuels is shown in Table 4. Interestingly, no sulfur-containing compounds have been identified. However, the gel was effective at removing many of the polar N- and O- compounds identified by Hazlett as key players in the formation of insolubles. These compounds have been identified as mainly substituted phenol and amine compounds.

A less obvious use of the TS scale is in the evaluation of jet fuel additives. TS of the fuels and the relative increase in their TS as a result of additives can now be more easily quantified as to how much improvement was achieved, and appropriate wighting schemes for the individual tests can now be determined.

CONCLUSION

By using a ranking procedure, the results of TS tests can be compared to one another without resorting to a normalization that amounts to an assumption of linearity that may not exist. Once the ranking system is established, it becomes apparent that several of the TS tests yield results that are similar to each other. That is, the concept of TS of a jet fuel may be reasonably well-defined, independent of the conditions. A TS scale indicative of the average of six TS test measurements was developed. The noise associated with TS has been established. Analytic tests, alone and in combination, have been shown to reproduce the TS scale as well as the individual TS tests (i.e., to within the same noise level as the TS tests).

A series of analytic tests for oxygenates/polar materials showed several important correlations with the TS scale. In particular, there was a very strong correlation with phenols and polar sulfur. Analysis of the polar material showed that a majority of it is phenolic in nature with secondary quantities of amine-type material. Despite the importance of polar sulfur material shown by its correlation with the TS scale, no sulfur compounds have yet been identified. Tests for TAN and peroxides showed only slightly better than random chance at correlating fuel TS.

Tests for polar oxygen and carbon showed better than random chance correlations, but they were not as good as any TS test at measuring the TS scale.

Several pairs of analytic tests were found to adequately describe the TS scale. Each pair which exhibits good comparison to the TS scale contains at least one analytic test which measures phenols or polar-sulfur compounds.

The importance of polar-sulfur compounds appears obvious from D_j for the polar sulfur test and from the two parameter correlations but becomes less obvious during multiple regressions. Peroxide and TAN are not strongly related to thermal stability. A set of five analytic tests gave a 0.94 correlation to the TS scale.

The removal of phenols appears to be crucial to the development of higher thermal stability fuels. The importance of as yet unidentified polar-sulfur compounds is probably important, but the correlation is not as well-established.

ABBREVIATIONS

ASTM	American Society for Testing and Materials	JFTOT	Jet Fuel Thermal Oxidative Tester
AED	Atomic Emission Detection	JPTS	Jet Propellant, Thermally Stable
D_j	Difference measurement for jth test	MCRT	Micro Carbon Residue Test
D	D_j averaged over j tests	MS	Mass Spectroscopy
GC	Gas Chromatography	QCM	Quartz Crystal Microbalance
HLPS	Hot Liquid Process Simulator	r^2	Correlation Coefficient
i	index of fuels	R, r	Integer, Average Rank
j	index of tests	TS	[illegible] Stability
ICOT	Isothermal Corrosion Oxidation Test	TAN	[illegible]ber
		UV/VIS	U[illegible]olet/Visible

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Table 1. Test Fuels

POSF#	Type	Comments
2976	JPTS	Jet Propellant -Thermally Stable
2747	Jet A-1	Meets super K-1 kerosene spec
2827	Jet A	
2922	Jet A	Hydrotreated
2926	Jet A	
2928	Jet A	contains 15% hydrocracked stock
2934	Jet A-1	High acid number
2936	JP-5	
2959	Jet A	Merox-treated
2963	JP-5	Copper-spiked 50 ppb
2980	Jet A	Merox-treated
2985	JP-5	High nitrogen

Table 2. Thermal Stability Test Results

Fuel	ICOT mg/L	MCRT mg/g	QCM-8hrs $\mu g/cm^2$	QCM-15hrs $\mu g/cm^2$	JFTOT Breakpoint C	HLPS $\mu g/cm^2$
2976	0	0.5	0.3	0.8	427	6
2747	5	1.2	0.6	0.85	332	7
2827	87	3	2	3.6	282	48
2922	104	1.7	1.8	2.4	277	18
2926	64	2.2	3.2	4	288	43
2928	89	1.8	3	3.2	279	36
2934	358	1.9	5	5.7	266	121
2936	72	1.6	4	6.9	277	65
2959	43	1.4	1.4	2.5	293	113
2963	485	1.9	5.4	6.1	232	153
2980	83	2.1	5	6.2	288	52
2985	755	3.9	9.5	10.5	266	127

Table 3. Analytic Test Results

Fuel	TAN μg KOH/g	Phenols mmole/l	UV-VIS	Peroxide μmole/L	Carbon Area	Sulfur Area	Oxygen Area
2976	3	0	0.07	3	3.4	1.4	6.1
2747	0	0.4	0.10	0	2710	8.5	10.1
2827	1	2.6	0.9	29	7650	91.5	25.4
2922	4	0.2	0.25	12	2012	21.1	8.5
2926	2	0.8	0.32	27	2450	26.8	9.0
2928	13	1	0.50	25	4990	43.2	21.4
2934	43	7.1	2.65	0	11800	13.8	85.3
2936	14	3.6	0.77	0	2140	28.9	14.6
2959	2	1.5	0.33	31	4130	20.1	21.5
2963	4	2.1	0.67	22	2766	71	14
2980	1	2.1	0.80	34	14200	34	80
2985	3	16	3.69	33	33600	122	128

Table 4. Identifiable Polar Compounds and Their Number of Occurrences in the Base Fuels

Compound	Occurrences	Compound	Occurrences
Phenol	3	Methyl aniline	3
Methyl phenol	8	Ethyl aniline	3
Dimethyl phenol	10	Dimethyl aniline	2
Ethyl phenol	8	Diethyl aniline	1
Trimethyl phenol	5	Propyl aniline	1
Propyl phenol	3	C3 aniline	1
C3 phenol	9	C4 aniline	1
C4 phenol	10	C5 aniline	1
C5 phenol	6		
C6 phenol	3	C4 pyridine	1
C4 benzenemethanol	1	Ethylmethyl pyridine	2
1-methoxy-4-1-methylpropylbenzene	1	Propyl pyridine	1
Bis 2-ethylhexylpthalate	1	Trimethyl pyridine	2
C3 benzodioxole	1	T-butyl pyridine	1
C3 cyclohexanone	1	Dimethyl pyridine	1
Ethoxybenzaldehyde	1	C4 pyridine	2
Methoxy benzenes	1		
Trimethyl bicyclohytanone	1	Trimethyl quinoline	1
Phenol ethyl benzene ethanomine	1	Tetrahydro 3-methyl isoquinoline	1
Indoles	1	Dimethyl tetrahydro quinoline	1
C3 benzoic acid methyl ester	1	Napthalamine	1

Table 5. Integer Ranking (R_{ij}) of Fuels by Thermal Stability Tests

Fuel	ICOT	MCRT	QCM 8hrs	QCM 15hrs	J FTOT	HLPS	Average ranking (r_{iave})	Rank of average (R_{iave})
2976	1	1	1	1	1	1	1	1
2747	2	2	2	2	2	2	2	2
2959	3	3	3	4	3	9	4.17	3
2922	9	5	4	3	8	3	5.33	4
2928	8	6	6	5	7	4	6	5
2926	4	10	7	7	4	5	6.17	6
2827	7	11	5	6	6	6	6.83	7
2936	5	4	8	11	8	8	7.33	8
2980	6	9	9	10	4	7	7.50	9
2934	10	7	9	8	10	10	9.00	10
2963	11	7	11	9	12	12	10.33	11
2985	12	12	12	12	10	11	11.50	12
(D_j)	1.33	1.75	0.42	1.00	1.42	1.17		

Table 6. Integer Ranking (R_{ij}) of Fuels by Analytic Test

Fuel	TAN	Phenols	UV/VIS	Peroxide	Carbon	Sulfur	Oxygen
2976	6	1	1	4	1	1	1
2747	1	3	2	1	5	2	4
2959	4	6	5	10	7	4	8
2922	8	2	3	5	2	5	2
2928	10	5	6	7	8	9	7
2926	4	4	4	8	4	6	3
2827	2	9	10	9	9	11	9
2936	11	10	8	1	3	7	6
2980	3	7	9	12	11	8	10
2934	12	11	11	1	10	3	11
2963	8	7	7	6	6	10	5
2985	7	12	12	11	12	12	12
Difference(D_j)	3.67	1.58	1.17	3.50	2.33	1.67	2.17

Table 7. Correlations: 2 Parameter Analytic Test to r_{iave} in Lower Triangle, 1 parameter to r_{iave} on Diagonal, and Difference Measurements (D_j) of 2 Parameters Tests in Upper Triangle.

	Oxygen	Sulfur	Carbon	Phenols	Peroxide	TAN	UV/VIS
Oxygen	0.44	1.83	2.17	1.50	2.17	2.00	1.16
Sulfur	0.67	0.57	1.67	1.50	1.67	1.67	1.16
Carbon	0.44	0.64	0.40	1.50	2.33	1.67	1.33
Phenols	0.70	0.78	0.66	0.70	1.50	1.50	1.33
Peroxide	0.44	0.58	0.40	0.69	0.14	2.17	1.17
TAN	0.56	0.70	0.61	0.67	0.48	0.18	1.67
UV/VIS	0.80	0.79	0.74	0.74	0.73	0.77	0.73

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BEHAVIOUR OF CONDUCTIVITY IMPROVERS IN JET FUEL

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ABSTRACT

Dangerous accumulation of electrostatic charge can occur due to high speed pumping and microfiltration of fuel. This can be avoided by increasing the electrical conductivity of the fuel using conductivity improver additives. However, marked variations occur in the conductivity response of different fuels when doped to the same level with conductivity improver. This has been attributed to interactions of the conductivity improver with other fuel additives or fuel contaminants. The present work concentrates on the effects of fuel contaminants, in particular polar compounds, on the performance of the conductivity improver. Conductivity is the fuel property of prime interest. The conductivity response of model systems of the conductivity improver STADIS 450 in dodecane has been measured and the effect on this conductivity of additions of model polar contaminants sodium naphthenate, sodium dodecyl benzene sulphonate, and sodium phenate have been measured. The sodium salts have been found to have a complex effect on the performance of STADIS 450, reducing the conductivity at low concentrations to a minimum value and then increasing the conductivity at high concentrations of sodium salts. This work has focused on characterising this minimum in the conductivity values and on understanding the reason for its occurrence. The effects on the minimum conductivity value of the following parameters are investigated: (a) time, (b) STADIS 450 concentration, (c) sodium salt concentration, (d) mixed sodium salts, (e) experimental method, (f) a phenol, (g) individual components of STADIS 450. The complex conductivity response of the STADIS 450 to sodium salt impurities is discussed in terms of possible inter-molecular interactions.

1 INTRODUCTION

Jet fuel has very low natural electrical conductivity, usually less than **5pSm^{-1} (CU).** It is well known that dangerous accumulation of electrostatic charge can occur due to high speed pumping and microfiltration of jet fuel (1,2). This can be overcome by increasing the electrical conductivity of the fuel which is achieved by the use of conductivity improver additives.

Two additives have been used, namely, Shell ASA-3 , employed outside the USA since 1962 and DuPont STADIS 450 which was introduced in the mid 1970's. Both additives were considered for US Military use only after service tests in 1978. Shell discontinued supply of ASA-3 at the end of 1991 and for this reason, since January 1992, this work has concentrated entirely on the behaviour of STADIS 450.

Considerable variations are observed in the conductivity response of fuels from different crude sources when doped with the same concentration of additive. It was for this reason that the UK MOD tasked the Royal Military College of Science to investigate interference with additive performance.

2 AIMS OF THE WORK

The aims remain similar to those in our earlier published work (3):

(a) to investigate the influence of fuel components on the performance of conductivity improver additive and

(b) to attempt to understand the nature of important intermolecular interactions.

Earlier (3) we reported on the effects of a wide range of additives and compounds, representative of naturally-occurring fuel components, on the electrical conductivity of solutions of conductivity improvers. Large reductions in conductivity can be caused by dodecylbenzene sulphonic acid (DDBSA) and other highly polar substances. For example, preliminary results on the sodium salt of DDBSA showed this to have a large antagonistic effect on 3 ppm STADIS 450 in dodecane.

The acidity in fuel is due to the presence of naturally-occurring phenols and naphthenic acids plus sulphonic acids which are refinery produced by certain processes. In addition the presence of sodium salts is also a possibility. Data indicate that clay treatment of fuels, whilst giving substantial reduction in naphthenates and probably sulphonates, rarely removes substantial amounts of phenolic components.

Table 1 is a summary of our knowledge on the concentration of these highly polar constituents observed in jet fuel. We note the following:

Naphthenates show a large concentration range but with a fairly modest maximum concentration. However, there is a possibility of some salt being present, at estimated concentrations of 1ppm or greater.

Phenolics show a very large concentration range and very large concentrations. Here there is no information on phenate concentration and 10ppm has been estimated.

Sulphonates occur only at low concentrations, possibly up to 0.3ppm. Some higher total sulphonate values, up to 5ppm, have been reported (4).

In our research programme it is our intention to examine these substance types in detail. However, in this paper we shall concentrate on the influence of the most highly polar types, namely salts, on the conductivity of STADIS 450 in dodecane solutions. For this purpose we have used a sodium naphthenate, for which extensive measurements are presented, sodium dodecyl benzene sulphonate and a sodium phenate. The parameters studied were : (a) time, (b) STADIS 450 concentration, (c) sodium salt concentration, (d) salt mixture concentration and (e) STADIS component effects.

3 EXPERIMENTAL

3.1 Materials

Details and purification of most substances used here are as previously described (3).

STADIS 450 was supplied by **Instar/DuPont.**

The sodium phenate (NaP) was prepared by neutralisation of dodecylphenol (Aldrich) by sodium hydroxide in methanolic solution followed by recovery of the solid phenate by rotary evaporation of the methanol. Sodium naphthenate (NaN) has been prepared in a similar way. A sample of the latter was acquired from Kodak which is used in this work. Sodium dodecyl benzene sulphonate (NaDDBS) is a Sigma product. m-cresol was obtained from BDH Chemicals.

STADIS 450 fractions: Gel Permeation Chromatography of STADIS 450 showed that three major components were present of high, medium and low molecular weight. Selective precipitation was used to separate the three molecular weight fractions.

3.2 Conductivity Equipment and Conditions

Previously (3) we discussed in some detail the difficulties caused by adsorption effects on conductivity measurements and described how these were taken into account in the interpretation of data. Adsorption was a particular problem with ASA-3. For STADIS 450 however, adsorption losses were small. In this work STADIS 450 has been used exclusively and conductivity losses due to adsorption are generally insignificant. Measurements were made with the range of apparatus already described (3) and temperature controlled at 25 C unless stated otherwise.

The experimental conditions were selected in order to examine the general behaviour of these systems, rather than to mimic any special field conditions.

4 RESULTS AND DISCUSSION

4.1 Effects of Salts on the Conductivity of Dodecane

The effects of each of the three salts alone, on the conductivity of dodecane, are shown in figure1. NaDDBS gives a significant increase in conductivity which is substantially larger than the small increase caused by NaN. NaP has virtually no effect.

4.2 Time Effects on the Conductivity of STADIS 450 Solutions Containing Salt

Addition of salts to a stable conductivity solution of STADIS 450 causes the conductivity to change with time as illustrated by the data for NaN shown in figure 2. Similar behaviour is observed for NaDDBS and NaP though there are quantitative differences. We note that below a certain concentration of salt, conductivity *decreases* with time, eventually reaching a constant value. Above this certain concentration, conductivity *increases* with time to a constant value. These time dependencies cannot be accounted for in terms of time-for-mixing, nor can they be explained by any adsorption effects on cell surfaces. They are real solution effects which are probably a consequence of the time dependence of conformational changes induced in the polymer components and which will be discussed further in sections 5.3 and 5.5. Conductivities reach constant values after about 5 to10 minutes from the additions and remain constant for many hours. For experimental purposes, additions were made at 5 minute intervals. This procedure provides a satisfactory basis for comparisons to be made.

4.3 Dependence of Conductivity on Salt Concentration at Constant STADIS Concentration.

The behavior of NaN and NaDDBS are shown respectively in figures 3 and 4. There are striking qualitative similarities. The general behaviour is characterised by a depression of conductivity at low salt concentration leading to a minimum, then an increase, until the net effect is enhancement relative to the initial STADIS value. We note the considerable range of behaviour which is possible. In particular, and possibly most important, is the large antagonistic effect at low salt concentrations.

4.4 Dependence of Conductivity on STADIS 450 Concentration

In these experiments we observe the conductivity response of STADIS 450 additions to dodecane containing prepared concentrations of sodium salts. These experiments are more relevant to field use of the additive. Data from such experiments are shown in figures 5 and 6. It can be seen that, in the absence of salts, the conductivity increases approximately linearly with STADIS concentration.

At low concentration of salts, <10ppm, the conductivity of the STADIS solution is lower than in the absence of salts for STADIS concentrations <20 ppm. Above 20ppm STADIS the differences are probably not significant when the uncertainties in measurements are taken into account.

At high concentration of salts, ~200ppm, a large increase in the conductivity of STADIS solutions occurs for STADIS concentrations <20ppm. At STADIS concentrations >20ppm the conductivity decreases with increasing STADIS concentration and is considerably lower than the value expected without the sodium salts.

4.5 Effect of STADIS Concentration on the Position of the Minimum Conductivity.

Figures 3 and 4 illustrate the effects of both salt and STADIS concentration.

Sodium naphthenate. Fig 3 shows a pronounced shift in the conductivity minimum to higher sodium salt levels as the STADIS concentration increases. The gradient of the initial part of the curve, where the conductivity is decreasing, is approximately constant for each concentration curve. As shown in Table 2, the ratio of the concentration of STADIS to NaN at the minimum of each curve is approximately constant. Also the depth of the minimum is approximately constant if allowance is made for the uncertainty in the conductivity values, when normalised for the concentration of STADIS.

Sodium dodecylbenzenesulphonate. Figure 4 shows that the ratio for STADIS to NaDDBSA has a similar effect to NaN on the conductivity of STADIS solutions.

4.6 Effects of Salt Mixture Combinations on the Conductivity of STADIS Solutions

The effects of sodium salt mixtures, covering the ranges: naphthenate 0.1-10 ppm, phenate 100-500 ppm and suphonate 1-2 ppm, on solutions of STADIS in dodecane show that the magnitudes of observed conductivities are close to those predicted assuming additivity of individual salt conductivities. Data for one series of measurements are included in figure 5. The 212ppm of mixed salts includes: 200ppm NaP, 10ppm NaN and 2ppm NaDDBS.

4.7 Effects of a Parent Phenol on the Conductivity of STADIS 450 Solutions

Preliminary measurements on dodecylphenol and meta-cresol up to a concentration of ~1000ppm are shown in figure 7. Conductivity decreases non-linearly with phenol concentation and the two phenols show differences in behaviour. Comparison with the low concentration effects of NaP illustrates the considerable difference, mole for mole, between phenol and salt. No minimum is observed for the phenol.

4.8 Comparison and Verification of Behaviour for Research and Field Equipment

The conductivity measurements outlined in section 4.3 were repeated using the EMCEE Portable Conductivity Meter and the procedure given in ASTM D2624. The same dependence of conductivity on salt concentration, and the minimum in conductivity were found . The results were similar to those shown in figures 3 and 4 from the research equipment.

4.9 Conductivity Response of Individual Components of STADIS 450 to Sodium Salts

DuPont patents published in 1975 and 1977 (5,6) suggest that in STADIS 450 the two major components for conductivity performance are the polysulphone and the polyamine, with a sulphonic acid as the third major component, thought to act as a stabiliser. STADIS components, separated as described earlier in section 3.1, are a high molecular weight fraction assumed to be mainly polysulphone, a medium molecular weight fraction assumed to be mainly polyamine and a low molecular weight fraction which seems to be the sulphonic acid.

The conductivity response of each of these fractions and their sensitivity to sodium salts were measured. Each fraction was used at 3ppm in dodecane.

The *high molecular weight fraction* gave the greatest increase in conductivity. A minimum occurs with each salt. The stability of this fraction seems to be impaired by separation from the other components. In all cases the conductivity increases with time, rapidly at first, and only after approximately 2 hours is the conductivity sufficiently constant to begin the addition of salts. It seems likely that this polysulphone fraction is responsible for the minima observed with solutions of fully-constituted STADIS 450.

The *medium molecular weight fraction* shows a minimum with the salts but this is much less pronounced than is the case for the polysulphone fraction. This may be due to traces of polysulphone still being present. A decrease in conductivity occurs with NaDDBS.

The *low molecular weight fraction* shows a small increase in conductivity on addition of each salt, but a minimum does not occur.

These observations are illustrated by the data for NaN in figure 8.

4.10 Practical Significance for Fuels.

Although these results are for model dodecane systems, the trends could be significant for fuels. For fuels containing low concentrations of salt impurities, <10ppm, the performance of STADIS might be reduced. Adding more STADIS would cause the conductivity to increase less than would be expected if no salts were present. High concentrations of salts, >100ppm, could greatly enhance the conductivity performance of STADIS. In some cases the conductivity at 3ppm to 5ppm STADIS could be so high that values would be off-scale on the EMCEE Portable Conductivity Meter, when measured according to ASTM D2624. In the unlikely situation of high concentrations of STADIS, >30ppm, combined with high concentration of salts, >10ppm, the addition of further STADIS will give little or no increase in conductvity.

5 SPECULATION ON THE MECHANISM OF ION PRODUCTION IN SALT-STADIS 450 SOLUTIONS

5.1 General Comments

The general factors which determine ion concentration are:

(a) the intrinsic ability of a molecule to produce ions combined with
(b) the ability of the system to stabilise ions.

The latter we suggest is related to the tendency for molecules to aggregate and to incorporate ions into the aggregates formed. The factors which control aggregation of substances in non-aqueous hydrocarbon solutions have recently been reviewed (7). In the case of surfactant-type molecules the driving force for aggregation in non-aqueous solutions differs from that in aqueous solutions. In the latter case, the so-called hydrophobic interaction between water and hydrocarbon groups is the major factor which gives rise to a favourable entropy increase, whereas for non-aqueous solutions it has been argued that the dipole-dipole interaction between polar head groups provides the major interaction (8-11). An important consequence of this is that in non-aqueous solutions aggregates form at very low concentrations with a range of sizes. This size range changes continuously and slowly with concentration and there is no critical micelle concentration as seen in aqueous solutions.

Consider a sodium salt of general formula NaX. The aggregation process can be then conceived as follows:

$$2NaX \rightarrow (NaX)_2 \qquad \text{(i)}$$

$$NaX + (NaX)_2 \rightarrow (NaX)_3 \qquad \text{(ii)}$$

$$NaX + (NaX)_{n-1} \rightleftharpoons (NaX)_n \qquad \text{(iii)}$$

These equilibria involve only uncharged dipoles. Ions are then produced via processes such as:

$$(NaX)_n \rightleftharpoons [(NaX)_p Na]^+ + [(NaX)_q X]^- \qquad \text{(iv)}$$

where $n = p + q + 1$

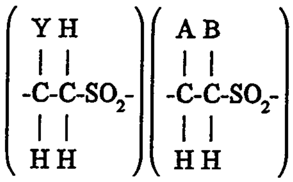
Charged groups such as these will, of course, be present at extremely low concentrations and will give rise to electrical conductivity. Theoretical treatment of such equilibria is being examined but will not be reported in this paper.

5.2 STADIS 450

In a previous paper (3) we briefly discussed the conductivity-improving mechanism of STADIS 450 and argued that an increase in acid strength of one carboxyl can occur due to the combined activating influence of neighbouring sulphone and carboxyl groups. This effect, combined with the proton-acceptor properties of the polyamine component, could lead to ion production. However, polyamine is not essential for conductivity improvement and polysulphone alone is sufficient (6). The polysulphone present in STADIS 450 and that described by Johnston (6) are apparently identical and contain the carboxyl group.

5.3 Conformational Properties of the Polysulphone Component of STADIS 450.

The polysulphone component is a co-polymer of an alkene with suphur dioxide of general formula:



$$\left(\begin{array}{c} Y\ \ H \\ |\ \ | \\ -C-C-SO_2- \\ |\ \ | \\ H\ \ H \end{array}\right)\left(\begin{array}{c} A\ \ B \\ |\ \ | \\ -C-C-SO_2- \\ |\ \ | \\ H\ \ H \end{array}\right)$$

According to Mansfield (12) such polymers exist as random coils or helices depending on the presence or absence of groups A and B in trans positions. Sulphone groups which are present in helix structures interact co-operatively to give large dipole moments. For STADIS 450 the range of polysulphone structures can vary from 0% of (b), in which case the repeat unit has only a single side group and helix formation is favoured, to 10% of (b), in which case one-in-five repeat units has one side group on each of the two adjacent carbon atoms. The latter will be trans and will disrupt the helix structure. Any percentage between these values will clearly give a product mixture which includes some degree of helix development.

We can envisage that a given polysulphone molecule will contain a series of helical segments, each having a dipole moment determined by the number of repeating units present, joined by single units containing trans-configured carboxyl groups. The latter will add flexibility into the total chain and may allow helical segments from the same molecule to interact. We also note that the polysulphone can be considered as a polyelectrolyte and this is discussed in sections 5.4 and 5.5.

5.4 Polysulphone Conductivity

Since polysulphone alone is capable of imparting conductivity this implies that the polysulphone molecule itself is able to stabilise ions. The candidate group for this role, within the molecule, is the sulphone group which has been shown to have proton acceptor properties as indicated by its interaction with phenol (14). Phenolic hydroxyl groups are, in general, considerably weaker proton donors than carboxyl, as measured in both aqueous and non-aqueous solution (15). This suggests that sulphone-carboxyl interactions will be even stronger. We therefore suggest the following two-step process:

$$R\,COOH + R\,SO_2 \rightleftharpoons R\,COOH\,O_2SR \qquad \text{(v)}$$

where R represents the remainder of the polymer chain

$$R\,COOH\,O_2SR \rightleftharpoons [R\,COO]^- + [HO_2SR]^+ \qquad \text{(vi)}$$

Additional stabilisation will arise from interaction of ions with dipolar helical segments either from a part of the same or a different molecule. It is important to bear-in-mind that ion concentrations are always very low and that the majority of carboxyl groups remain undissociated.

5.5 Effect of Salts on STADIS 450

We interpret the effects as being due to interaction with polysulphone. The interaction of salts with this polyelectrolyte (polysulphone) is considered to involve ion exchange in which Na exchanges with H from a carboxyl group. The resulting sodium carboxylate has no proton donor properties so that reactions (v) and (vi) are no longer possible and the conductivity decreases. From equilibrium arguments we should expect the extent of exchange to depend directly on the salt concentration in solution. We note that the kinetics of this process need not be instantaneous and this may account for time-dependent effects.

Another effect of such exchange is that it is accompanied by a considerable change in polarity, expected to influence the coil and cause it to extend. Any ions stabilised by such extended chains will now have reduced mobilities and this will also contribute to a reduction in conductivity.

A given concentration of STADIS corresponds to a certain concentration of carboxyl groups and replaceable hydrogen. As salt concentration increases the number of hydrogens replaced will increase to a limit determined by carboxylate concentration. We therefore expect the conductivity to *decrease* to a limit. However, as salt concentration increases, ion stabilisation via aggregation processes, similar to reaction (iv), may increase in importance. Self aggregegates of salt may be of secondary importance and we suggest that the primary stabilisation of ions is due to interaction with the polysulphone and /or polyamine. In the former case favourable sites could be strong helix dipoles.

We suggest that the combined influences of polymer chain expansion, proton reduction and sodium ion increase, provide a qualitative explanation of the conductivity minimum.

5.6 Effect of Parent Phenol

We suggest that the detrimental effect of dodecylphenol is caused by reduction in the availability of sulphone groups due to complexation with phenol in reactions similar to that represented by equation (v). In this instance however, the phenol complex does not undergo the ion-producing step, principally because it is a much weaker proton donor.

6 CONCLUSIONS

6.1 Sodium salts of acidic species, present in jet fuel, interfere with the conductivity improving properties of STADIS 450.

6.2 The precise effects on conductivity depend on both STADIS 450 concentration and salt concentration. In general, increasing salt concentration causes the conductivity of the STADIS solution to fall to a minimum and thereafter to increase continuously.

6.3 For normal doping levels of STADIS 450, conductivity losses of up to 50% are observed at 'low' salt concentrations.

6.4 Related to 6.3 is the fact that at low salt concentrations the conductivity response, to STADIS 450 addition, is much reduced.

6.5 For normal doping levels of STADIS 450, significant conductivity enhancement occurs at 'high' salt concentrations.

6.6 Phenols can have a large detrimental effect on STADIS performance. Conductivity losses of up to 70% have been observed at phenol concentrations 'typical' of those in jet fuel.

6.7 The conductivity of these solutions has been explained in terms of the ionisation propensity of groups, the ability of other molecular groupings to stabilise ions and the conformational properties of polyelectrolytes.

7 ACKNOWLEDGEMENTS

The authors wish to thank additive manufacturers and oil companies, especially BP, for their helpful cooperation and supply of additives and fuels. They would also like to express their gratitude to the sponsors of this work, The Procurement Executive, M O D, Dept. F S(AIR) 53, St Giles Court, London WC2H 8LD under Contract FS 1a/375,1993.

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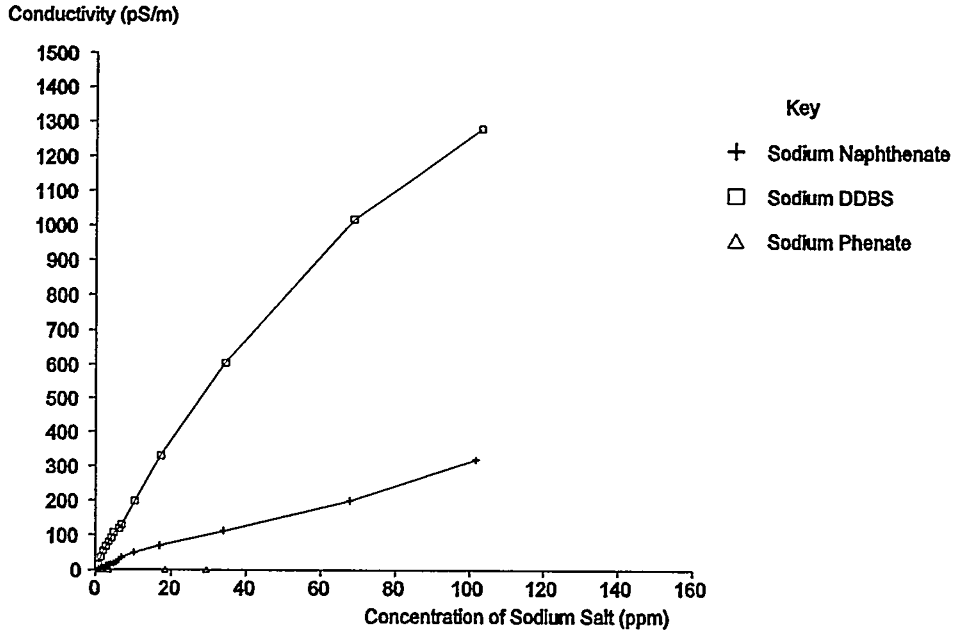

Figure 1 Effect of Sodium Salts on the Conductivity of Dodecane

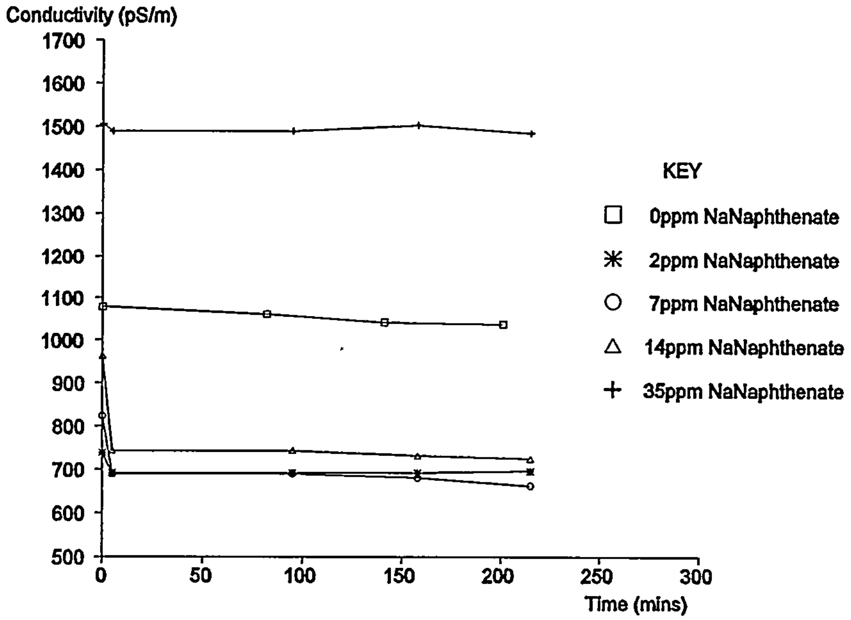

Figure 2 Change in Conductivity with Time for 3ppm STADIS/Dodecane Solution Containing Sodium Naphthenate

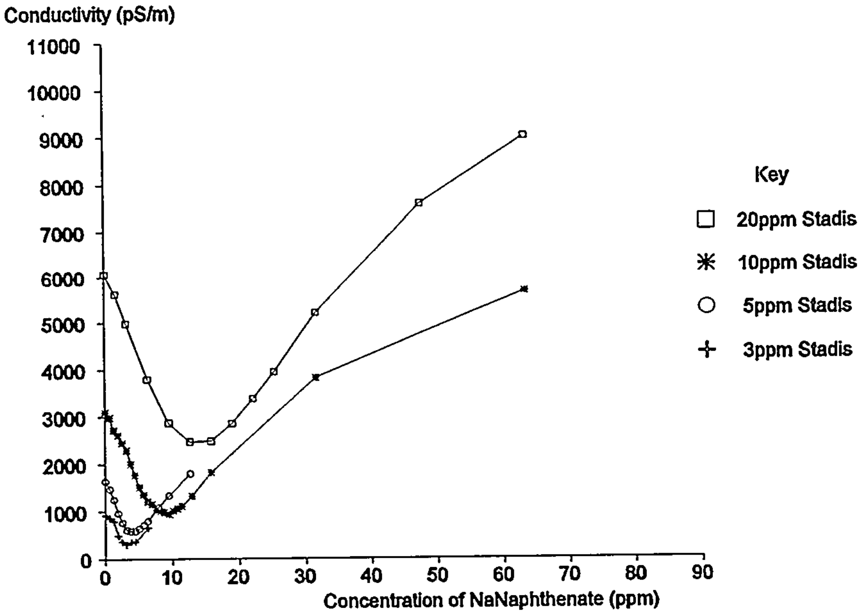

Figure 3 Change in Position of Conductivity Minimum with STADIS Concentration for STADIS/Dodecane/NaNaphthenate Systems

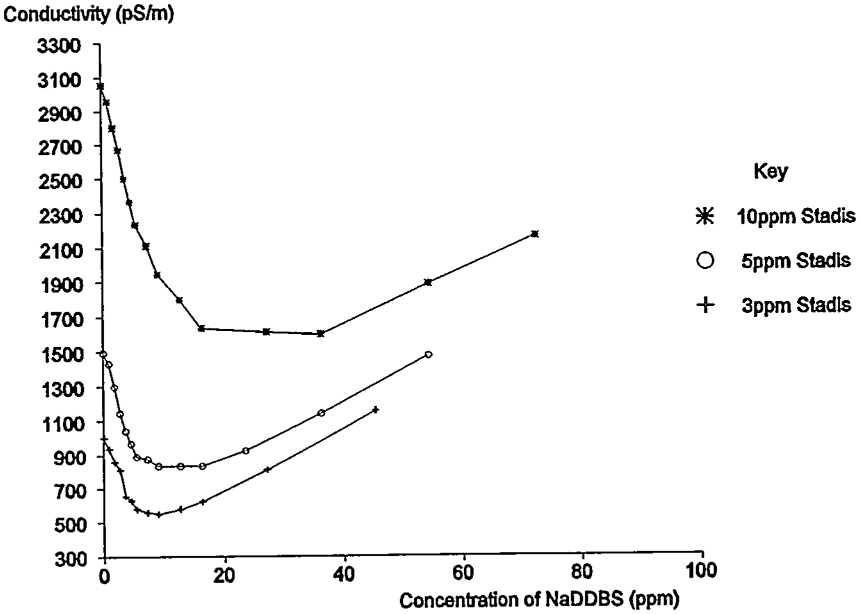

Figure 4 Change in Position of Conductivity Minimum with STADIS Concentration for STADIS/Dodecane/NaDDBS Systems

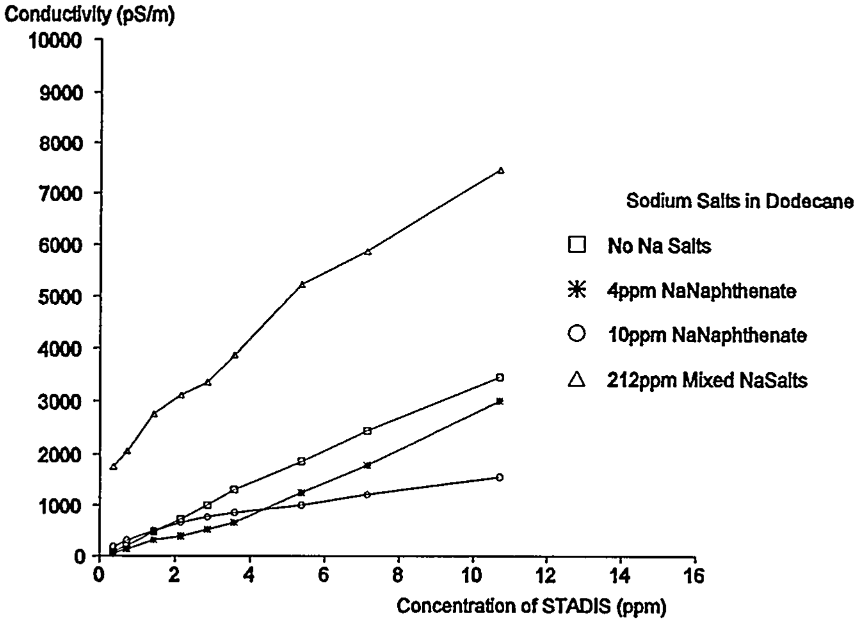

Figure 5 Additions of STADIS to Dodecane Containing Sodium Salts Effect on Conductivity

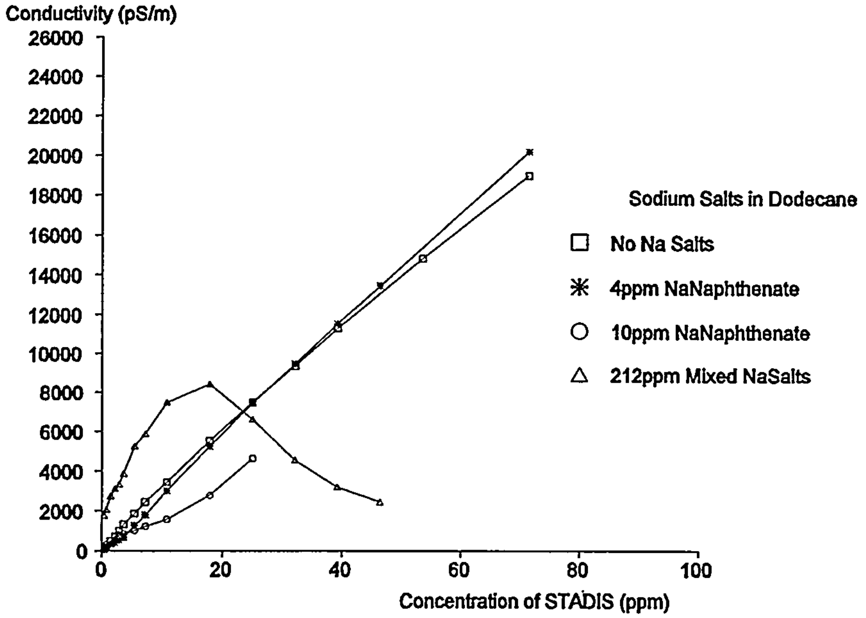

Figure 6 Additions of STADIS to Dodecane Containing Sodium Salts Effect on Conductivity

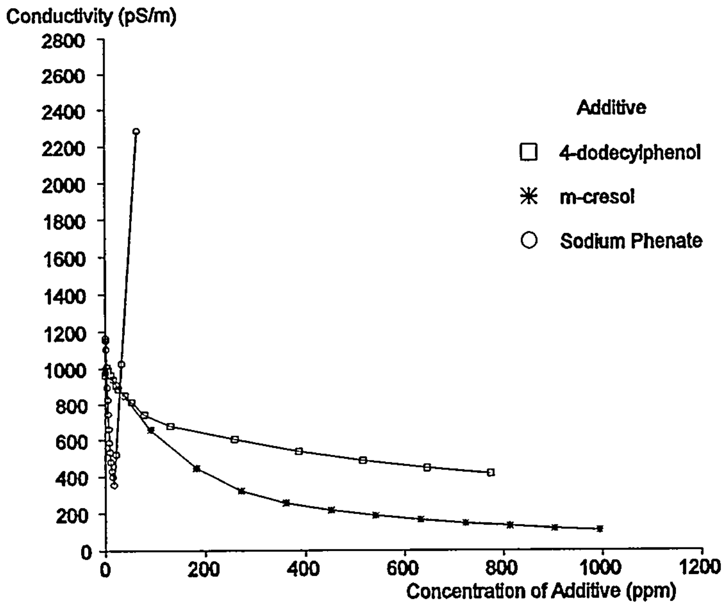

Figure 7 Effect of Phenols on the Conductivity of 3ppm STADIS in Dodecane

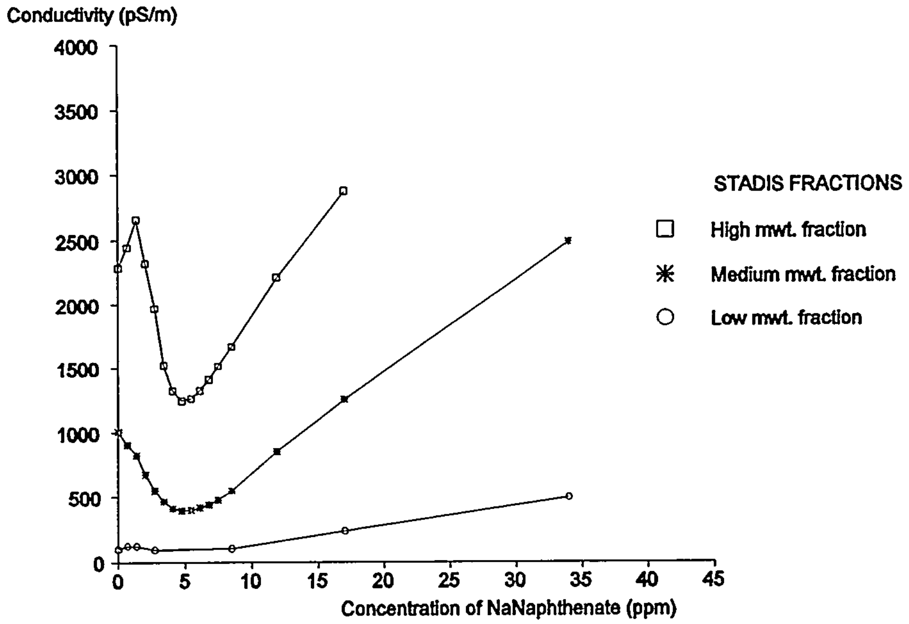

Figure 8 Effect of NaNaphthenate Concentration on the Conductivity of STADIS Fractions in Dodecane

Substance type	**Merox Fuel**
Naphthenic Acid + Naphthenate	<0.1 to 10ppm
Sodium Naphthenate	to ~10ppm
Phenol + Phenate	160 to 750ppm
Sodium Phenate	to ~10ppm (?)
Sulphonic Acid + Sulphonate	~0.3ppm[1] [2]

Table 1 **Suggested Concentrations of Polar Constituents in Jet Fuel**

Parameters at minimum in conductivity curves	**Concentration of STADIS in Solution**			
	3ppm	**5ppm**	**10ppm**	**20ppm**
Concentration of Sodium Naphthenate (ppm)	3.2	4.2	9.4	14.2
Ratio of STADIS (ppm) to Sodium Naphthenate (ppm)	0.9	1.2	1.1	1.4
Conductivity at minimum (pSm^{-1})	305±12	580±23	960±39	2400±96
Conductivity at minimum normalised for concentration of STADIS (pSm^{-1})/ppm	101±4	116±5	96±4	120±5
Depth of minimum (pSm^{-1})	616±49	1057±89	2138±161	3658±338
Depth of minimum normalised for concentration of STADIS (pSm^{-1})/ppm	205±16	211±18	214±16	183±17

Table 2 **Values of Parameters at Minima in Conductivity Curves for STADIS/NaNaphthenate/Dodecane Solutions.**

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[1] By methylene blue method. Determination limit is 0.03ppm. Only surfactant sulphonates are detected and therefore some sulphonates could be missed.

[2] Higher values for strong acids, 5 to 14ppm, have been measured for two sweetened fuels (ref.4).

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STADIS® 450 IN MEROX-SWEETENED JET FUELS

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ABSTRACT

Stadis® 450 has been used in aviation fuels since 1983, and in many cases is the additive of choice due to conductivity retention of treated fuels during distribution, and other characteristics. In the past several years, manufacture of Shell ASA-3 (the other aviation-approved static dissipator additive) has been discontinued; current stores are being drawn down and for some refiners conversion from ASA-3 to Stadis® 450 is underway. In fuels sweetened by hydrogen-treating, Stadis® 450 performs very well and there are few reported difficulties. Chemically sweetened fuels sometimes contain trace materials not removed by the sweetening process. When treated with Stadis® 450 some of these fuels have exhibited two behaviors which are being addressed: in one case, the formation of a precipitate which disarmed coalescers; in several other cases, reduced conductivity response and loss of conductivity during storage coupled with unusually large effects on the microseparometer water separation properties. In late 1992, a Coordinating Research Council (CRC) Panel on Coalescer Deactivation was formed to address these problems. The results of DuPont and CRC efforts are discussed, along with actions taken and underway to eliminate these problems.

HISTORY

Stadis® 450 has been increasingly used in aviation turbine fuels since 1983, when approvals by turbine and airframe manufacturers were obtained and followed by ASTM, the United Kingdom Ministry of Defence, International Air Transport Association, Canadian General Standards Board, and the United States Air Force acceptance. This culminated a nine-year effort, during which more background data were generated in support of acceptance than for any other additive before or since that time. These data included studies of compatibility with co-additives, effects on aircraft fuel system materials, extensive electrostatic performance studies, and so on.

Use of Stadis® 450 in aviation fuels which are hydrotreated has not presented known difficulties; in fact, in most fuels Stadis® 450 provides superior retention of conductivity during distribution and minimally affects water separation properties. In 1984, however, it became clear that jet fuels from certain refineries presented difficulties in meeting both conductivity and water separation requirements. These refineries used Merox™ processes to sweeten fuel. Fuels produced

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by this process sometimes give poor initial conductivity response, and/or show loss in conductivity during storage, and often have greater reduction in the ASTM D3948 water separation rating than hydrotreated fuels. The overall effect is to make it difficult to deliver fuel to airports meeting both conductivity and water separation requirements. Studies of these fuels resulted in several conclusions.

- **The Merox process itself did not add trace materials.**

This conclusion resulted from studies at three refineries where fuel samples were obtained before and after Merox processing; in all cases Stadis® 450 gave better performance in the fuel samples obtained following the complete process. For purposes of this discussion, the "Merox Process" is defined as the typical combination of caustic pre-wash, exposure to the sweetening catalyst, water wash, salt drying, and clay filtration. In addition, Merox-sweetened fuel from another refinery using Stadis® 450 with no difficulties was evaluated; in that case, the feed to the Merox process also gave lesser performance. The Merox process (and probably, other less-studied chemical sweetening processes) simply fails to remove trace contaminants as effectively as hydrotreating.

- **Refinery Chemicals can be the cause of conductivity/MSEP interactions.**

This conclusion resulted from analysis of trace fuel components from one refinery's fuel, and from comparison with the effects of a filming amine used in the refinery.

- **Studies showed similarity in the behavior of Stadis® 450 and ASA-3.**

Figure 1 shows data previously published[1] from addition of several refinery additives to a clean Jet A fuel. These data showed, surprisingly, that some materials which affected Stadis® 450 also gave similar results with ASA-3. The antifoulants and filming amine corrosion inhibitor used in this study were obtained from a refinery where they were in use. Other conductivity additives, not approved for aviation fuels, also are affected by trace materials in fuels.

In spite of these findings, however, a period of equilibrium was established, during which refiners and others evaluated both Stadis® 450 and ASA-3 in their fuel, chose the one which gave the better performance, and went their way - even though, in a few cases, they may not have been happy with their choices.

RECENT FINDINGS

In 1991, the equilibrium changed. Shell announced that manufacture of ASA-3 was being discontinued, and refiners and others who had been using that product began a transition to use of Stadis® 450. Most refiners, regardless of the sweetening process in use, are able to provide fuel in which the performance of Stadis® 450 is satisfactory. One has had continuing problems; some have "spot" problems which come and go, apparently due to crude slate.

In the meantime, another concern was raised: coalescers from the Munich airport were found to contain a significant quantity of a fuel-insoluble sulfonate, ultimately identified as sulfonates of dodecylbenzenesulfonic acid, which is a component in Stadis® 450. These materials appear to originate from an interaction of a fuel component with dodecylbenzenesulfonic acid - which normally remains dissolved in the fuel - to form a viscous liquid precipitate which tends to collect on coalescer elements.

The sulfonate precipitate is thought to be a salt. The primary fuel supply for Munich is from one refiner, who produces a Merox-processed high-quality fuel in all other aspects; it is derived from Libyan crude oil and generally has aromatics content in the 12-14% range. Isolation of the cation from the sulfonate has not been possible. Examination of coalescers from several other locations has revealed traces of dodecylbenzenesulfonates, which are expected due to simple absorption by the filtration media, but many times less than the level found on the coalescer from the Munich airport fuel system. Figure 2 shows results from analysis of toluene extracts from the Munich and other filters. "Sulfonate" levels refers to the total strong acid content of the filter, determined by a spectrophotometric technique. "Solids" are the content of dissolved, non-volatile material determined by evaporation of the toluene extract. "DDBSA" is the actual level of dodecylbenzenesulfonates, determined by HPLC. These data show that the DDBSA content of the Munich filter is higher than that from other filters in long service. Similar levels of "sulfonates" and DDBSA were found on the inner filter pleats and the outer fiberglass wraps.

As a consequence of these concerns, a CRC Panel on Coalescer Deactivation was formed to gather knowledgeable individuals and address both types of problems. This group is currently co-chaired by Edward Matulevicius, Exxon R&E, and Victor Hughes, Shell- Thornton. The group has met several times in the USA and in Europe. This group has work underway to identify interfering species in fuels leading to both types of concerns, and other efforts; in addition, the group provides a vital advisory function to help guide DuPont and recommend industry action.

The conductivity/water separation difficulties and the insoluble sulfonate problem require separate approaches, and hereafter will be discussed separately. These differ both in origin and the nature of the solution(s) to be applied. The sulfonic acid in Stadis® 450 is present as a storage stabilizer for the neat additive; when the additive has been diluted to use concentration it is no longer essential, although it has an obvious effect on water separation properties. The conductivity/water separation problems, however, are due to trace contaminants which interact with all the major components in Stadis® 450.

INSOLUBLE SULFONATES: PROBLEM DEFINITION AND SOLUTION

The sulfonates on a Munich airport filter were extracted with hot toluene. Sodium was the only metal cation present in high concentration relative to toluene extracts from other filters, although the sodium content of the fuel was known to be very low, in the 10 to 15 parts-per-billion range. Unless pre-dissolved in a solvent such as ethanol, sodium sulfonate has very poor solubility in jet fuel. It appears possible that sodium may be involved along with perhaps other materials such as amines, which in the relatively low aromaticity fuel have poor solubility as dodecylbenzenesulfonates.

ÖMV, the primary fuel supplier to the Munich airport, has carried out a number of refinery tests and has developed a rig test to further define the circumstances under which insoluble sulfonates occur. The rig test involves passing 700 liters of dry fuel through a section of a coalescer, then challenging the coalescer section with a fuel/water emulsion to determine if it is disarmed. If not disarmed, the fuel is considered to have passed; if disarmed, the result is considered a failure. Results are summarized as follows. Visual assessment is a primary criteria, as in a single element coalescer test.

- **Stadis® 450 in Berghausen fuel fails.**
- **Stadis® 450 components without dodecylbenzenesulfonic acid pass.**
- **Dodecylbenzenesulfonic acid alone fails.**
- **Stadis® 450 in a hydrotreated jet fuel passes.**
- **Stadis® 450 formulated with dinonylnaphthylsulfonic acid in place of dodecylbenzenesulfonic acid passes.**
- **Fuel Blends containing regular Stadis® 450 in hydrotreated fuel and modified Stadis® 450 in the Berghausen fuel pass.**

These results have led us to consider modification of the Stadis® 450 formulation to use dinonylnaphthylsulfonic acid (DINNSA) in place of dodecylbenzenesulfonic acid (see Figure 3). Substantial efforts have been carried out to evaluate the modified formulation; this has included comparison of electrostatic charging properties, comparisons of conductivity-improving performance and effects on water separation in various Merox-processed and other fuels, verification that thermal stability is not affected, and evaluation of compatibility with other additives used in aviation fuels. These studies have not revealed any flaws in the modified formulation.

Metal salts of DINNSA are well-known to have uniquely good solubility properties in hydrocarbons. A C23 alkylbenzenesulfonic acid was also evaluated and gave improvement, and it is likely a source of such acid could be found which would give satisfactory results. However, DINNSA has several advantages - while more expensive, it is a higher-quality, uniform product which can be expected to remain consistent as a component in Stadis® 450; formulations containing it gave somewhat better conductivity, and DINNSA is registered on all the major chemical inventories.

Utilization of this approach to solve the insoluble sulfonate problem is considered necessary because of failure to identify the cation responsible for the problem, and because formation of very minute levels of insoluble sulfonates is not easily detectable by the usual aviation fuel quality control tests or other laboratory tests suitable for quality control purposes.

Additional testing has been completed in ÖMV facilities to determine whether commingling of fuels containing regular and modified Stadis® 450 give satisfactory performance. Results were satisfactory.

In the meantime, data to support the modified formulation has been presented to representatives of fuel suppliers, airlines, and equipment manufactures at the December 1993 meeting of ASTM Committee D-2 Subcommittee J on Aviation Fuels[2]. There were no objections to field trials with modified Stadis® 450. Test quantities are being supplied to coalescer manufacturers and others on request, and a field trial will hopefully be arranged at the Munich Airport. If satisfactorily completed, it is expected that the modified product will become the only product manufactured, following full acceptance by equipment manufacturers and specification bodies.

An alternate solution to modification of the acid component in Stadis® 450 would be to use the other components independently, so that the storage stabilizer is not needed. This approach was not considered practical. Still another approach would be to eliminate the causative factor from the fuel. Unfortunately, that could be accomplished with assurance only by a requirement to hydrogen treat, or by development of an appropriate test to determine whether fuel would react to form insoluble sulfonates. Thus far, this has not been possible. Overall, the use of DINNSA-modified Stadis® 450, where one alkyl aryl sulfonic acid is substituted for another alkyl aryl sulfonic acid, is the best solution. In terms of chemical activity, these two materials are very similar. The primary difference is in the size of the hydrocarbon moiety, which affects solubility of sulfonate salts in hydrocarbons.

CONDUCTIVITY/MSEP INTERACTIONS

Having some assurance of an ultimate solution of the insoluble sulfonate problem, our full attention is now turning to resolution of the conductivity/water separation interaction concerns. We are assuming that extraordinary measures to resolve these concerns are inappropriate. Thus, for example, a recommendation to install hydrogen-treating facilities to replace Merox or other chemical sweetening units is not a satisfactory solution, since the cost of these units for that purpose alone is totally unreasonable.

In general, conductivity/MSEP interactions do not appear to be a continuing problem for many refiners. We are aware of one refiner who encounters serious, ongoing interactions to the point of extreme difficulty in meeting conductivity/MSEP requirements using Stadis® 450. ASA-3 also causes problems at this location, but when conductivity declines with ASA-3 the MSEP values recover, so that re-doping is more practical. Several others have moderate but tolerable ongoing concerns. The most frequent occurance is at refineries where Stadis® 450 is normally used with no problems - then for reasons not yet defined but perhaps due to crude oil slate, poor conductivity/MSEP values are occasionally obtained. In such cases, the quality of the Stadis® 450 in use is often questioned, and in all cases to date it has proved to be typical.

Modified Stadis® 450 may provide some relief for these refiners; however, preliminary results show that a change in the stabilizer acid component does not result, on average, in improved behavior in problem Merox-sweetened fuels. However, there are some fuel-to-fuel differences which might be of benefit for some refiners. Other changes in Stadis® 450 composition are probably not acceptable without re-initiating the entire approval process. An effort is underway to assure that the individual components in Stadis® 450 are optimized within the bounds of the "aviation approvals" so that effects on water separation are minimal.

Conductivity-improving performance and the effect on water separation should not be used as independent parameters for the purpose of evaluating this phenomenon. The primary concern is not the amount of additive needed to achieve a conductivity of 50 pS/m or more when measured; it is the balance of conductivity improvement and effect on water separation which interests refiners and others. It is helpful to use a combined parameter which has been dubbed the "Conductivity Microsep Factor", or "CMF"(see Figure 4).

A DuPont test method has been written[3] to define CMF and cites an experimental procedure to obtain CMF values, which are defined as follows:

$$\mathrm{CMF} = \frac{\Delta\ \mathrm{CONDUCTIVITY}}{\Delta\ \mathrm{MSEP\ VALUE}}$$

CMF values are simply pS/m of conductivity obtained in a fuel per unit of ASTM D3948 loss. Preferably, these values are obtained on fuels which are first treated with 1 mg/L of Stadis® 450, then stored for a period of two weeks. The conductivity after two weeks will at least substantially indicate any trace materials, if present, which cause a loss in conductivity during storage. The D3948 MSEP test is carried out on the fuel; a CMF value can then be calculated which reflects both conductivity improvement (including storage effects), and water separation effects. The weak link in this test is the MSEP value; the test should be replicated at least twice.

Typically, the CMF values for clean, hydrotreated Jet A-1 fuels are 15 to 30, which means that when treated to give a conductivity of 150 pS/m, an MSEP loss of 5 to 10 units is obtained; clearly acceptable performance. As CMF values approach 10, less favorable results are expected. For values of less than 5, significant difficulties are likely since to achieve a conductivity of 150 pS/m or more, a MSEP loss of more than 30 is obtained.

When the current effort was initiated, it appeared that low CMF values were likely due to carryover of refinery chemicals such as filming amines. In a few instances that has indeed been the case, and refiners should be aware of this possibility when low CMF values occur. A more likely cause, it appears now, is carryover of trace materials from the crude oil. Several ways to eliminate or reduce these impurities which have been explored to date.

Clay filtration under vigorous laboratory conditions, such as in ASTM Test Method D3948 Appendix X1, has in nearly every case removed trace materials and resulted in fuel which gives high CMF values. In the refinery, however, it appears that clay filtration begins to pass through some interacting species more quickly than strongly polar surfactants. Nonetheless, the refiner should review the operation of the Merox unit, examining the adequacy of the caustic wash, water wash, and the condition of the clay tower.

Several other approaches have been examined to date; each has shown some promise in limited evaluations.

- **Alumina filtration as a follow-on to clay filtration.**

Results from laboratory long-term filtration through clay has shown that its capacity to remove interacting species is quickly exhausted with some fuels. Supplemental filtration through alumina, a more active absorbent, has proven effective; the alumina activity is long-lived and it might be re-generated. If regeneration proves practical, alumina filtration economically competitive when clay disposal costs are also considered. See Figures 5 and 6, which illustrate results of laboratory filtration.

- **Improved water wash is effective.**

Three refiners' fuels were satisfactorily improved by simply water washing the fuel.

- **Dilute acid wash can be effective.**

Caustic washing is part of the Merox process and effectively removes acid species. Some amines are not removed by caustic or water washing; use of an acidic water wash (containing sodium dihydrogen phosphate or citric acid, for example) removed interacting species from two refiner's fuel. This solution may be appropriate if caustic carryover to water wash is minimal. Figure 7 illustrates the degree to which amines are removed from fuels by washing fuel with aqueous solutions of various pH. In general, water or dilute acid washed fuel should be passed through a laboratory salt dryer before evaluating Stadis® 450 performance. What is now needed, however, is an examination of these solutions over a period of time at specific refineries, so that effects of varying crude slates are understood.

Overall, it appears that modest improvements to the Merox process may overcome all but the most recalcitrant fuels. We are working closely with a few refiners to seek solutions to their particular cases. In the meantime, we welcome discussions with other refiners regarding specific circumstances at their locations. Two DuPont test methods[4,5] have been developed and written to determine trace levels of acidity and basicity in jet fuels; these are known to affect Stadis® 450.

We are suggesting that refiners who find significant conductivity/MSEP interactions should carry out response evaluations over a period of time so that the scope of the issue at their location is understood. We are quite willing to work cooperatively with anyone so interested. A package of literature has been developed for that purpose which is available on request.

As an aside, findings about the effect of sulfur dioxide on Stadis® 450 have been recently disclosed[6]. These results show that concentrations of SO2 which might result from inadequately scrubbed flue gases used to inert shipments of jet fuel can interact with Stadis® 450 components to give a 50-70% loss in conductivity. Further studies showed that clay-filtering of shipped fuel removes sulfur dioxide and subsequent treatment with Stadis® 450 is unaffected. These findings are in agreement with other studies which show strong suppression of conductivity from acidic species[7].

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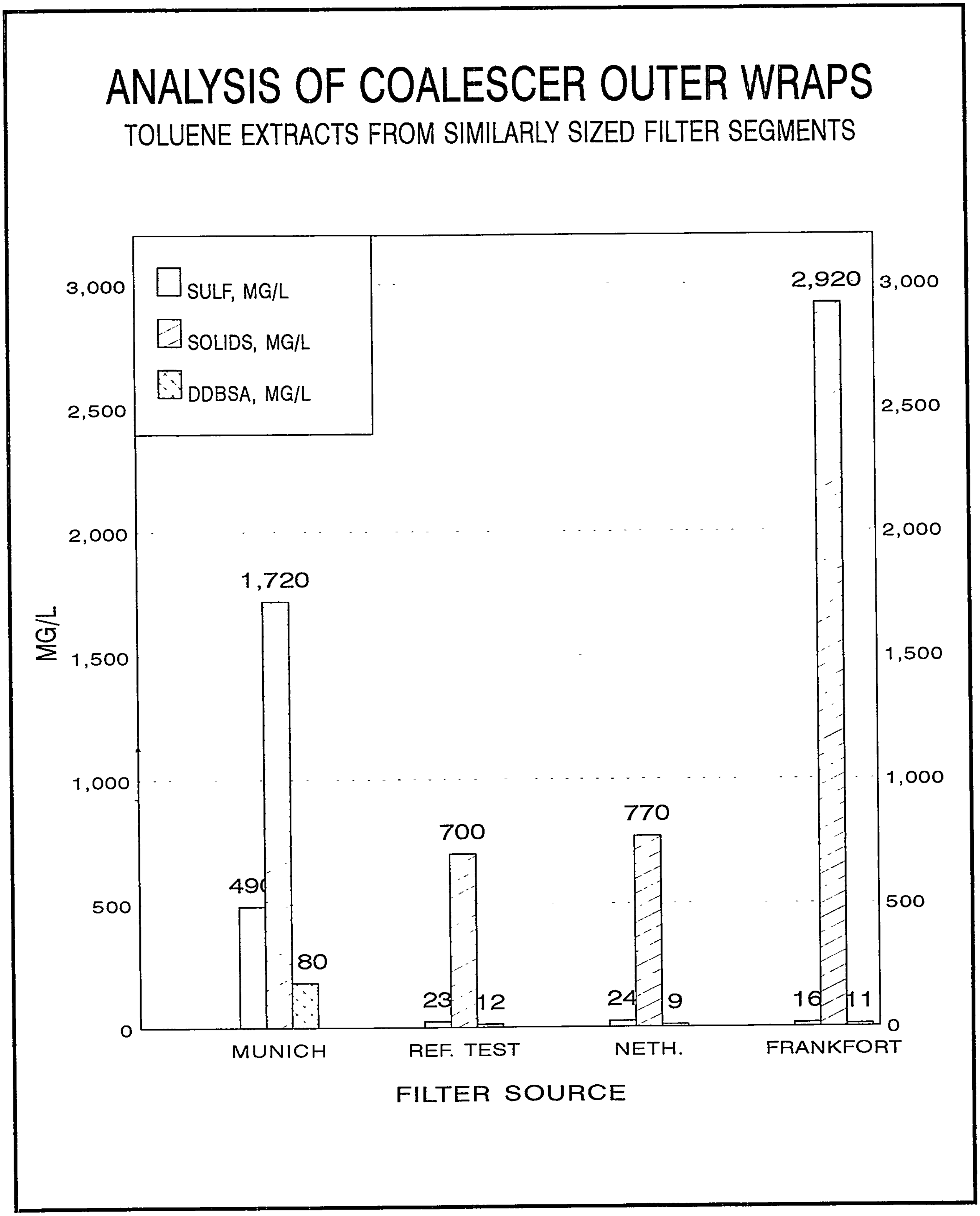
FIGURE 1

SOME ADDITIVES GIVE EFFECTS OBSERVED IN MEROX FUELS

COADDITIVE (CONC,PPM)	COND. ADD. (0.7 MG/L)	INITIAL pS/m	7 DAY pS/m	MSEP D3948
NONE	ASA-3	238	242	92, 95
NONE	S450	200	208	93, 95
ANTIFOUL.1 (5)	ASA-3	94	26	60
	S450	59	71	55
ANTIFOUL.2 (5)	ASA-3	250	215	88
	S450	195	178	84
CORR.INH. (5)	ASA-3	185	65	56
(FILMING AM.)	S450	155	128	66
NaOH (2)	ASA-3	250	190	91
(1% IN WATER)	S450	210	175	99
WATER (200)	ASA-3	270	255	94
	S450	225	221	94

FIGURE 2



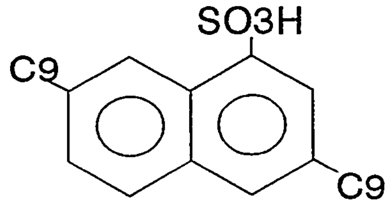
ANALYSIS OF COALESCER OUTER WRAPS
TOLUENE EXTRACTS FROM SIMILARLY SIZED FILTER SEGMENTS
SULF, MG/L
SOLIDS, MG/L
DDBSA, MG/L
MG/L
3,000
2,500
2,000
1,500
1,000
500
0
1,720
490
80
700
23
12
770
24
9
2,920
16
11
MUNICH
REF. TEST
NETH.
FRANKFORT
FILTER SOURCE

FIGURE 3

PRECIPITATE PROBLEM
HOW TO SOLVE?

1. IDENTIFY AND ELIMINATE CO-REACTANT FROM FUEL
    - -- NOT POSSIBLE TO DATE
    - -- MAY NOT BE PRACTICAL
2. ELIMINATE THE OTHER CO-REACTANT IN STADIS®450
    - -- ELIMINATE DDBSA
    - -- USE ALTERNATE ACID

DINONYLNAPHTHYLSULFONIC ACID
(DINNSA)



DODECYLBENZENESULFONIC ACID
(DDBSA)

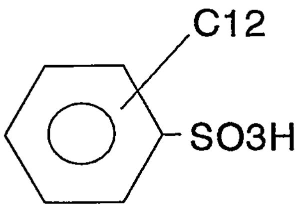


FIGURE 4

PROBLEM DEFINITION

EVALUATION OF FUEL TO DEFINE BEHAVIOR

- DETERMINE BASE FUEL CONDUCTIVITY AND D3948 MSEP RATING
- DETERMINE CONDUCTIVITY WITH 1 MG/L STADIS®450
  (500 ML OR 1 L TEFLON® BOTTLES)
- STORE TWO WEEKS AT ROOM TEMPERATURE
  (PROTECT FROM LIGHT EXPOSURE)
- RE-MEASURE CONDUCTIVITY AND DETERMINE MSEP VALUES
- CALCULATE CONDUCTIVITY/MSEP FACTOR

CMF = 2 WK CONDUCTIVITY/MSEP LOSS

$$= \frac{\Delta \text{ CU}}{\Delta \text{ MSEP}}$$

EXAMPLE: BASE FUEL MSEP = 95

2 WK CONDUCTIVITY = 275 PS/M

MSEP = 82

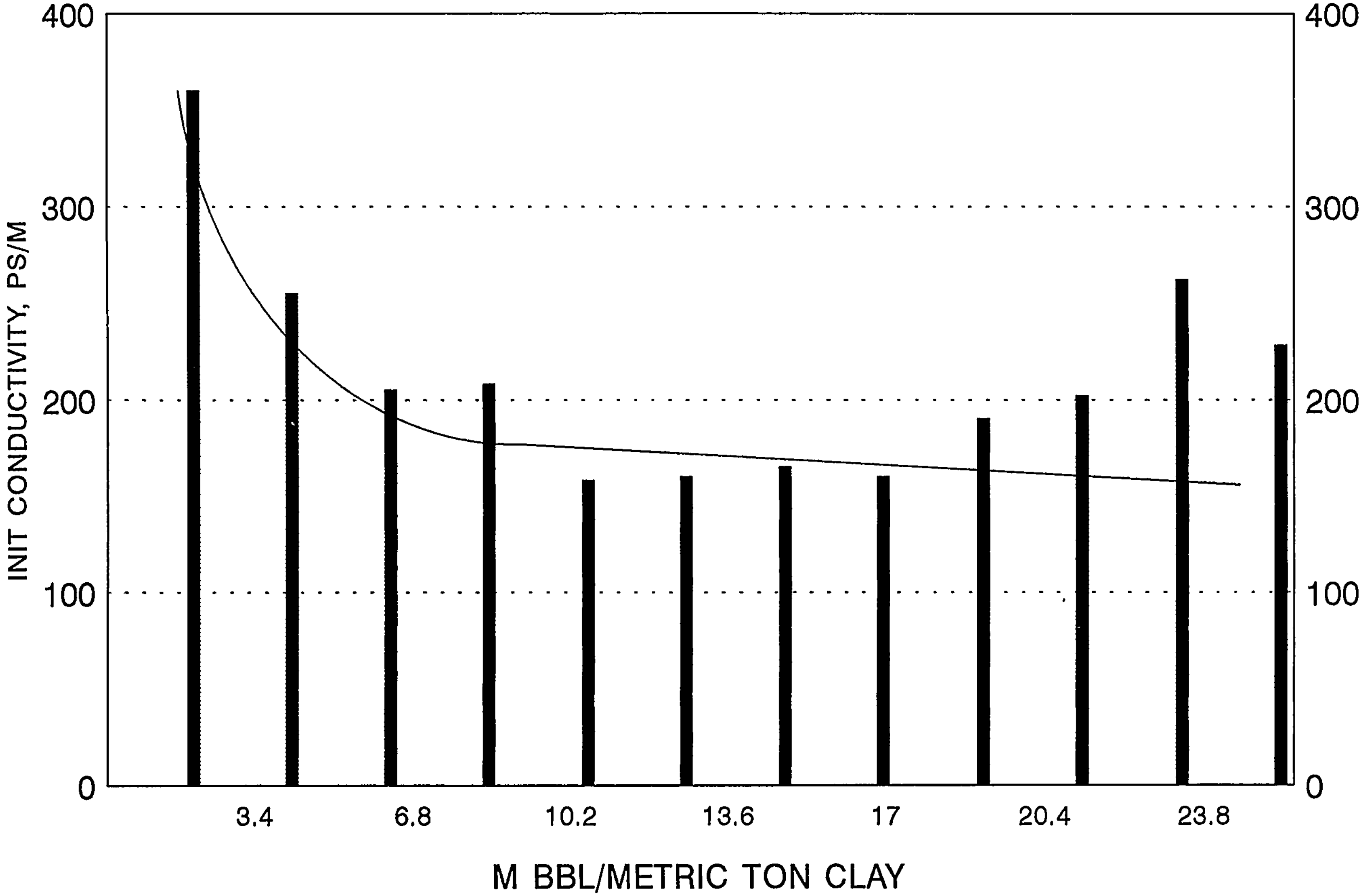
CMF = 21

CMF < 4 = PROBLEMS

FIGURE 5

MEROX FUEL THROUGH CLAY COLUMN

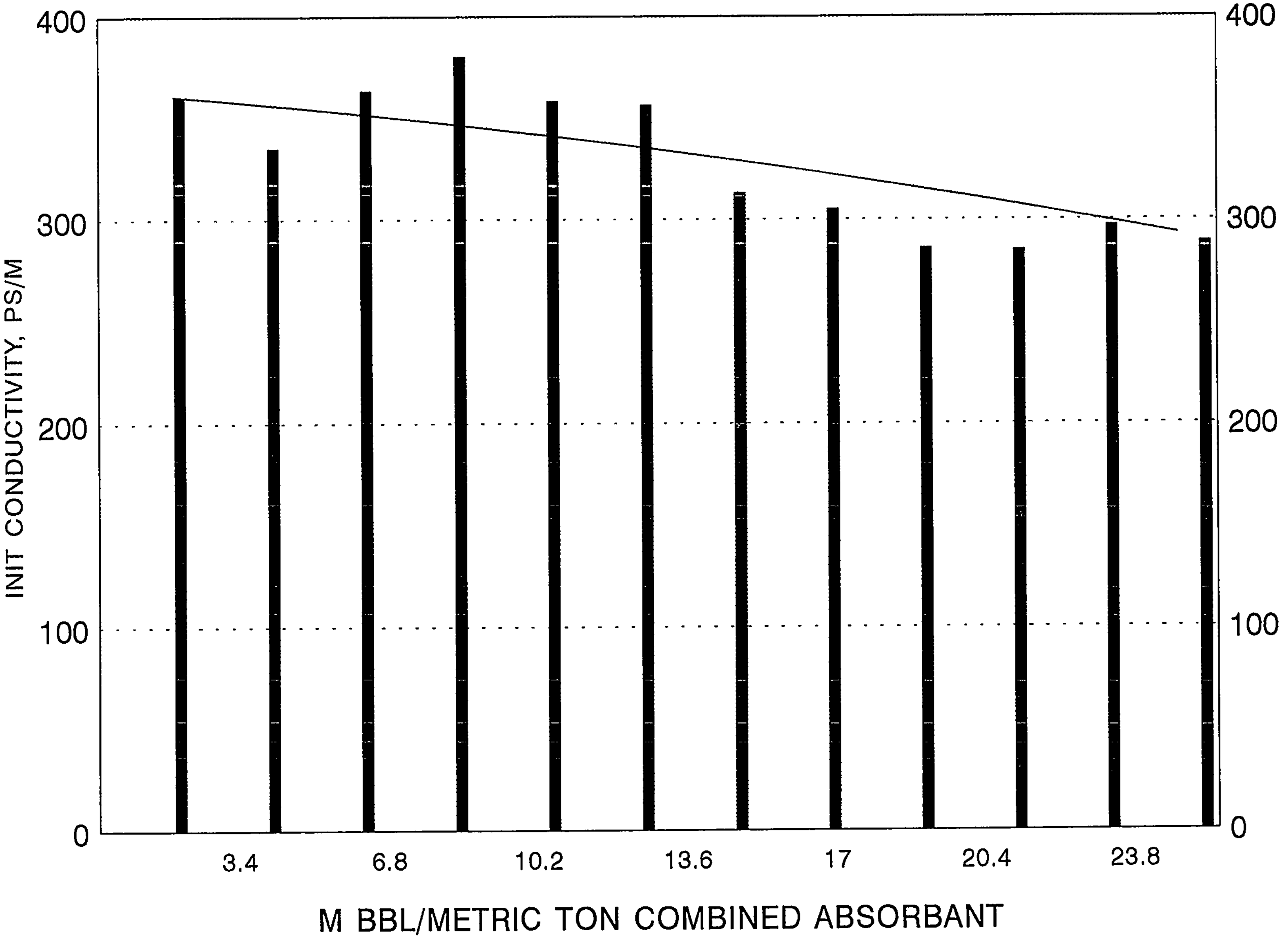
FUEL NOT CLAY TREATED AT REFINERY



15 G CLAY, 1.5 X 13.5 CM COLUMN
AVE FLOW RATE 5 ML/MIN --> 4 ML/MIN
INITIAL AMINE ABS. 0.33

FIGURE 6

CLAY + 20% ALUMINA COLUMN

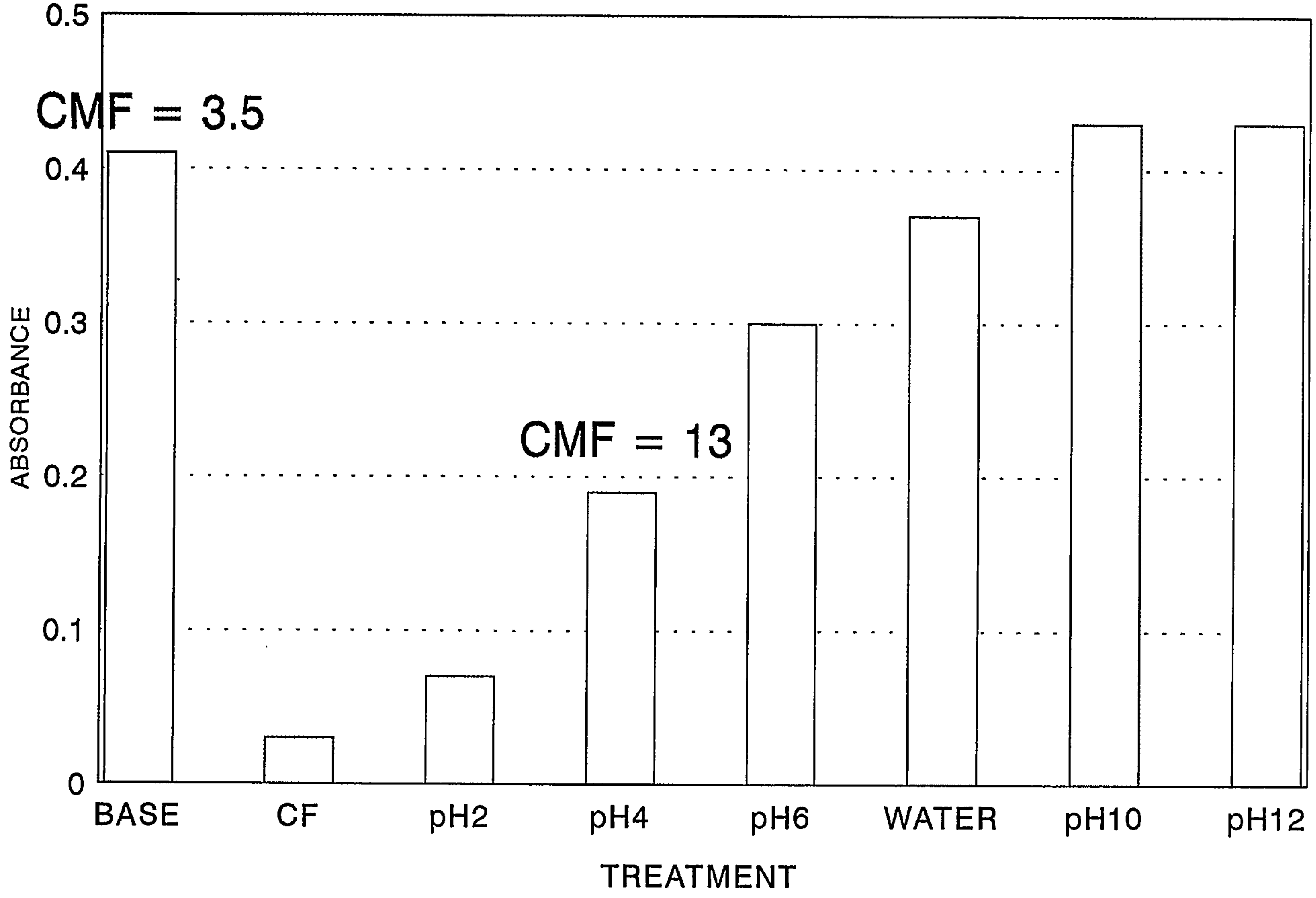


12 G CLAY, 3 G 60 MESH BASIC ALUMINA
AVE FLOW RATE 3 ML/MIN

FIGURE 7

SURFACTANT AMINE IN P92-682 JET A-1

EFFECTS OF CLAY FILTRATION AND WASHING



WASH WITH PH SOLUTION THEN 3X WATER WASH

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

FACTORS AFFECTING THE SILVER CORROSION PERFORMANCE OF JET FUEL FROM THE MEROX PROCESS

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ABSTRACT

The Natref refinery at Sasolburg, South Africa, which is 63,6% owned by Sasol and 36,5% by Total, is producing Jet A-1 fuel at a rate of 80 m^3/h by means of a UOP Merox process. A substantial part of the crude oil slate is made up from crudes which have been stored for considerable times in underground mines. Since the 1970's, Natref has experienced sporadic non-conformance of its treated jet fuel to the silver corrosion (IP 227) test. Various causes and explanations for the sporadic silver corrosion occurrence have been put forward but a direct causal link has remained obscure. The paper addresses these possible causes for silver corrosion and some of the process changes which have been made to alleviate the problem. Emphasis is placed on the most recent approaches which were taken to identify the origin of the sporadic silver corrosion. An inventory of all the potential causes was made, such as bacterial action, elemental sulphur formation in storage, etc. and experiments designed to test the validity of these causes, are discussed. A statistical evaluation which was done of the historical process data over a 2 year period, failed to link the use of mine crudes directly to Ag-corrosion occurrence. However, a correlation between elemental sulphur and H_2S levels in the feed to the Merox reactor and Ag-corrosion was observed. Finally, the outcome of the experiments are discussed, as well as the conclusions which were reached from the observed results.

1. INTRODUCTION

The Natref (National Petroleum Refiners of South Africa (Pty) Ltd) refinery at Sasolburg, South Africa, is 63,6% owned by Sasol and 36,4% by Total South Africa. A substantial part of its jet fuel is produced by means of the UOP Merox process. The refinery processes crude oil at a rate up to 570 m^3/h, while the feed to the Merox unit is 70-80 m^3/h. A substantial part of the crude oil feed frequently consists of crude which has been stored in underground mines for considerable time periods. Alternative sources of jet fuel at the refinery is from the diesel hydrotreating unit when it is on kerosene mode and by means of the distillate hydrocracker, as illustrated in Figure 1.

Since the late 1970's, Natref has experienced sporadic non-conformance of its Merox treated jet fuel to the silver corrosion test for aviation turbine fuels, the IP 227 test[1]. Although the sporadic occurrence of silver corrosion non-conformances on kerosene treated by the Merox process has received much attention over the years, the actual cause or set of causes have remained obscure.

In April 1993, a research project was undertaken by Sasol in conjunction with chemists from the CSIR (Council for Scientific and Industrial Research) to identify the causes of silver corrosion occurrence in treated kerosene. It was believed that the cause would firstly have to be established and proven by experiments before the subsequent elimination thereof could be considered.

2. HISTORICAL BACKGROUND

Over the past 20 years, adherence to the silver corrosion specification has cost Natref a considerable amount of money in terms of limiting refinery flexibility, enforced sub-optimal production options, capital investments, reprocessing costs and management time.

Various changes to the Merox plant have also been made in an attempt to eliminate the intermittent non-conformance of the product to the Ag-corrosion test. The most noteworthy of these was the installation of a clay filter in 1984 and the installation of a Merichem contactor (Napfiner) upstream of the pre-wash in February 1992. Although the quality of the rundown has improved due to these process changes, the sporadic occurrence of off-specification Ag-corrosion ratings (values of 2 or higher) has persisted.

In the past, the use of crude oil which has been stored for a number of years in underground mines, has often been blamed for silver corrosion problems in the Merox treated rundown. High elemental sulphur, $S°$, levels in the feed to the process could be correlated to the use of mine crudes in 1992. Also, very high $S°$ levels in the rundown could be correlated to the occurrence of non-zero Ag-corrosion. However, statistical analysis of the historical data of 1992 and 1993 could not link the use of mine crudes directly to non-zero Ag-corrosion in the rundown.

3. DESCRIPTION OF THE PROBLEM

At this refinery, the rundown from the Merox process is monitored two times per day for silver corrosion by means of a standard 4 hour IP 227 test. All the jet fuel tanks, transit as well as final product tanks, are monitored for silver corrosion on a daily basis. The rundown seldom shows anything other than zero Ag-corrosion. For example, during the period May 1991 to May 1993 only 5,3% of the time Ag-corrosion results of 1 were obtained, with only two results (0,3%) being rated as 2 (off specification). The tanks, however, test sporadically positive to silver corrosion. This leads to costly reprocessing or re-routing of the kerosene to the diesel pool.

Sometimes distinct deterioration of the jet fuel is observed upon storage. Conventionally the assumption would be that this is caused by microbiological processes, such as sulphate reducing bacteria (SRB). However, this phenomenon has also been observed in freshly cleaned tanks, from which water is drained meticulously, and in which no SRB's and other micro-organisms were found. Since silver corrosion is mainly caused by H_2S and elemental sulphur, the measurement of these compounds received much attention and procedures have been developed for their analysis at parts per billion levels. However, analytical difficulties are experienced in the measurement of H_2S and S° at p.p.b. levels in the presence of total sulphur at p.p.m. levels. Since the Merox process converts mercaptans to disulphides, it does not decrease the total sulphur level in the kerosene.

4. RECENT APPROACH

A comprehensive study was made of all the various possible causes which have been postulated regarding the sporadically occurring Ag-corrosion at the Natref refinery. The theories were grouped together and prioritized in an order of decreasing importance, as follows.

4.1 H_2S as Cause of Ag-Corrosion

The most corrosive compound towards silver is hydrogen sulphide. The silver surface is also much more sensitive (in terms of discolouration) towards H_2S than towards elemental sulphur. It has been shown that 100 p.p.b. of H_2S will cause off-specification Ag-corrosion[2].

H_2S can be formed in kerosene by the following mechanisms:

4.1.1 H_2S from sulphides by a decrease in pH

H_2S can be liberated from sulphides such as NaHS and Na_2S by a decrease in pH. This decrease in pH can be due to: (a) acidification by metabolic products from aerobic bacteria, e.g. acetic, lactic acids, (b) acidification by atmospheric contamination e.g. CO_2, (c) by separation of alkaline water upon storage and cooling of the kerosene; and (d) by acidifying chemical reactions.

4.1.2 H_2S from sulphate reducing bacteria

Anaerobic bacteria are capable of reducing any sulphates to H_2S. It has been shown that they can still be active at relatively high oxygen concentrations of a few parts per million[3].

4.1.3 H_2S from FeS

H_2S can be generated by the hydrolysis of iron sulphide under neutral conditions and more easily under acidic conditions:

$$FeS + 2H_2O \rightarrow H_2S + Fe(OH)_2. \tag*{1)}$$

Iron sulphide can be formed due to the action of H_2S on the steel under the corrosive conditions at the top of the crude distillation unit. It can also be generated in the storage tanks due to either bacterial or chemical corrosive action.

4.1.4 H_2S from mercaptan and/or elemental sulphur chemical reactions

Mercaptan and/or elemental sulphur reactions that may produce H_2S or generate H^+ are expected to take place under reducing conditions. Examples are:

$$2\ RSH \rightarrow H_2S + R_2S \tag*{2)}$$

$$2\ RSH + S^\circ \rightarrow R\text{-}SS\text{-}R + H_2S. \tag*{3)}$$

These reactions are believed to be unfavourable under the relatively mild conditions and short times that kerosene is in storage. The thermal decomposition of disulphides to olefins and H_2S is also unlikely under these conditions.

4.2 Elemental Sulphur as a Cause of Ag-Corrosion

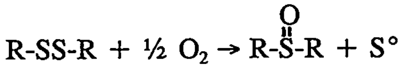
The corrosive action of elemental sulphur (S°) in kerosene upon silver has been studied intensively[4,5,6]. The synergistic effect between H_2S and S° has been universally accepted, since various investigators have found that mixtures of very low concentrations of S° and H_2S are more corrosive to the IP 227 test than the separate components[2,7].

Since S° (and H_2S) levels are determined daily in samples from the Merox treated rundown, reactions which could generate S° upon storage were considered. These are:

Oxidation of mercaptans:

$$RSH + \tfrac{1}{2}\ O_2 \rightarrow ROH + S^\circ \tag*{4)}$$

Oxidation of disulphides:



$$R\text{-}SS\text{-}R + \tfrac{1}{2}\ O_2 \rightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{S}\text{-}R + S^\circ \tag*{5)}$$

or

$$R\text{-}SS\text{-}R + 2O_2 \rightarrow R_2SO_4 + S^\circ \tag*{6)}$$

Oxidation of H_2S:

$$H_2S + \frac{1}{2} O_2 \rightarrow S^\circ + H_2O. \qquad 7)$$

It will be noted that most of these reactions are an overoxidation of the central Merox reaction which could be caused by an excess of oxygen in the reactor.

4.3 Process Related Causes for Ag Corrosion

These are incidents of contamination due to process upsets or physical contamination due to leaking valves, the sharing of pipes, pumps etc. Another cause may be operator errors, since these would be able to explain the irregular occurrence of the Ag-corrosion problems. Since the refinery is operated and maintained under strict guidelines, both these causes are considered to be of lower probability.

4.4 Ag-Corrosion Caused by Specific Corrosive Compounds

A literature search yielded no information on sulphur compounds other than S° and H_2S whose presence in kerosene can cause silver corrosion. In fact, experimental evidence suggests that most of the other sulphur compounds in kerosene seem to have inhibiting effects on Ag-corrosion.

4.5 Ag-Corrosion Due to Absence of Natural Corrosion Inhibitors

It is possible that the occasional absence of some inhibiting compound, which is normally present in the jet fuel, might cause the sporadic Ag-corrosion non-conformances. It is known that most anti-tarnishing compounds used in commercial silver polishes are C_{16} to C_{18} mercaptans or mercaptan derivatives. Examples are octadecyl thioglycolate and octadecyl mercaptan. Under certain process conditions it may be possible that too much of these are removed from the kerosene.

5. STATISTICAL ANALYSIS

A first Ag-corrosion cause analysis approach was to do a statistical analysis of the Merox process data for a 2-year period (May 1991 to May 1993) by means of a statistics software package named SAS. Correlations between the key process parameters and the occurrence of non-zero Ag-corrosion on the rundown were sought. For this purpose, the percentage of each crude in the slate for a specific day was also viewed as a process parameter.

A correlation was found between elemental S° in the feed to the process and Ag corrosion of the product. No correlation was found between feed rate to the process versus Ag-corrosio, or between crude type and Ag-corrosion.

Unfortunately, a correlation could be obscured by inherent flaws in the data being gathered at the refinery. Most process data are spot measurements of the parameter which is taken once every 24 h and is then assumed to depict the value of that parameter for the full period. The feed rate, for example, is the average value over the 24 h period. All fluctuations in feed rate have been lost from the data. The same is true for most of the other parameters. It is therefore not surprising that the statistical evaluation of the process data yielded somewhat inconclusive results.

6. EXPERIMENTS

Laboratory and plant experiments were designed and carried out in order to prove or disprove the different theories, where possible. A simplified scheme of these, together with some implications of positive results on the process, is shown in Figure 2.

7. RESULTS FROM EXPERIMENTS

7.1 H_2S Liberation by Addition of Acid

The results of the experiments to determine the liberation of H_2S as a function of pH, are presented in Table 1. During October 1993 the untreated kerosene feed had a low elemental sulphur content and during February 1994 the sulphur content was high. Even with excessively large amounts of acetic acid only small amounts of H_2S were liberated during October. However, during February, significantly more H_2S was released and in July even more. The maximum amount obtained (85 μg/kg) after the addition of 1 ml acetic acid, would suffice to make the product off - specification. The amount of acetic acid used was however so large that it is highly unlikely that bacteria could release similar amounts of acids. Although we have shown that acidification of the product does release H_2S, the amount is normally small and excessive quantities of acid are required. In another experiment, investigating H_2S liberation by acidification due to CO_2, no H_2S was liberated by purging kerosene samples with CO_2 for a period of 4 hours. The experiment to investigate acidification due to aerobic bacteria also yielded negative results. No microbial activity could be detected over a 7 day period. Tests for SRB's were also negative.

7.2 H2S precursors in Spent Reactor Caustic

The reactor spent caustic was titrated with strong acid to a pH of 4 while the H_2S liberated during the titration was measured, as shown in Table 2. The maximum amount of H_2S that was liberated was 200 p.p.b. This low amount contradicts the theory that the spent caustic contains a substantial amount of H_2S precursors which may be transferred to the kerosene. Also no substantial difference was found between the October experiments (kerosene feed with low S° content) and the February experiments (kerosene feed with high S° content).
A qualitative GC-MS analysis of the organic components of the reactor spent caustic solution was also done. A large number of phenolic compounds were identified. The main components were:

- phenol
- 3-methyl phenol
- 4-methyl phenol
- 3,4-dimethyl phenol
- 3-ethyl phenol

- 3-ethyl-5-methyl phenol
- 2,5-dimethyl phenol
- 4-ethyl-2-methyl phenol
- 3,5-diethyl phenol
- 2-methyl-6-propyl phenol
- 2-methyl-5-(1-methylethyl) phenol

No sulphur containing compounds such as mercaptans and disulphides could be identified, nor any naphthenic or carboxylic acids. None of these were present at levels high enough for detection by the instrument (100 p.p.m.). The results do not substantiate the theory that organic sulphur compounds, acting as H_2S precursors, may be present in the reactor spent caustic. The high phenolic content of the reactor caustic will lead to contamination of jet fuel with phenolates, unless optimum performance of the salt and clay filters are ensured. Phenolates are strongly hygroscopic and therefore the water content of the fuel will increase when the phenolate concentration increases.

7.3 H_2S Generation by Hydrolysis of FeS

This experiment showed that no H_2S was formed by the hydrolysis of FeS in the kerosene/water system over a period of 3 hours. An acidic environment is apparently required to liberate H_2S from FeS in the storage tanks. Even if the hydrolysis reaction does not take place in the kerosene system, FeS should still be considered as a H_2S precursor. Thus iron sulphide should not be allowed to contaminate kerosene and maintenance and cleaning of tanks should receive appropriate attention.

7.4 Formation of S° in Merox Reactor

The results in Table 3 show that no definite trend of elemental sulphur formation in the Merox reactor could be observed. However, it is not believed that this change in S° plays a major role in the occurrence of Ag-corrosion problems, since very high S° levels have historically been tolerated (2 000 p.p.b. and higher) in the merox rundown without causing problems. This observed formation of S° may only contribute to the problem at times when the S° content of the feed to the Merox reactor becomes very high. The experiment which investigated the formation of S° upon oxidation in storage, yielded only negative results. The scatter observed in the measured S° values made them statistically non-significant.

7.5 Ag-Corrosion Inhibition by Long Chain Mercaptans

The results of an experiment, testing the hypothesis that certain mercaptans may act as natural corrosion inhibitors, are shown in Table 4.

Octadecylmercaptan was used since it is commercially more freely available than the C_6 to C_{11} mercaptans which should actually be present in kerosene (Bp. 150° - 250 °C). The results obtained from Merox samples from the final jet fuel tank, F29597, which showed non-zero Ag-corrosion readings, indicated at first that the mercaptan did have a beneficial effect on Ag-corrosion. Unfortunately, no naturally off-specification samples of the Merox rundown were available during this period to test the effect of the long chain mercaptan on them.

In the samples which were made artificially corrosive to silver by the addition of either 1 000 p.p.b. S° or 80 p.p.b. H_2S (Ag-corrosion ratings of 2 and 1, respectively) the addition of 125 p.p.m. octadecylmercaptan had no visible inhibiting effect. It is unlikely that the shorter chain mercaptans (C_8 - C_{11}) would have an inhibiting effect at more realistic levels (20 - 30 p.p.m.). Of special interest are the results in which 80 p.p.b. H_2S was added to Merox rundown sample. In this low sulphur-containing product, this amount of H_2S was not enough to cause off-spec silver corrosion, but only a rating of 1. This means that low S^0 jet fuel may have a bigger tolerance or buffering capacity for H_2S than what was previously believed. At Natref it was assumed that 40-50 p.p.b. H_2S causes Ag-corrosion of 2 or higher. Unfortunately this experiment does not prove the hypothesis that long-chain mercaptans will improve Ag-corrosion ratings when they are present at permissible levels of 20-30 p.p.m.

7.6 Plant experiments

7.6.1 Effect of air reduction in the Merox reactor on the product quality.

The air flow rate to the Merox reactor was reduced from 0.12 Nm^3 air/m^3 kerosene feed to 0.012 Nm^3 air/m^3 kerosene. No effects on RSH concentration could be measured down to a flow rate of 0.053 Nm^3 air/m^3 kerosene feed. Below this value the RSH concentration increased and at 0,012 Nm^3 air/m^3 kerosene feed, this concentration exceeded the specification of 30ppm. It can therefore be concluded that the process parameters are not very sensitive to the air flow rate, while exceeding this minimum air requirement.

7.6.2 Effect of NaOH recirculation through the reactor on RSH levels.

During normal operation of the Merox reactor the caustic solution is cycled through the reactor once a day. The purpose of this experiment was to evaluate the quality of the jet fuel (RSH and H_2S content) depending on the time lapse after the last caustic circulation. During the circulation and in regular intervals before the next circulation, samples were taken before and after the reactor. In each sample the amount of H_2S, RSH and S° was determined. No significant differences were observed in concentrations of these three chemicals during the total time interval between two caustic circulations. It can therefore be concluded that the quality of the jet fuel is not affected by cycling the caustic solution through the reactor once a day.

8. CONCLUSIONS

The results of the experiments carried out in October 1993 and in February 1994 led to the following conclusions :

- Products derived from untreated kerosene feed with a higher S° concentration can liberate more H_2S with the addition of modest quantities of acetic acid than product derived from untreated kerosene feed with a lower S° concentration. The amounts were twice as large in February as during the October experiments. Provided acidification occurs, such amounts of H_2S can cause considerable silver corrosion. Although the amounts were still significantly smaller than expected, this cause can not be ruled out as the major cause for Ag Corrosion.

- The build up of H_2S precursors in the Merox reactor spent caustic is not significant and is independent of the S° concentration in the untreated kerosene feed. The expectations that the caustic would extract H_2S precursors from the product were not met.

- Significant amounts of phenolates did accumulate in the Merox reactor spent caustic. The phenols are not a cause of Ag-corrosion. Entrained phenolates in the product would however increase the water content of the treated product and may have a detrimental effect.

- When untreated kerosene high in S° is used as feedstock, it must be anticipated that the following systems will be contaminated sooner and therefore need rigid monitoring :

- a) spent reactor caustic
  It must be expected that other sulphur compounds accumulate in the caustic, thereby reducing its strength sooner compared with the use of low S° kerosene feeds.

- b) salt filter
  High S° kerosene feed is expected to lead to more entrainment of ionic species in the fuel. Such species will contain water, which depletes the salt filter.

- c) clay filter
  The clay filter removes probably more sulphur compounds, thereby decreasing its useful life expectancy.

- The plant experiments have shown that flexibility exists in the actual amount of air to be used for the Merox process. Furthermore it was shown that the process is tolerant to the frequency of the cycling of the caustic through the reactor.

This project has confirmed the complex and integrated nature of the link between the Merox process and the occurrence of Ag-corrosion. It also confirmed the synergistic value of a combined engineering and chemistry approach in addressing problems of this nature.

The experimental testing of the theories on the possible causes of Ag-corrosion has resulted in an improved understanding of the problem and, by reducing the number of possible causes, led to a more focused approach to the routine operation of the

Merox unit.

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FIGURE 1 : NATREF JET FUEL PROCESSING SCHEME

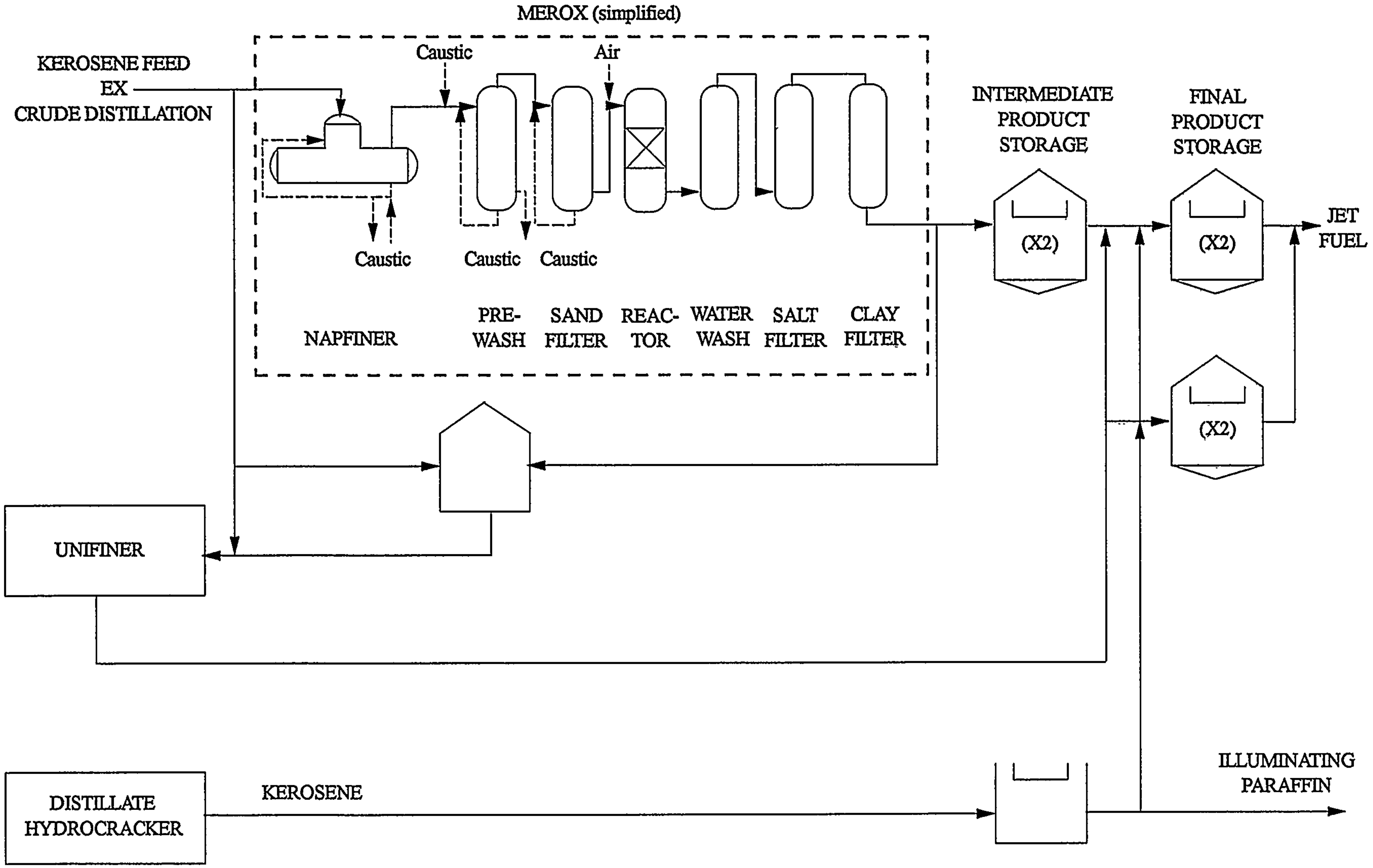
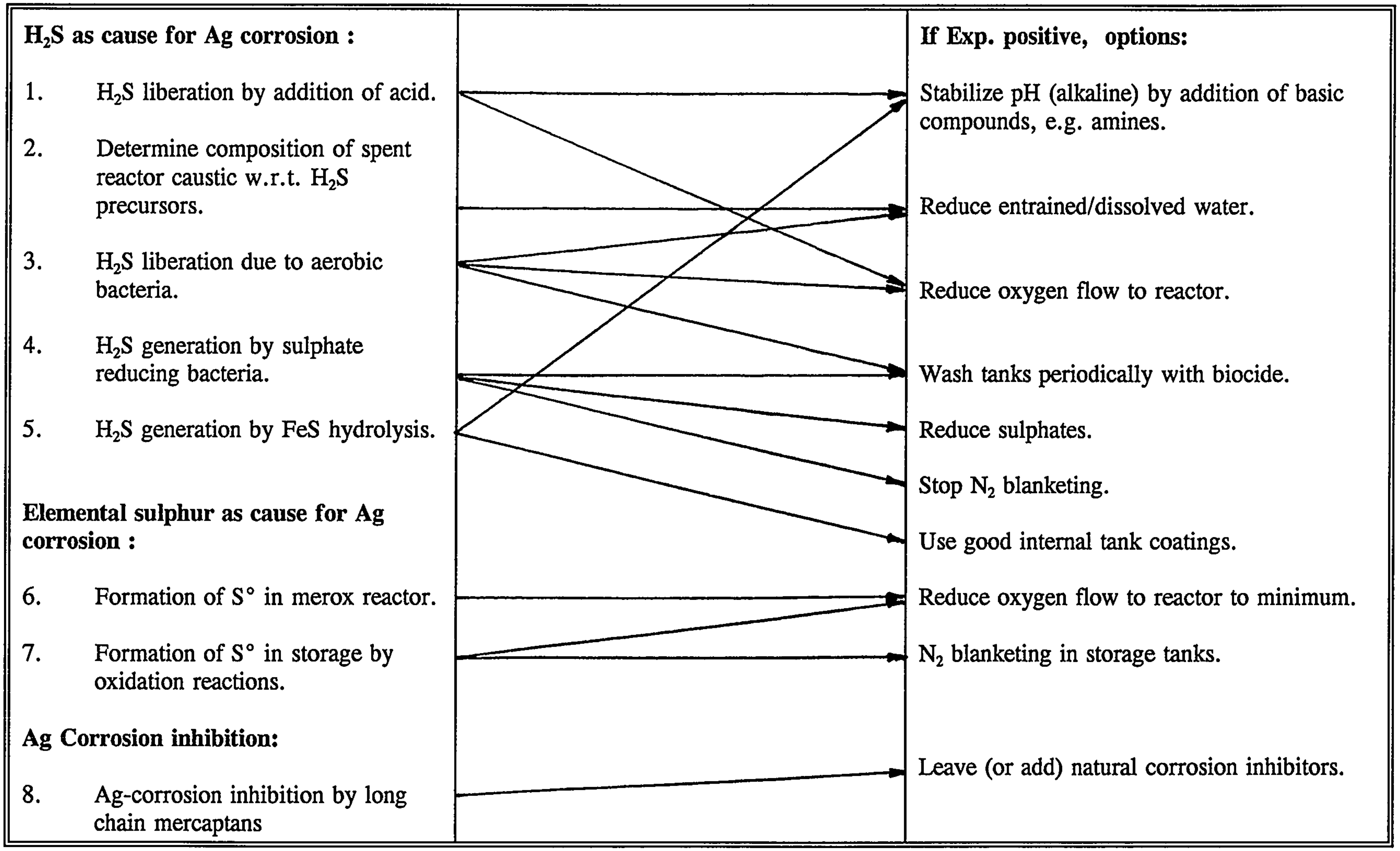


FIGURE 2: SCHEME OF EXPERIMENTS



H_2S as cause for Ag corrosion :

1. H_2S liberation by addition of acid.
2. Determine composition of spent reactor caustic w.r.t. H_2S precursors.
3. H_2S liberation due to aerobic bacteria.
4. H_2S generation by sulphate reducing bacteria.
5. H_2S generation by FeS hydrolysis.

Elemental sulphur as cause for Ag corrosion :

6. Formation of S° in merox reactor.
7. Formation of S° in storage by oxidation reactions.

Ag Corrosion inhibition:

8. Ag-corrosion inhibition by long chain mercaptans

If Exp. positive, options:

Stabilize pH (alkaline) by addition of basic compounds, e.g. amines.

Reduce entrained/dissolved water.

Reduce oxygen flow to reactor.

Wash tanks periodically with biocide.

Reduce sulphates.

Stop N_2 blanketing.

Use good internal tank coatings.

Reduce oxygen flow to reactor to minimum.

N_2 blanketing in storage tanks.

Leave (or add) natural corrosion inhibitors.

TABLE 1: H_2S liberation by the addition of acid to 500ml samples of treated kerosene

Date	Acetic Acid added	H_2S µg/kg	S° µg/kg
18/10/93	0	<4	39
	0,50 ml	8	39
26/10/93	0	<4	83
	1 ml	<4	88
03/11/93	0	<4	163
	0,25 ml	<4	234
	0,50 ml	25	237
	1,0 ml	25	229
	2,0 ml	25	232
22/2/94	0	<4	492
	0,25ml	15	525
	0,50ml	19	520
	1,00ml	38	560
25/2/94	0	<4	234
	0,10ml	15	300
	0,25ml	19	375
	0,50ml	30	400
	1,00ml	46	440
27/7/94	0	<4	645
	0,25ml	38	650
	0,50ml	67	660
	1,00ml	85	680

TABLE 2: Composition of Merox reactor spent caustic (100ml samples)

Date	Composition of spent caustic	Final pH	H_2S liberated ($\mu g/kg$)
15/10/93	Free NaOH :5,7% Tot. Alkal:6,3% Spent: 9,5%	4	130
22/2/94	Free NaOH : 22,8% Tot. Alkal:24,2% Spent: 5,8%	4	200
24/2/94	Free NaOH : 6,8% Tot. Alkal: 8,3% Spent: 18,1%	4	<30

TABLE 3: Formation of S° in reactor. The samples were taken before 1) and after 2) the Merox reactor.

Date		S° $\mu g/kg$	H_2S $\mu g/kg$	RSH mg/kg
13/10/93	1)	61	<4	54
	2)	91	<4	8
14/10/93	1)	78	<4	53
	2)	116	<4	9
28/2/94	1)	55	<4	79
	2)	150	<4	11
4/3/94	1)	311	<4	76
	2)	198	<4	14
6/3/94	1)	319	<4	71
	2)	190	<4	16

TABLE 4: Influence of added mercaptans on Ag Corrosion

Date	Sample (250 ml)	Ag Corr before treatment	Duration of 1st Ag Corr test	H_2S added p.p.b.	S° added (mg)	$C_{18}H_{17}SH$ added (mg)	Ag Corr after treatment	Duration of 2nd Ag Corr test
13/10/93	Product tank	1	4 hrs	nil	nil	25	0	4 hrs
20/10/93	Product tank	1	16 hrs	nil	nil	25	0	4 hrs
21/10/93	Untreated kerosene	2+	4 hrs	nil	1 000	25	2+	4 hrs
24/10/93	Treated kerosene	0 0	4 hrs 4 hrs	nil nil	1 000 1 000	nil 25	2+ 2+	4 hrs 4 hrs
25/10/93	Treated kerosene	0 0	4 hrs 4 hrs	nil nil	1 000 1 000	nil 25	2 2	4 hrs 4 hrs
04/11/93	Treated kerosene	0 0	4 hrs 4 hrs	80 80	nil nil	nil 25	1 1	4 hrs 4 hrs

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AUTOXIDATION OF JET FUELS; IMPLICATIONS FOR MODELING AND THERMAL STABILITY

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The study and modeling of jet fuel thermal deposition is dependent on an understanding of and ability to model the oxidation chemistry. Global modeling of jet fuel oxidation is complicated by several facts. First, liquid jet fuels are hard to heat rapidly and fuels may begin to oxidize during the heat-up phase. Non-isothermal conditions can be accounted for but the evaluation of temperature versus time is difficult. Second, the jet fuels are a mixture of many compounds that may oxidize at different rates. Third, jet fuel oxidation may be autoaccelerating through the decomposition of the oxidation products. Attempts to model the deposition of jet fuels in two different flowing systems showed the inadequacy of a simple two-parameter global Arrhenius oxidation rate constant. Discarding previous assumptions about the form of the global rate constants results in a four parameter model (which accounts for autoacceleration). This paper discusses the source of the rate constant form and the meaning of each parameter. One of these parameters is associated with the pre-exponential of the autoxidation chain length. This value is expected to vary inversely to thermal stability. We calculate the parameters for two different fuels and discuss the implication to thermal and oxidative stability of the fuels. Finally, we discuss the effect of non-Arrhenius behavior on current modeling of deposition efforts.

INTRODUCTION

The evaluation and prediction of jet fuel thermal stability has been the subject of many experimental studies[1-3]. Recently, the development of computational fluid dynamics whith chemistry (CFDC) code has provided a useful tool to aid in the understanding of the fundamental phenomena of jet-fuel degradation[4,5]. The successful application of CFDC codes requires the establishment of a global chemistry model to account for the complicated deposition process.

Current models rely on the well-established notion that deposition processes are initiated by the oxidation reactions[3]. Since the chemical kinetics of the autoxidation process are complex, a global oxidation process has normally been used to represent a series of elementary reactions to initiate the deposition process. Typically, the reaction rate parameters of the global kinetics model are assumed to be Arrhenius and independent of time and temperature. However, the Arrhenius-type approach has been found to be lacking in general predictive power when applied to disparate temperatures and flow conditions. In particular, when CFDC codes were calibrated using data collected from the "Phoenix rig"[6] and then applied to a near-isothermal flowing test rig (NIFTER),[7] the results while intriguing were not particularly good (Figure 1). The shape of the curves appears to be an excellent match, but the time scale for deposit appearance is significantly shortened in the model calculations.

To account for this discrepancy, a new global oxidation model has been developed which does not assume that the global reaction rates are Arrhenius in form. Rather, an underlying mechanism for oxidation is assumed to have elementary rates that are Arrhenius, and the global oxidation rate law for the disappearance of oxygen is derived. The global oxidation rate law shows a time dependence and an apparent activation energy that changes with both time and temperature. A key parameter in the global rate is the chain length of autoxidation, a parameter that has been linked to fuel thermal stability[2]. We will discuss the meaning and possible value of each parameter, and evaluate key parameters of oxidation for two fuels. Finally, we will show how the new model, when incorporated into CFDC codes, results in good fits for both oxidation and deposition of a jet fuel over a range of temperatures.

EXPERIMENTAL DATA

The U.S. Air Force (USAF) acquired, stored, and made available to several researchers fuels (designated F-2827 and F-2747) for baseline thermal and oxidative stability studies. One of these, F-2827, has been the subject of several studies concerning its oxidation and thermal deposition[1]. Two studies have been used to evaluate global oxidation and deposition models[6,7].

Jones et al.[7] used a single-tube heat exchanger and a slow flow that was capable of maintaining an isothermal temperature profile along at least 80% of the tube length. Since the wall and bulk fluid are essentially the same temperature for a large fraction of the flow path, the temperature and residence time at that temperature are well characterized. Jones measured the fraction of oxygen remaining in the fuel at a given temperature as a function of time. Oxygen concentration was measured using on-line gas chromatography (GC)[8]. Reaction (residence) time is varied by increasing or decreasing the flow speed. These are the best available data for kinetic interpretations of the oxidation of this particular jet fuel.

Heneghan et al.[6] used a faster-flowing, single-tube heat exchanger. This system (dubbed the Phoenix rig) uses high wall temperatures (up to 300C) and a rapid flow to heat fuel to near 200C at the end of a 46-cm tube. The residence time is about 6.3 seconds, and the heating rate is about 30C/sec. As a result of the high wall temperatures and rapid heating rate, there are temperature gradients transverse to the flow as well as in the direction of the flow. The flow characteristics in the Phoenix rig are further complicated by the transition from laminar to turbulent flow and buoyancy effects[9]. To study the oxygen consumption, the wall temperature is raised at a constant flow rate, resulting in an increased heating rate, increased output bulk-fuel temperature, and decreased oxygen level. The oxygen concentration is measured using a GC system identical to that used by Jones et al.[7]. The measured data are oxygen concentration vs. output bulk temperature for a fixed flow speed.

The deposits along the tube in both the Phoenix rig and the NIFTER have been collected for F-2827. Deposits for F-2747 have been collected only in the Phoenix rig due to the low level of deposits formed in the NIFTER. The oxygen consumption data have been collected using both systems for both fuels. These experiments cover a range of temperatures from about 150C (bulk fuel temperature) to 240C and flow conditions from laminar to transitional with buoyancy.

AUTOXIDATION MECHANISM

The autoxidation mechanism used in the following analysis is given as follows.

initiation	Initiation of $R\cdot$ (R_i)	(i)
propagation	$R\cdot + O_2 \rightarrow RO_2\cdot$	(2)
	$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$	(3)
termination	$RO_2\cdot + RO_2\cdot \rightarrow$ products	(t)
chain-transfer reactions	$RO_2\cdot + AH \rightarrow RO_2H + A\cdot$	(3t)
autocatalysis	$RO_2H + RO_2H \rightarrow ROH + RO_2\cdot + H_2O$	(b)
	$RO_2H \rightarrow RO\cdot + OH\cdot$	(u)

THEORETICAL DESCRIPTION OF OXIDATION

The rate of chain oxidation for a hydrocarbon is known to follow Equation 1.

$$\frac{-d[O_2]}{dt} = k_3\left(\frac{R_i}{2k_t}\right)^{0.5}[RH] \qquad 1)$$

Jones et al.[7] have shown that, in a fuel, the rate of initiation, R_i, increases with time and is proportional to the square of the disappearance of oxygen (Equation 2).

$$R_i = k_b([O_2]_0 - [O_2]_t)^2 + k_i \qquad 2)$$

where k_i, the baseline initiation rate, is assumed to be a normal Arrhenius rate and is independent of the oxygen concentration. The term k_b is the bimolecular rate constant associated with a reaction that forms radicals from the oxidation products. Jones et al.[7] have indicated that this is probably a bimolecular peroxide reaction discussed by Walling[10].

Heneghan and Zabarnick[2] have shown that in a strongly terminated oxidation system the rate of oxidation can be given by Equation 3.

$$\frac{-d[O_2]}{dt} = \frac{k_3[RH]R_i}{k_{3t}[AH]} \qquad 3)$$

In this case, Jones data support a unimolecular reaction and Equation 4.

$$R_i = k_u([O_2]_0 - [O_2]_t) + k_i \qquad 4)$$

where k_u is a unimolecular process associated with the decomposition of the oxidation products that produces radicals. The low concentrations of peroxides formed in fuels due to the limited oxygen availability in Jones' system strongly favor the unimolecular decomposition over the bimolecular pathway. It is worth reiterating that this analysis depends on Equation 4 and/or Equation 2. If there is no autoacceleration ($k_u = 0$ and $k_b = 0$), global kinetic parameters will provide an excellent description of the oxidation rates and the activation energy is a valid parameter for extrapolation to new temperatures.

Inserting R_i (Equations 2 and 4) into the time derivative of oxygen concentration (Equations 1 and 3) leads to either of two cases (Equations 5 and 6). These equations show similar behavior. Equation 6 was chosen to represent the global oxidation because we believe it is more theoretically sound.

$$\text{Case 1}\ \frac{-d[O_2]}{dt} = k_3\left(\frac{k_b(\Delta O_2)^2 + k_i}{2k_t}\right)^{0.5}[RH] = \qquad 5)$$

$$\text{Case 2}\ \frac{-d[O_2]}{dt} = \frac{k_3[RH](k_u\Delta O_2 + k_b)}{k_{3t}[AH]} \qquad 6)$$

where ΔO_2 is $[O_2]_0 - [O_2]_t$.

If oxygen consumption is considered as a global parameter with no dependence on the oxygen concentration, the global rate constant can be considered as in Equation 7.

$$k_o = \frac{k_3[RH](k_u\Delta O_2 + k_b)}{k_{3t}[AH]} = k'(k_u\Delta O_2 + k_i) \tag*{7)}$$

where $k' = \frac{k_3[RH]}{k_{3t}[AH]}$, a unitless ratio

The difference in oxygen, ΔO_2, is related to the global oxidation rate and the time of the reaction, t, by Equation 8. Assuming that k_o is independent of time, Equation 8 can be integrated to show that ΔO_2 equals $k_o t$.

$$-d[O_2] = k_o dt \tag*{8)}$$

Substituting $k_o t$ for ΔO_2 in Equation 7 yields Equation 9, which can be solved for the global oxidation rate constant k_o (Equation 10).

$$k_o = k'(k_o k_u t + k_i) \tag*{9)}$$

$$k_o = \frac{k'k_i}{1-k'k_u t} \tag*{10)}$$

A brief check of the units shows that no gross injustice has been done. The terms k' (unitless), k_i (moles/L-sec), k_u (sec^{-1}), and t (sec), yield k_o in (moles/L-sec), a zero-order rate constant.

The first item of note in Equation 10 is that k_o is a function of time in contradiction of our assumption. Returning to Equation 7 and inserting the integral form of ΔO_2 (not assuming a constant k_o) from Equation 8 gives Equation 11. This can be solved by first differentiating and noting that the constant of integration can be determined by recognizing that, at time zero, k_o is $k'k_i$. The solution is given in Equation 12.

$$k_o = k'(k_u\left(\int k_o\, dt\right) + k_i) \tag*{11)}$$

$$k_o = k'\, k_i \exp(k'\, k_u\, t) \tag*{12)}$$

The time t in this oxidation model is the residence time of the oxygen molecule in the system under study. In flowing systems, such as the NIFTER and Phoenix rigs, the residence time of the oxygen molecule at a given location is not well defined because it is path-dependent, and the pathway is affected by convective and diffusive motions in the flow field. To apply the model more simply in the present study, t was estimated by integrating the convective time of the oxygen molecule along the streamwise flow direction. (Equation 13).

$$t = \left(\int_{\tau=0}^{\tau=t} d\tau \right) = \left(\int_{x=0}^{x=x_t} dx/v(x) \right) \qquad 13)$$

EVALUATION OF THE OXIDATION MODEL

The global oxidation rate (k_o) parameters from Equation 12 are $A'A_i$, $A'A_u$, $E'+E_i$, and $E'+E_u$. These parameters were determined using NIFTER data at temperatures 428K, 438K, 448K, and 458K. These data are shown in Figure 2. First, Jones[7] estimated $A'A_i = 2x10^{11}$ l/mole-s and $E'+Ei = 35.8$ kcal/mole by fitting the initial slopes to an Arrhenius equation. Values for A' and E' from Zabarnick[11] for a strongly terminated oxidation system are $A' = 2x10^4$ and $E' =$ 5 kcal/mole. An average value for A_u and E_u are from Benson's[12] ($A_u = 1x10^{15}$ l/mole-s, and $E_u =$ 42 kcal/mole). A best fit to the data was found by adjusting k_u. The best fit shown in Figure 2 is based on $A'A_i = 2x10^{15}$ l/mole-s, $A'A_u = 1.4x10^{19}$ s^{-1} $E'+E_i = 40.8$ kcal/mole, and $E'+E_u = 45$ kcal/mole.

The above parameters were used to calculate the behavior of the oxygen depletion in the Phoenix rig. A comparison of the experimental and predicted result is shown in Figure 3. The good general agreement over a wide temperature range, initial conditions, and flow conditions shows that the oxidation process is adequately modeled by Equation 12.

DEPOSITION

The new oxidation model was incorporated into the CFDC model. The deposition model proposed by Katta et al.[5] includes five steps for bulk-fuel reactions and three steps for wall reactions. This deposition model was calibrated based on the Phoenix rig experiments using a 16-ml/min flow rate. and two block temperatures (608K and 543K). Using this deposition model and the new global oxidation model, the deposition profiles for a flow rate of 4 ml/min and two block temperatures (608K and 543K) were calculated. The results are shown in Figure 4. The prediction from the deposition model using the old two-parameter Arrhenius global oxidation model is also shown. At the high temperatures and short residence times in the Phoenix rig, either oxidation model is sufficient to account for the deposition changes with flow rate and temperature.

The two global oxidation models are further compared in Figure 1 by predicting the deposition profiles at low temperatures (458K) and flow rates (0.125 ml/min and 0.5 ml/min) in the NIFTER. It is evident that the old two-parameter model (dashed curves) failed to predict the correct locations of the deposition peaks for both flow rates. The predictions from the model using the new oxidation model (solid curve) match the measurement extremely well.

A key parameter from the oxidation model that may impact deposition modeling is the value A', the pre-exponential of the chain length. This parameter has been assigned a value that corresponds to about 100 ppm (concentration) based on earlier analysis by Heneghan[2] and Zabarnick[11]. By maintaining k_u and E' constant, and measuring $k'k_i$, the autoxidation parameters for a new fuel can be determined by adjusting only A'. According to Heneghan and Zabarnick,[2] the parameter A' should be proportional to fuel thermal stability. According to Jones[13], the parameters log(A'A) and E'+E are 16.3 and 45.2 kcal/mole, respectively, for fuel F-2747. Fitting data from the Phoenix rig using these parameters and allowing only A' to vary yields $A' = 10^{5.7}$ — an increase by a factor of 25 for F-2747 versus F-2827[14]. This result is in agreement with our prediction because F-2747 is known to be significantly more thermally stable than F-2827.

ACTIVATION ENERGY

The acceleration of oxidation with time observed by Jones[7], modeled by Zabarnick[11], and incorporated into CFDC models here has some interesting implications for the activation energy of deposition. In global modeling, an assumption of Arrhenius behavior is equivalent to an assumption that the activation energy is constant with temperature (that is, that a plot of ln(k) versus 1/T is a straight line). Any deviation from this expectation is considered to be due to a change of mechanism. The apparent activation energy of Equation 12 can be easily calculated (Equation 14) using the definition of activation energy (the differential of the Arrhenius equation).

$$E = RT^2 \frac{\partial \ln k}{\partial T} \qquad 14)$$

Application of this to Equation 13 yields Equation 15.

$$E_o = E_3 - E_{3t} + E_i + (E_3 - E_{3t} + E_u)k'k_u t \qquad 15)$$

Equation 15 shows that the activation energy is expected to be constant versus temperature only at time (t) equals 0, will increase with time, and will increase faster with higher temperatures as both k' and k_u increase with temperature. Since deposition reactions follow the oxidation reactions and the time scales of the reactions are usually changed to account for differing flow conditions and temperatures, it is not surprising to find that the apparent activation energy for deposition reactions changes with temperature. Just such an increase of activation energy with temperature was observed by Katta et al.[5].

CONCLUSION

The ability to predict the oxygen consumption is, not surprisingly, critical to modeling deposition reactions. However, it is not always possible to extrapolate, in time and temperature, the oxidation reactions using only a two-parameter Arrhenius global oxidation reaction mechanism. Careful analysis of the expected mechanism, including the acceleration of the initiation process, reveals a four-parameter non-Arrhenius global oxidation equation with time dependence. We have calculated the four parameters for the new model using an isothermal flowing system. The measured values are consistent with estimates from theoretical considerations. Using these parameters, we can accurately account for the consumption of oxygen and the deposition profile at a variety of temperatures and flow conditions. The model predicts that the observed activation energy for oxidation is not expected to be constant with time, and will only be constant with temperature at zero time. The predicted behavior of fuel thermal stability increasing with the pre-exponential of oxidation chain length has been verified for two fuels.

NOMENCLATURE

AH	Antioxidant Molecule
A	Arrhenius A-Factors
CFDC	Computational Fluid Dynamics with Chemistry
E	Arrhenius Activation Energies
GC	Gas Chromatograph
k	Rate Constants
NIFTER	Near-Isothermal Flowing Test Rig
$R\cdot$	Hydrocarbon Radical

RH Fuel Molecule

Subscripts, Superscripts

- b values associated with bimolecular autoacceleration reactions
- i values associated with initiation reactions
- u values associated with unimolecular autoacceleration reaction
- ' values associated with chain length

τ time scale associated with the flowing molecule

t time scale associated with the flow through the tube

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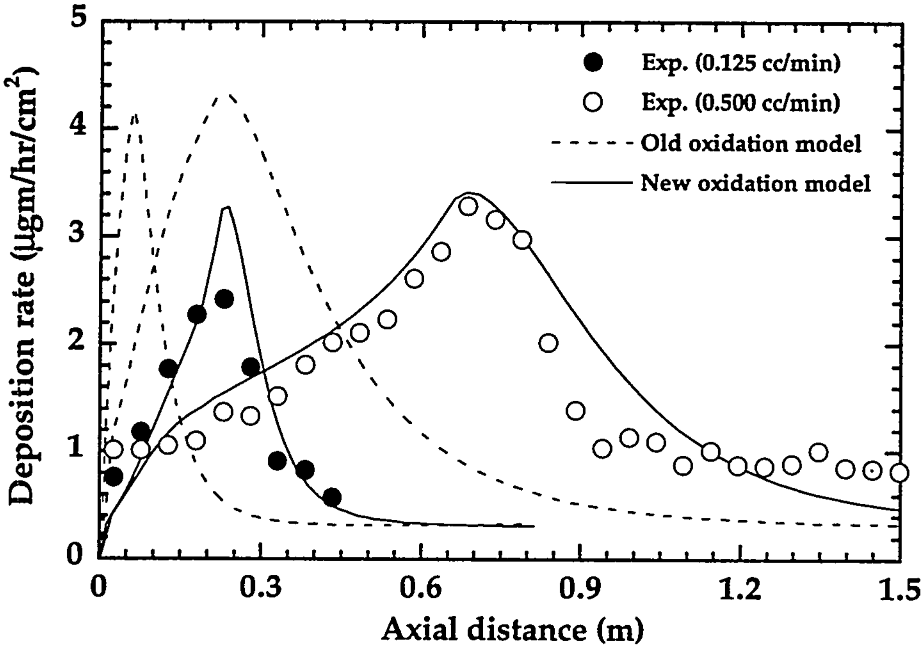

Figure 1. Prediction of deposition in NIFTER using Arrhenius assumptions, calibrated data from Phoenix rig, and CFDC code.

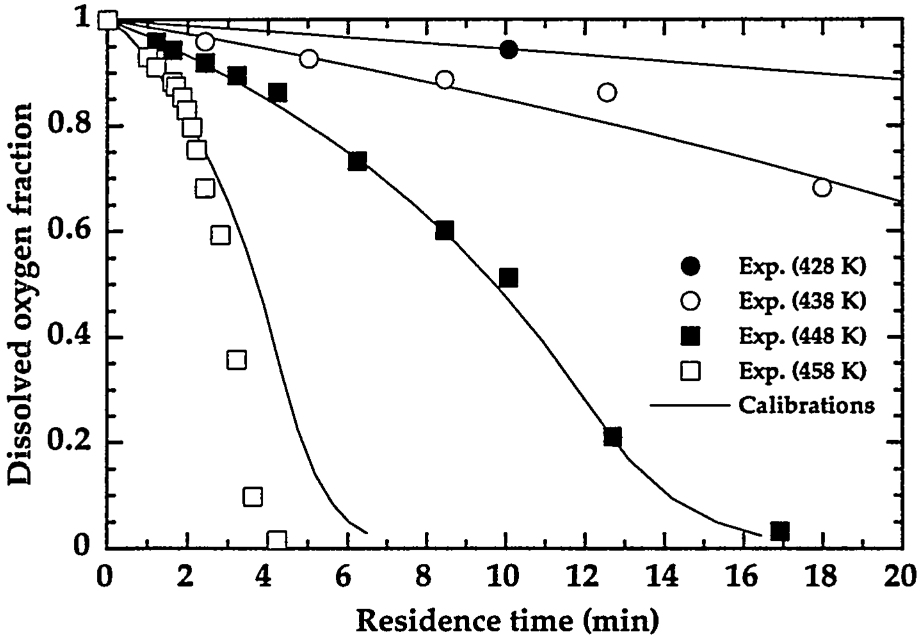

Figure 2. Calculated oxygen depletion vs. time at varying temperatures compared to measured values (from Jones[7])

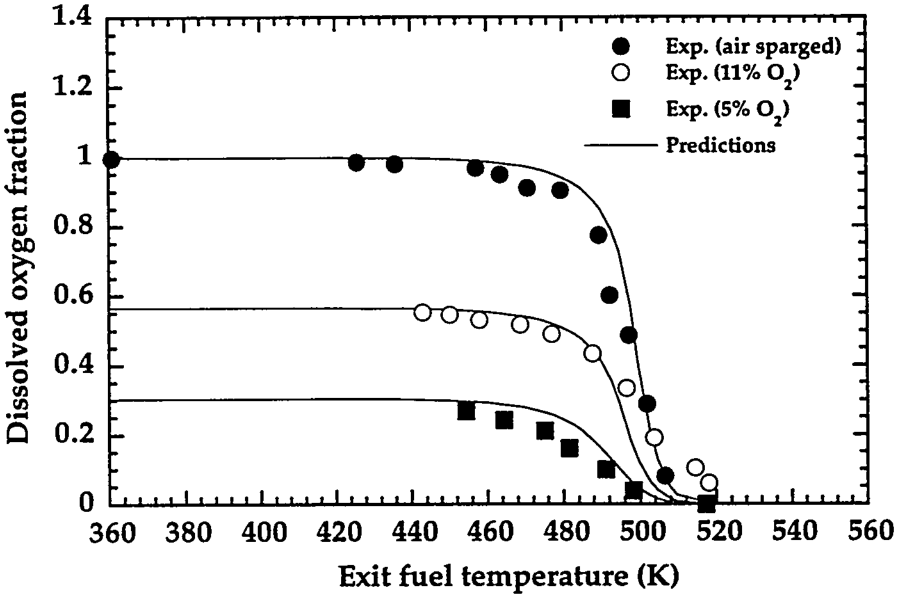

Figure 3. Comparison of the Phoenix rig oxygen consumption experimental and predicted values.

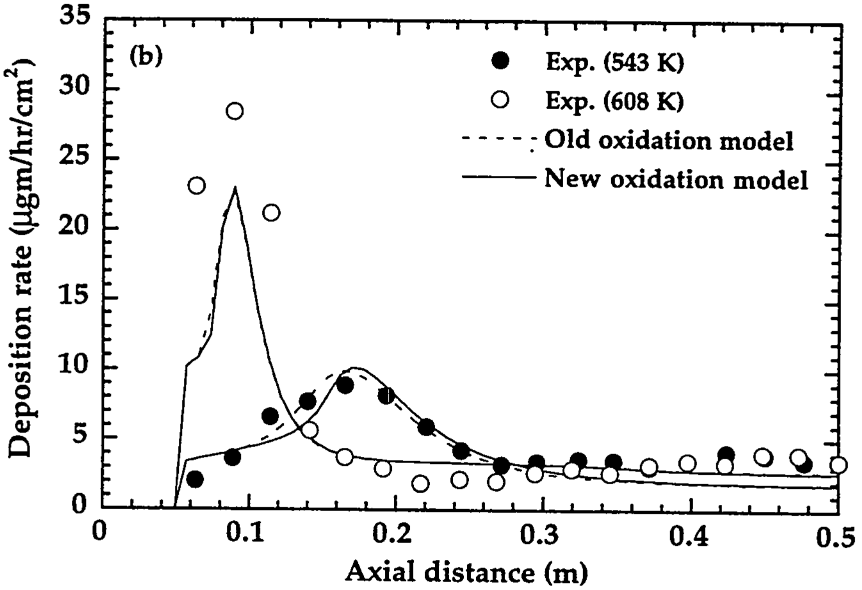

Figure 4. Calculated and predicted results for Phoenix Rig at 608K and 543K and flow rate of 4 ml/min. for two oxidation models.

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SAFE, ACCEPTABLE ANTI-MICROBIAL STRATEGIES FOR DISTILLATE FUELS.

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Microbiological fouling, spoilage and corrosion have for years been considered as end-user problems but they have now become endemic up-stream affecting cargoes, tank farms and terminals. Trading agreements to share storage and distribution facilities impose the need to mutually agree antimicrobial strategies which satisfy all health, safety and environmental regulations wherever that fuel is distributed and used. Also agreed must be the infection levels at which antimicrobial action is initiated. Physical decontamination methods are described and the use of biocides discussed in relation to increasing regulatory restrictions.

1. Introduction

In the 1980's, in response to a perceived increase in microbial fouling and spoilage problems of distillate fuels, the Institute of Petroleum formed a Fuels Task Force which reported its findings[1] concluding that "there is no correlation of numbers of organisms with some fuel performance characteristic that allows some logical guideline on the acceptability of certain numbers". Nevertheless a number of widely different limit values obtained by a variety of test methods have been proposed. Not surprisingly, fuel traders are confused, particularly as the relationships between numbers, types of organisms, test methods, and sampling points, to operational problems (fouling, corrosion, down stream spread of contamination) have not been made clear to them.

Whatever methods are adopted, as soon as norms or limits are in place there will be pressure to meet them for bulk fuel and this may entail remedial measures when they are exceeded. Remedial measures are already widely used by end users afflicted with fouling and corrosion problems. How to conduct these measures safely and acceptably, particularly for bulk fuel, against an increasingly regulated background, is the main topic of this paper. Where trading agreements exist to share storage facilities, loading racks and pipe-lines, limit values and any anti-microbial strategies implemented must be mutually agreed between the parties involved. However some comments on the relationship of microbial numbers to problems and the influence of sampling points on results are perhaps timely as these are largely ignored by most bulk fuel traders who tend to take microbiological test results at face value.

2. Microbial Numbers and Fouling

It is often assumed that microbial numbers can be equated to fouling potential. Not only does this ignore the difference in size between bacteria, yeasts and moulds but it also fails to recognise that microbial by-products, particularly bio-polymers and surfactants, are major causes of operational problems.

Whatever the microbial 'count' of the bulk fuel and however it is determined it is only an indication that all is not well and it cannot predict if and when large masses of interfacial slime or biofilm will find their way into the supernatant fuel.

It is the spasmodic release of major fouling into the fuel which is the cause of most serious end-user problems.

3. Factors Affecting the Numbers of Microbial Particles Detected in Fuel.

3.1 Physical Decay.

All particles, including microbial particles (living or dead), are progressively sedimented from fluids. The kinetics are explained in section 5.1.1. The depth at which a sample is taken and the settling time elapsed will affect the size and numbers of microbial particles detected.

3.2 Biological Decay (Loss of Viability)

Any test method which inherently estimates 'viable' microbes does so at the time of testing not at the time of sampling. In the intervening period some increase in viable units is possible if free water is present; conversely microrganisms, particularly bacteria, may lose viability in water free fuel.

4. Action Criteria

Thus when interpreting test results on samples due regard must be paid to the implications of Physical Decay, and, if the test method is a viable count proceedure, to Biological Decay also. Additionally the high inherent inaccuracies in microbiological test methods must be appreciated. It therefore follows that introducing any simple limit value for microorganisms which triggers anti-microbial measures, without also specifying test method(s) and confidence limits, sample taking and handling is not a tenable proposition. These factors will be explored in detail at this symposium[2].

The experienced petroleum microbiologist will consider all of these factors, take into account visual and microscopic charactereristics and consider the risks to facilities (including downstream facilities), transport and potential end-users. If available, he may conduct supplementary "fitness-for-use" tests such as filterability. On the basis of this overall assessment he may then propose one or more anti-microbial strategies. These must be safe, environmentally acceptable and conform to local and national regulations.

5. Antimicrobial Strategies

Obviously the greenest and safest strategy is avoidance by Good Housekeeping. If however fuel is deemed to be unacceptably contaminated by microorganisms, active anti-microbial measures are needed. The objectives of these could be one or more of the following:

Return fuel to a fit for use condition.

Decontaminate storage tanks, pipe-lines, and transports and, at the point of use, end-user equipment.

Prevent microbial corrosion, particularly by SRB.

Minimise the contamination of facilities downstream.

For bulk fuel this is usually planned as a 'crash' programme but there are circumstances when preventive measures are appropriate. These strategies will be considered in out-line only as incidents vary widely in their severity, urgency, microbial nature and availability of equipment (including spare tanks) waste disposal facilities and chemicals.

5.1 Physical Methods

As these avoid the use of toxic chemicals, they are user friendly and have little environmental impact. They have the disadvantage that they do not decontaminate the facility in which infected fuel is stored or used and there is no ongoing downstream affect.

5.1.1. Settlement.

The friendliest and simplest physical method is gravitational settlement; the principles of this are governed by Stoke's Law. This determines the "Terminal Velocity" (V_S) of a falling particle, i.e. the maximum vertical velocity which a particle attains before drag restricts further acceleration.

$$V_S = \frac{p.g.d^2}{18\mu}$$

p = density of particle (g/cm^3)
g = acceleration due to gravity (cm/s^2)
d = equilavent spherical diameter (cm)
μ = viscosity of fluid (g/cm s^{-1})
V_S = terminal velocity (cm/s)

Note A non-spherical particulate will be subject to greater drag and V_S will be smaller. A "slip factor" should be applied to very small particles but can be ignored practically. The density of microbes and microbial debris varies from 0.9 - 1.3 gm/cm^3 ; most wet particles approximate to 1.05 gm/cm^3 and 'dry' particles to 1.1 gm/cm^3, both considerably greater than the density of normal gas oil. For practical purposes $V_S = k.d.^2$

To convert this formula to usable figures, for diesel fuel of 4.5 cSt viscosity at 25°C, and V_S expressed as cm h^{-1} and particle diameter expressed as micron (μm), then K = 0.046.

For an individual bacterium of 2 μm diameter,

$V_S = 0.18$ cm h^{-1}

For a yeast cell or fungal spore 5 μm diameter,

$V_S = 1$ cm h^{-1}

For a microbial aggregate 100 μm diameter (just visible)

$V_S = 460$ cm h^{-1}

Thus it is obvious from the above that in a quiescent tank not only will microbial aggregates and microbial debris gravitate progressively to the tank bottom but that as time progresses, any viable microbial units detected in upper fuel will actually be very small units and have reduced fouling significance.

A rule of thumb time allowance of one foot tank depth per hour of settlement is often quoted but this would not suffice for microbial aggregates less than 25 μm in diameter. The water and sludge can then be drawn off, thus removing the main 'factory' which could generate more microbes and their products. With time, both physical and biological decay (see sections 3.1 and 3.2) continue; any remaining suspended particles will be very small. Very heavy microbial contamination accompanied by prolific bio-surfactant synthesis can seriously impede the settlement process.

Settlement of small particles can be reversed by fuel movements such as convection currents. Settled particles will accumulate at the fuel/water interface or on the tank bottom from where they could be locally redistributed by turbulence, for example by operating tank drains. On a few occasions large aggregates of microbes and debris have exhibited positive buoyancy due to gas production and gas entrainment.

The concentration of contamination into the lower fuel may necessitate supplementary treatment of this, for example, by filtration.

5.1.2. Filtration.

Transportable filter trains have become available and have been used for processing large volumes of fuel at a rate up to 5000 m^3 p.d. A final filtration stage of c. 1 μm will completely decontaminate aviation kerosene; a final stage of c. 5 μm may be considered adequate for producing acceptable gas oil. Filtration may be the only practical option for fuels when biocide treatment is undesirable. Filtration is often part of an overall strategy, for example coupled to settlement - only the lower fuel is filtered, or coupled to biocide treatment to remove dead microbes and debris.

A small magnetic filter (the De-Bug Unit) has been advocated for end-users but refereed supportive technical papers have not yet appeared in the literature.

5.1.3. Heat Treatment.

In-line heat exchangers are sometimes available as surplus equipment at refineries. In a vacuum configuration, large volumes of contaminated fuel have been successfully processed at high flow rates. Heat treatment is usually part of an overall strategy which includes settlement and partial filtration.

5.2. Chemical Methods

Anti-microbial chemicals may be used in fuel as long lasting preservatives or decontaminants. In either case they migrate into water associated with fuel. This presentation will not address the merits or de-merits of preservation or shock treatment or of the various products available but only the environmental and health issues. Of prime importance is compliance with local, national and multi-national regulations.

Despite the health and environmental implications of using biocides they are often the only treatment available or appropriate and safe and acceptable strategies can be devised and implemented.

5.2.1. EC Regulations.

In the EC all the following control or will control the use of biocides added to fuel and to water used to wash tanks, ships and pipes.

The Biocide Directive (7th Amendment to the Dangerous Substances Directive 1993; Common Principles for the Evaluation and Risk Assessment of Biocidal Products 1994). The common principles group biocides together and propose a common data requirement for each group. Proof of efficacy is required; there should be "consistent and measurable benefits" substantiated by standard or in-house test procedures or experience. The Directive should be in force by 1997.

EC Classification, Packaging and Labelling of Dangerous Preparations, 1988. A standardised Material Safety Data Sheet must be supplied with all biocides.

Marpol 73/78 Discharge of Noxious Liquids. Refers to discharges into international waters.

Various national Health and Safety at Work regulations, Control of Substances Hazardous to Health Regulations and Duty of Care (Waste Disposal) Regulations; these reflect EC Directives.

5.2.2. National Regulations.

As fuel containing a biocide may move from country to country during distribution or use, national regulations must be considered. For example the German "Decree on Chlorine and Bromine Compounds as Fuel Additives, 1992 (19th BImSchV)" prevents the addition of certain biocides to automotive fuels.

Biocides added to water to decontaminate facilities need only be assessed for safety and environmental impact at the point of use. Biocide added to fuel will deplete progressively from the fuel into contaminating water at the point of use and at all points downstream wherever they may be. Thus there may be an obligation to notify downstream purchasers and users of the presence of a toxic chemical; there may also be an obligation to notify them of strategies for de-toxifying drain water/waste sludges before they are discharged.

5.2.3. Compliance.

For most commonly used fuel biocides there is adequate de-toxification guidance from the suppliers. For example isothiazolinone and oxazolidine fuel biocides can be neutralised with calculated amounts of bi-sulphites. Oxidising biocides (chlorine, bromine, chlorine dioxide etc) used in aqueous washes, can be neutralised with sodium thiosulphate. For other biocides, compliance with environmental regulations may necessitate substantial dilution of waste streams until they have negligible environmental impact; it could be argued that this is hiding a problem not solving it. The responsibility for compliance with regulations lies with the biocide user; he must interpret the information on Material Safety Data Sheets and convert it into a strategy which is safe and environmentally friendly. Unfortunately most of the concentrations quoted will be for LD_{50}'s (concentration which kills 50% of a life form) and not NOEL's (no observed effect level). For example, a MSDS for one fuel biocide quotes on LD_{50} for rats of 2285 mg/kg body weight; this implies that if men (average weight 75 kg) drank 428 litres of fuel containing 400 ppm of the biocide (the recommended dose), half of them would die. It can be assumed that accidentally imbibing a little of this biocide would not be a health issue for toxicity although it could be for irritancy, sensitisation etc. NOEL's are important for controlling environmental discharges but are rarely quoted by biocide suppliers.

5.2.4. Monitoring

Biocides equilibrate between fuel and water phases according to relative solubilities and relative phase volumes. The concentration present in the water phase can be simply assessed on site[2,3]; the concentration in the fuel phase can be deduced by testing water derived after a standardised aqueous extraction. Concentration testing on site prevents under-dosing or over-dosing and also assists assessment of environmental impact.

6. References

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CASE STUDY: USE OF ISOTHIAZOLINONE AND NITRO-MORPHOLINE BIOCIDES TO CONTROL MICROBIAL CONTAMINATION IN DIESEL AND GASOLINE STORAGE AND DISTRIBUTION SYSTEMS

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Abstract: Responding to feed-back from its retail outlet network, a major, vertically integrated petroleum company undertook to diagnose and remediate diesel and gasoline performance problems. Analysis of samples from tanks at refinery, distribution terminal and retail outlet sites established that uncontrolled microbial contamination was rampant throughout the distribution system. The company then developed and instituted a two-phase action plan. During Phase I, all tanks received corrective (shock) biocide treatment preceding mechanical tank cleaning and fuel polishing. An ongoing Phase II program currently includes routine sampling and analysis combined with periodic preventive biocide treatment. This paper describes the initial problem diagnosis, corrective action plan and preventive program; recommending the Phase II program as a model for all companies involved with refining , distribution or retailing gasoline.

Introduction: Microbiological contamination has generally been perceived as a periodic problem that can be easily dealt with by just removing water and once in a while treating the water in a tank with a biocide. In a perfectly controlled environment, these tactics would be successful to a limited degree and succeed by temporarily keeping Mother Nature at bay. However, the ever changing petroleum environment has rendered this practice ineffective at best and dangerously misleading at worst. Recent changes in fuel chemistries, environmental laws (emissions control), and poor tank design, have contributed to the recent rash of reported biological problems both in diesel and in gasoline.

Generally, these reported problems have come about only after contamination's reached catastrophic consequences such as severe corrosion and filter plugging. The most surprising revelation was the extent of the problems discovered in a major gasoline distribution system. These problems were found originating at the refinery and extending to every phase of the distribution system. Up until now biological attacks on gasoline systems were extremely rare and usually insignificant.

The difference in biological contamination as opposed to other forms of contaminants, is that each storage vessel (tanks, filters, pipe lines and vehicles) are separate and distinct ecologies having no necessary relationship other than the common source of food; the fuel. This meant that in the case of this particular system, a program had to be devised to deal with biological attacks both in diesel fuel and gasoline. In addition, because of the various Government regulations and the differences in the two fuels, the program had to be flexible enough to adjust to these unique circumstances. The term unique has been used because in the case of gasoline the solution had to involve both regulatory and technical ramifications.

Materials and Methods. To begin with the US Clean Air Act of 1990, mandated the use of substantially similar chemistries be used in Gasoline. This eliminated the use of an Isothiazolinone based biocide because it does not fall into the sub-sim category. A Nitro-Morpholine additive was then selected as an effective replacement based on efficacy test data. The Isothiazolinone was kept for use in the diesel fuel. The chemical phase of the solution involved the use of both biocides to kill existing biologicals in the different fuels and a strategy to clean up contaminants at the retail level. While the diesel fuel posed no special problems, gasoline was another matter. Because of the volatility, extra safety precautions had to used during tank cleaning and filtration. The methodology of recirculating gasoline through the 3" fill and pump tank holes had to be developed by trial and error. The difficulty of "pulling" gasoline up 10' to 12' at a high flow rate, necessitated the development of a specially modified pump that could both pull and push with equal force.

Testing for active biologicals was done at each phase to ascertain both the additive effectiveness and the effectiveness of the physical cleanup at the retail level. These tests were conducted using convention and non-conventional methods. Bottom samples were taken from both ends of the tanks using a bomb-type device before and after the filtration operation. These samples were transferred into unused high density polyethylene (HDPE) sample bottles. All samples were shipped to a laboratory (Basic Fuel Services, Inc.) where analysis was conducted within 48 hours after the samples were taken. Aerobic and anaerobic bacterial and fungal (yeast/mold) titers were determined by the pour plate method. BACTO ™ Plate Count Agar, Anaerobic Agar and YM Agar (DIFCI Laboratories in Detroit MI) were used as growth media for the different microbial groups. Anaerobic sulfate reducing bacteria (SRB's) were estimated through serial dilution in BACTO Sulfate API Broth. Aerobic bacteria and fungi were incubated for 5 days. Anaerobic bacteria were incubated in an anaerobe incubator for 7 days. SRB,s were also incubated for 7 days. All plates were incubated at 32° C. A non-conventional catalase test was also performed. The catalase concentrations were determined using the method of Kraft et al. Precision tests were performed on catalase solutions (1.0 mg catalase/L 0.01M phosphate buffer; pH 7.2) Solutions ranging from 0.1 - 1.0 mg catalase/L were used to examine the relationship between pressure data and catalase concentration.

The fuels were recirculated at from 300 to 400 GPM and filtered to at least .5 microns. The results of this effort can be seen in the accompanying photographs. One major finding of this effort was the fact that over 50% of the tanks cleaned (over 1,000), were tilted opposite from the fill lines. This is extremely important because it is from the fill line location that samples are pulled and water finding checks are made.

If this statistic is representative, and we believe it is, then the majority of all water finding tests that are conducted at the retail level are inaccurate. While this may not be a major revelation to some, it does represent a dangerous signal. If, in fact, gasoline is now coming under biological attack because of the recent reformulating, the Petroleum industry is going to get a severe shock in the coming years if protective actions are not taken now. In the past, small amount of water were considered not to be a problem and were tolerated. Some facilities even felt that the water in a tank would prevent fuel leaks. With increasing disposal costs, many companies allow water to exist inside the tanks because of the regulatory requirements of disposal. While this practice may have had little consequence in the past, the current fuel re-formulations have removed the natural protections that previously existed (lead, higher aromatics, etc.). Bacteria like the oxygenates that we are now putting in our fuels. These bacteria multiply very rapidly in the proper environment and can turn a fuel very corrosive in a very short time. The ramifications of this are obvious and do not have to be discussed here in any detail. Suffice it to say this is not a good situation.

As can be seen by the data in the tables, killing biologics can be done rapidly and effectively with current biocide additives on the market. The problem is, the dynamic of the US system will allow for a rapid return if treatment is not done on a regular basis and more care is given to **HOUSEKEEPING** at **ALL** levels of the distribution system. The program that was utilized by the company in this paper has been successfully completed up to Phase I. Phase II is still on going and a follow-up paper will be presented at a later date.

Conclusions: Changes in fuel formulations have brought about an increasing likelihood that fuel systems (both diesel and gasoline) will come under biological attack. Regardless of the housekeeping at each level, biological contamination can occur in any vessel that contains even small amounts of water. If a fuel system is to remain contaminant free, a program of prevention rather than repair should be enacted. The consequence of inaction will without doubt, have far reaching effects on consumers in the coming years. In this instance, Mother Nature is not on the side of the oil companies.

BIOCIDE TREATMENT SUMMARY

- DIESEL TANKS WERE TREATED WITH 15 ppm (a.i.) CIT. GASOLINE TANKS WERE TREATED WITH 240 ppm (a.i.) NMEND.
- CATALASE ACTIVITY WAS MEASURED AS PRESSURE (psig) DEVELOPED IN REACTION TUBE, AFTER 15 MINUTES EXPOSURE TO H202.
- N.D.: NOT DETERMINED; NO SAMPLE DRAWN.
- BDL: BELOW DETECTION LIMIT:<1.00E=01 FOR AEROBES AND SRB; <0.1 FOR CATALASE ACTIVITY.
- BIOCIDE WAS ADDED 3 - 7 DAYS AFTER 07 OCT., 1993 SAMPLING
- BIOCIDE WAS ADDED 7 - 10 DAYS AFTER 30-31 OCT.; 09 NOV., 1993 SAMPLING

TERMINAL

BIOCIDE TREATMENT SUMMARY

- ➢ MID GRADE GAS:
  - 2 OF 3 SHOWED REDUCTIONS *
  - 1 SHOWED AN INCREASE

* LATER TESTING SHOWED 2 OF 3 TOTALLY ELIMINATED
1 OF 3 BECAME RE-CONTAMINATED.

- ➢ REGULAR GAS:
  - 3 OF 3 SHOWED REDUCTIONS
  - 2 OF 3 SHOWED TOTAL ELIMINATION

TERMINAL
BIOCIDE TREATMENT SUMMARY

- 17 OF 21 TANKS TESTED SHOWED POSITIVE BIOLOGICALS

- DIESEL: 7 OF 7 SHOWED POSITIVE ACTIVITY
  7 OF 7 SHOWED REDUCTION OF ACTIVITY
  4 OF 7 SHOWED TOTAL ELIMINATION OF ACTIVITY

- GASOLINE: 9 OF 14 TANKS SHOWED POSITIVE BIOLOGICALS
  PREMIUM GAS:
  4 OF 4 SHOWED REDUCTION OF ACTIVITY
  2 OF 4 SHOWED TOTAL ELIMINATION OF ACTIVITY

SERVICE STATION
BIOCIDE TREATMENT SUMMARY

- 20 OF 29 TANKS SHOWED ACTIVE BIOLOGICALS
- 18 OF 20 TANKS SHOWED SIGNIFICANT REDUCTION OR ELIMINATION OF BIOLOGICAL ACTIVITY AFTER FILTRATION AND BIOCIDE TREATMENT

BIOCIDE TREATMENT
TERMINAL TANKS

Table 2. Effect of treatment program on microbial loads in 21 terminal tanks.

Tank	Product	Test Dates	Treatment Date	Treatment (1)	Aerobe Titer (MPN/mL)	SRB Titer (MNP/mL)	Catalase Activity (2)
1	DIESEL	18-May-93	Jun-93	CIT	1.00E+05	N.D. (3)	N.D.
		11-Nov-93			BDL (4)	N.D.	N.D.
		8-Mar-94			BDL	N.D.	N.D.
		14-Jul-94			BDL	N.D.	N.D.
2	DIESEL	18-May-93	Jun-93	CIT	1.00E+05	N.D.	N.D.
		11-Nov-93			BDL	N.D.	N.D.
		8-Mar-94			BDL	N.D.	N.D.
		14-Jul-94			BDL	N.D.	N.D.
3	MID GRD	6-Oct-93	Oct-93	NMEND	BDL	BDL	34.0
		8-Mar-94	(5)		BDL	N.D.	N.D.
		14-Jul-94			BDL	BDL	3.6
4	PREM	6-Oct-93	Oct-93	NMEND	BDL	BDL	1.0
		8-Mar-94			BDL	BDL	BDL
		14-Jul-94			BDL	BDL	1.5
5	PREM. GAS	18-May-93	Oct-93	NMEND	1.00E+02	N.D.	N.D.
		6-Oct-93			1.00E+02	N.D.	0.6
		8-Mar-94			BDL	BDL	BDL
		14-Jul-94			BDL	BDL	1.5
6	MID GRD	18-May-93	Oct-93	NMEND	1.00E+01	N.D.	N.D.
		11-Nov-93			1.00E+04	BDL	4.0
		8-Mar-94	Mar-94		BDL	BDL	101.0
		14-Jul-94			BDL	BDL	BDL
7	PREM	18-May-93	Oct-93	NMEND	0	N.D.	N.D.
		11-Nov-93			N.D.	N.D.	N.D.
		8-Mar-94			BDL	BDL	BDL
		14-Jul-94			BDL	BDL	BDL

BIOCIDE TREATMENT TERMINAL TANKS

Table 2. Effect of treatment program on microbial loads in 21 terminal tanks.

Tank	Product	Test Dates	Treatment Date	Treatment (1)	Aerobe Titer (MPN/mL)	SRB Titer (MNP/mL)	Catalase Activity (2)
8	REG	18-May-93	Oct-93	NMEND	1.00E+02	N.D.	N.D.
		8-Mar-94			BDL	BDL	BDL
		14-Jul-94			BDL	BDL	BDL
9	DIESEL	11-Jun-93	Jun-93	CIT	1.00E+05	N.D.	N.D.
		1-Nov-93			1.00E+05	BDL	1.0
		2-Mar-94			1.00E+02	BDL	187.0
		27-Jul-94			N.D.	N.D.	N.D.
10	DIESEL	11-Jun-93	Jun-93	CIT	1.00E+05	N.D.	N.D.
		1-Nov-93			1.00E+01	2.00E+02	22.0
		2-Mar-94			1.00E+01	1.00E+03	99.0
		27-Jul-94			N.D.	N.D.	N.D.
11	DIESEL	11-Jun-93	Jun-93	CIT	1.00E+03	N.D.	N.D.
		1-Nov-93			BDL	BDL	1.0
		2-Mar-94			BDL	BDL	68.0
		27-Jul-94			N.D.	N.D.	N.D.
12	PREM	30-Oct-93	Nov-93	NMEND	1.00E+01	BDL	19.0
		2-Mar-94	(6)		BDL	BDL	48.0
		27-Jul-94			1.00E+01	BDL	13.8
13	MID	30-Oct-93	Nov-93	NMEND	1.00E+01	BDL	18.0
		2-Mar-94			BDL	BDL	15.4
		27-Jul-94			1.00E+01	BDL	0.6
14	REG	30-Oct-93	Nov-93	NMEND	1.00E+03	BDL	195.0
		2-Mar-94			1.00E+02	BDL	19.0
		27-Jul-94			N.D.	N.D.	N.D.

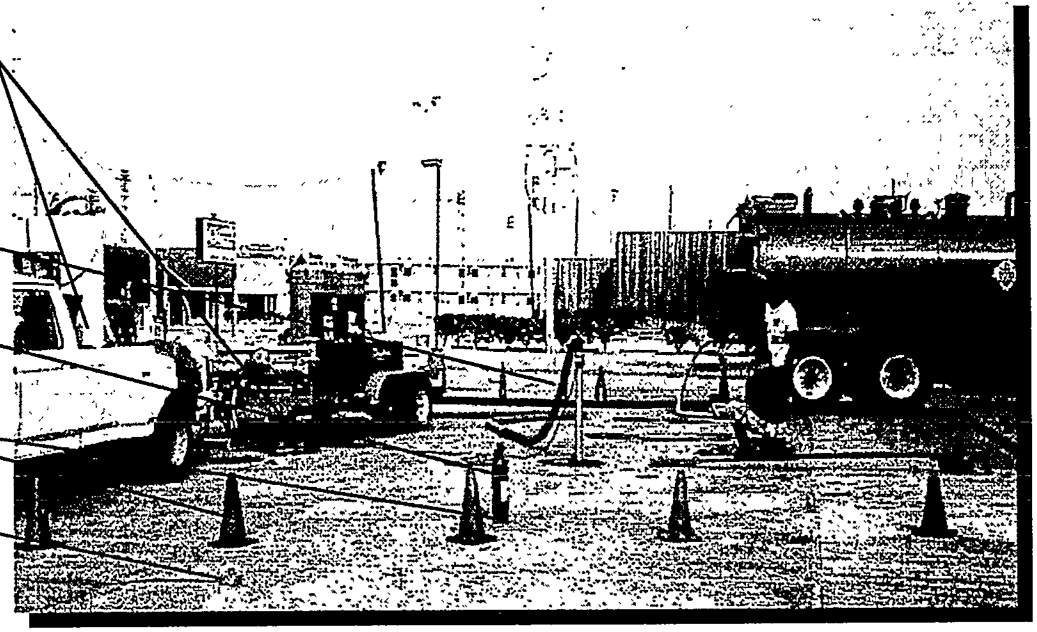
BIOCIDE TREATMENT
TERMINAL TANKS

Table 2. Effect of treatment program on microbial loads in 21 terminal tanks.

Tank	Product	Test Dates	Treatment Date	Treatment (1)	Aerobe Titer (MPN/mL)	SRB Titer (MNP/mL)	Catalase Activity (2)
15	REG	30-Oct-93	Nov-93	NMEND	1.00E+05	1.00E+02	196.0
		2-Mar-94			BDL	BDL	196.0
		27-Jul-94			N.D.	N.D.	N.D.
16	PREM	30-Oct-93	Nov-93	NMEND	1.00E+04	BDL	BDL
		2-Mar-94			1.00E+01	BDL	0.1
		27-Jul-94			1.00E+01	BDL	BDL
17	DIESEL	31-Oct-93	Jun-93	CIT	1.00E+05	1.00E+02	21.2
		2-Mar-94			1.00E+02	BDL	7.5
		27-Jul-94			BDL	BDL	1.0
18	PREM	9-Nov-93	Nov-93	NMEND	1.00E+05	BDL	0.0
		7-Mar-94			BDL	BDL	2.0
		6-Jul-94			1.00E+01	BDL	BDL
19	MID	9-Nov-93	Nov-93	NMEND	1.00E+02	BDL	BDL
		7-Mar-94			BDL	BDL	BDL
		14-Jul-94			BDL	BDL	BDL
20	REG	9-Nov-93	Nov-93	NMEND	BDL	BDL	0.2
		7-Mar-94			BDL	BDL	BDL
		14-Jul-94			BDL	BDL	BDL
21	DIESEL	9-Nov-93	Jun-93	CIT	1.00E+02	BDL	BDL
		7-Mar-94			1.00E+01	BDL	4.0
		14-Jul-94			1.00E+01	BDL	1.0

FIELD FILTRATION - GASOLINE

- GASOLINE FILTRATION AND TANK CLEANING REQUIRE SPECIAL ATTENTION TO SAFETY.



*EXPLOSION PROOF SYSTEM

*GROUNDING

*FIRE PROTECTION

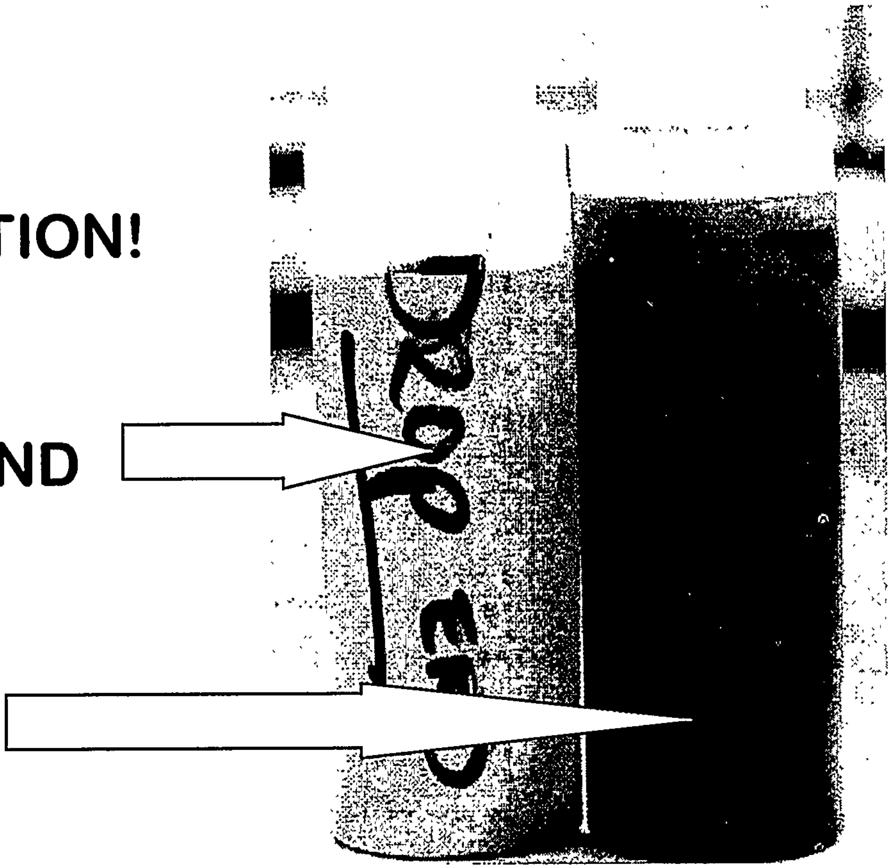
*PROTECTED AREA

*EMERGENCY SHUTOFF

PROTOTYPE FILTRATION SYSTEM

FILTRATION - GASOLINE

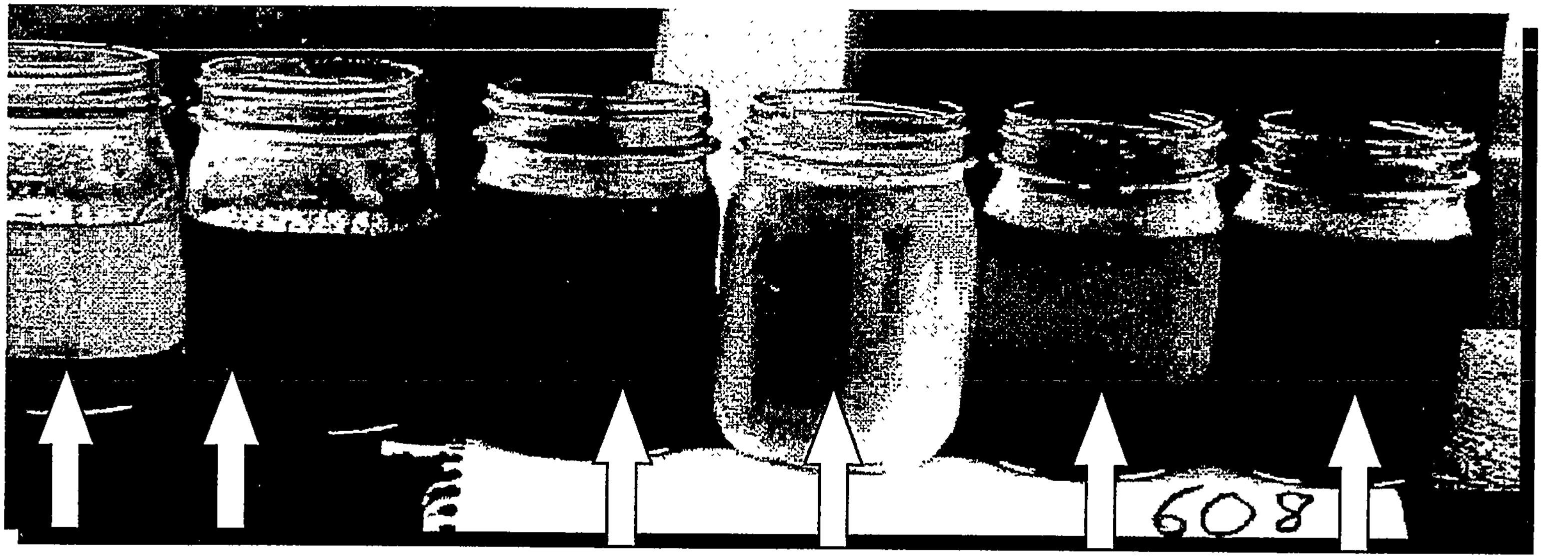
- SAMPLES TAKEN ONLY FROM ONE END OF A TANK CAN GIVE MISLEADING INFORMATION!



DROP &
SAMPLING END

PUMP
LOCATION

FILTRATION - GASOLINE



DROP - SUMP **DROP - SUMP** **DROP - SUMP**

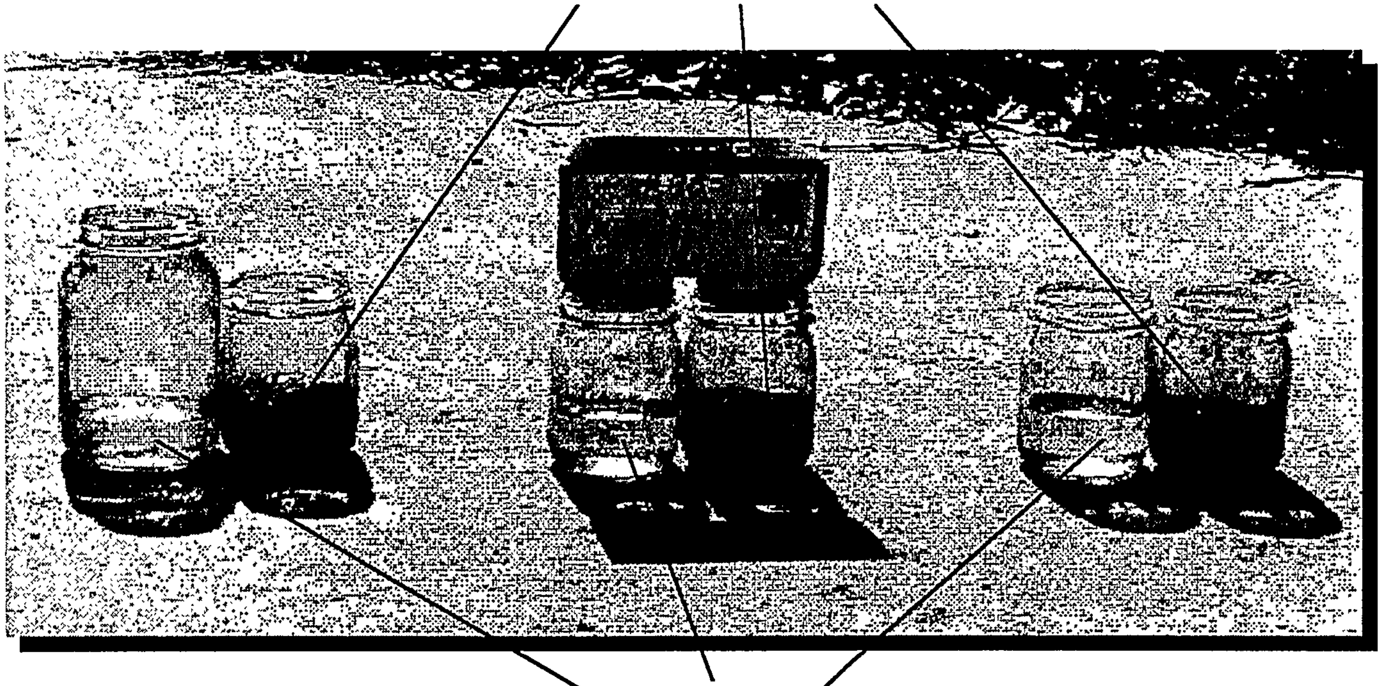
SUPREME **PLUS** **REG**

GASOLINE SAMPLES
STATION #608

FILTRATION - GASOLINE

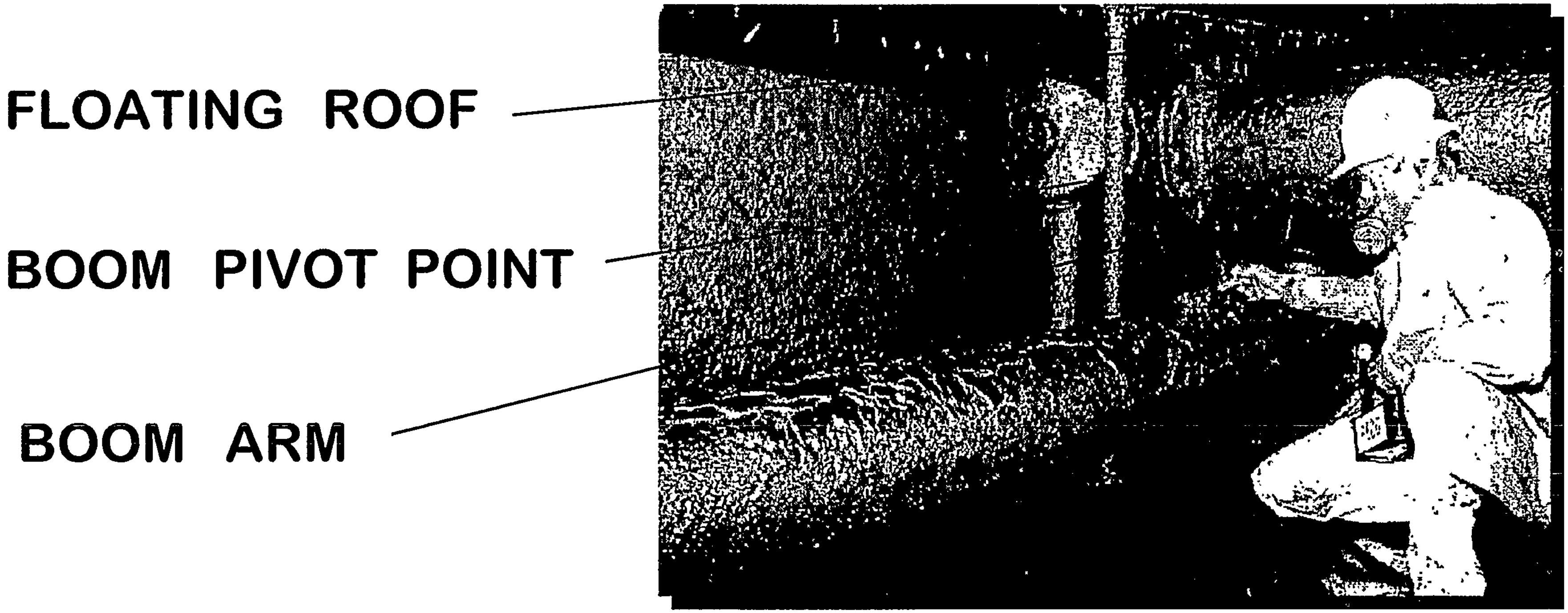
TANK SAMPLES

BEFORE



AFTER

BIOLOGICAL CONTAMINATION



5th International Conference on
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HARMONISATION OF MICROBIAL SAMPLING AND TESTING METHODS FOR DISTILLATE FUELS

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Increased incidence of microbial infection in distillate fuels has led to a demand for organisations such as the Institute of Petroleum to propose standards for microbiological quality, based on numbers of viable microbial colony forming units. Variations in quality requirements, and in the spoilage significance of contaminating microbes plus a tendency for temporal and spatial changes in the distribution of microbes, makes such standards difficult to implement. The problem is compounded by a diversity in the procedures employed for sampling and testing for microbial contamination and in the interpretation of the data obtained. The following paper reviews these problems and describes the efforts of The Institute of Petroleum Microbiology Fuels Group to address these issues and in particular to bring about harmonisation of sampling and testing methods. The benefits and drawbacks of available test methods, both laboratory based and on-site, are discussed.

1. INTRODUCTION

Microbiological spoilage of fuel and fuel components now increasingly poses problems in the refinery, storage facilities and for traders, distributers and end-user. In 1987 the Institute of Petroleum established the Fuels Task Force which concluded that the increase was at least in part merely perceived and due to a heightened industry awareness of microbial fuel spoilage[1]. This awareness unfortunately frequently lacks sufficient comprehension of the complex nature of the problem. Papers presented at the IP Microbiology Committee Conference on Microbiology of Fuels [2,3,4,5,6] indicate that changes in refining, blending and distribution practices, particularly co-mingling, plus the use of finer filters on diesel engines are likely to be additional factors in the escalation of spoilage incidents. In the early 1990's as a consequence of microbial contamination in a succession of Russian Gas Oil cargoes discharged at European ports, a confused industry, more familiar with compliance to chemical and physical specifications, called for implementation of microbial standards for fuels. Such were hastily proposed by various inspection companies, but lack of consistency in sampling procedures and methods used to assess microbial spoilage, sometimes even within the same organisation, casts some doubt on their worth.

2. THE IP MICROBIOLOGY FUELS GROUP

The IP Fuels Task Force reconvened in December 1992 as the Microbiology Fuels Group, inviting input from fuel suppliers, users, inspection companies and those offering treatment strategies, in an attempt to harmonise the procedures employed to detect microbial contamination. As a result, the IP385/88 "Code of Practice for Examination of Light Distillate Fuels for viable Microorganisms"[7] has been updated and retitled "Determination of the viable Microbial Content of Fuels and Fuel Components Boiling Below 390°C - Filtration and Culture Method" and is due for publication in the 1995 edition of IP Standard Methods of Analysis and Testing of Petroleum and Related Products, along with an additional procedure "Determination of Fungal Fragment Content of Fuels Boiling Below 390°C". Thus standard test methods for assessment of both viable microbial numbers (colony forming units) and fragments of fungal material (often called MBC) will be available. Test Methods are considered in more detail in section 5 below.

A supplementary document "Guidelines for the Investigation of Microbial Content of Fuels Boiling Below 390°C" will be published separately by the IP. This document will describe the ecology and consequences of microorganisms contaminating fuel in addition to specifying procedures for sampling various fuel systems for microbiological analysis. The two test methods specified above will be appended to the document, which will include comments on the interpretation of results of these tests plus comments on how data from other test procedures (e.g. filterability tests) may be used to interpret the significance of microbial infection. A brief review of measures for remediating microbial spoilage in fuel will also be included in the Guidelines document.

3. MICROBIOLOGICAL STANDARDS FOR FUEL

3.1 Existing Standards

Part of the remit of the IP Microbiology Fuels Group is to re-examine the issue of setting microbial standards for fuel. The previous Fuels Task Force concluded that it was not possible to set standards for fuels based on microbiological numbers as these could not be correlated with fuel performance characteristics. Nevertheless, there was a known guidance figure of 500 fungal fragments l^{-1} (a microscopic particle count, see section 5.1.3) used by the Royal Navy at that time to indicate the need for cleaning of on-board fuel tanks for gas turbine vessels. It was not a limit for acceptability for use. A similar method and figure was proposed for jet fuel by Cabral in 1980[8]. Whilst it is evident that upper limit values are of value to an end-user such as the Royal Navy for a particular fuel application, the current demand is for limit values to be set for bulk fuel which may have a host of different end use applications. The limit values offered by inspection companies to traders have differed, sometimes varying year by year. Examples are:

- 500 colony forming units ml^{-1} (500,000 cfu l^{-1})
- 500 cfu bacteria l^{-1}, 200 cfu yeasts l^{-1}
- 750 fibres l^{-1} (fungal fragment count)
- Any of:
    - 1000 fungal fibres 1^{-1} (fungal fragment count)
    - 1000 viable bacteria 1^{-1}
    - 1000 viable yeasts/moulds 1^{-1}
    - 1000 viable fuel degraders 1^{-1}
    - Sulphate reducing bacteria - any number.
- 3000 viable organisms 1^{-1}

Not surprisingly inspection companies are offering compliance testing. One company, as a convenient way of interpreting the result of its branded fuel test kit, has suggested that severity of infection is related to the diversity of microbial types. Whilst there is an element of truth in this, we still experience severe spoilage problems attributable to a few or even single species of microbes.

There is much merit in Laurenson's view[9] that one approach would be "to agree the levels of microbial contamination which could be achieved if good standards of housekeeping are maintained". However, it seems that the IP are most unlikely to issue microbiological standards for fuel in their Guidelines document. The best that could be hoped for are a range of guideline figures which should be interpreted in conjunction with other extenuating factors such as the fuel use, storage times and conditions. Upper limit values for acceptability could vary according to whether fuel was intended for gas turbines, marine engines, road vehicles, heating or power generation. Upstream, upper limit values could vary for short or long term storage, blending, co-mingling etc.. The reasons for the reluctance to set numerical limit values are apparent on consideration of the factors discussed in section 3.2.

3.2 Factors Complicating the Implementation of Microbiological Standards.

3.2.1 Lack of Correlation of Microbial Types with Spoilage Potential.

Whilst once microbial fuel contamination was almost entirely by the mould *Hormoconis resinae* (once known as *Cladosporium resinae*), a great diversity of bacteria, yeasts and moulds can now be recovered from fuel samples. The importance of each type in causing fuel spoilage is however usually not known. Some, but not all, moulds will proliferate at fuel/water interfaces causing filter plugging mats of mould mycelium. Other moulds may be present in high numbers as spores which will not proliferate and will present no operational problems. Likewise some yeasts form filamentous growth whilst others remain dispersed as small ovoid cells. It is likely that only a small percentage of bacteria recovered from fuel are capable of producing the polymer which has caused severe fouling in recent spoilage incidents, and even then they will only do so under certain nutrient or physical conditions. Different microbes cause different problems. Usually the tendency of microbial slimes to foul filters, orifices and gauges is of importance. Other concerns are the promotion of stable water haze by microbially produced surfactants and the generation of sulphide by Sulphate Reducing Bacteria which may result in tank corrosion and/or failure of fuel sulphide specifications. It is inconceivable that a single numerical standard could reflect the diverse consequences of contamination by a wide variety of microbial types.

3.2.2 Lack of Correlation of Microbial Numbers with Spoilage Potential.

Viable microbial counts of colony forming units cannot reveal how many bacteria or yeasts are aggregated into each viable "unit". Without some knowledge of this and of the relationship, if any, between amounts of solid microbial by-products (e.g. polymer) and living microbial cells, a viable count is only a vague indication of the amount of microbially related particulate matter present. Additionally many dead microbial cells could be present and not contribute to a viable count.

On the assumptions that simple microbial numbers are significant, that distillate fuels should not contain more than 2 mg l^{-1} particulates and that all of these particulates are microbes, then some rough approximations can be made:

> 2 mg l^{-1} particulates equates to 8 x 10^8 individual bacteria l^{-1} on a wet weight basis and 4 x 10^9 bacteria l^{-1} on a dry weight basis.
> 2 mg particulates l^{-1} equates to 4 x 10^7 individual yeasts l^{-1} on a wet weight basis and 2 x 10^8 yeasts l^{-1} on a dry weight basis.

Clearly, these figures are many orders of magnitude different from those proposed as standards in section 3.1. A recent publication[10] describes filter plugging experiments using fuel deliberately contaminated with microorganisms. It suggests that 10^6 - 10^7 l^{-1} organisms (0.1 - 0.7 mg l^{-1} bacteria/yeasts and 10 - 20 mg l^{-1} fungi) are required to induce poor filterability. In an incident where a vessel was subject to debilitating Main Engine filter plugging, we have authenticated that the problem was caused by filamentous yeast contamination and analysis of bottom samples from the bunker tanks indicated between 3.72 x 10^7 and 6.60 x 10^7 viable yeast cfu l^{-1} (analysis method was IP385, modified to include membrane elution as per the soon to be published update). Such figures are more in keeping with those based on gravimetric estimates of microbial particulate, quoted above.

A fungal fragment count (MBC) is not much better; recognition of fungal fibres under low power microscopy is not easy and whatever the size of the fibre it is recorded as one unit. Recognition and counting of individual bacteria or yeasts under low power microscopy is not practical and is not attempted. Direct microscopic counts include both living and dead units and therefore cannot indicate the potential for microbial proliferation.

3.2.3 Accuracy of Viable Counts

Methods for counting viable microbes in fuel employ procedures which assess the number of colony forming units (cfu) which grow on nutritive agar gels inoculated with sample material, or microbial particulate collected on a filter from sample material. One colony is equated to one viable microbial particulate and by consideration of the sample volume tested, the number of colonies on the agar plate is used to express numbers of cfu per litre or ml (usually the former) of sample. The widely used IP385/88 is such a method and it suggests fuel aliquots of 1 ml, 10 ml and/or 100 ml should be filtered. Many contracts to purchase fuel now include a microbial limit figure of 1000 cfu l^{-1}. Using these aliquot sizes and this limit figure the following confidence table can be calculated

Aliquot size	**No. colonies**	**cfu l^{-1}**	**95% confidence range**
1 ml	1	1000	0 - 4000
10 ml	10	1000	300 - 1800
100 ml	100	1000	820 - 1220
100 ml	120	1200	1000 - 1440

It would be a brave trader who rejected a fuel parcel or demanded that it required remedial treatment because it nominally contained 1200 cfu l^{-1}. Other test methods for viable microbes could be expected to show similar degrees of error.

3.2.4 Spatial Variations in Microbial Populations

Microbial contaminants are rarely distributed evenly within fuel systems. Microbes and microbial material have a specific gravity of 0.9 - 1.3 g cm^3 and hence, if suspended in fuel phase, tend to settle. This process is unpredictable, dependent on the size and mass of microbial aggregates. Settling can be impeded if biosurfactants have promoted emulsification. Generally, microbes concentrate in any water phase, particularly at the fuel/water interface. Disturbance of fuel, for example during tank filling, may result in the dispersion of slimes into fuel phase. The rather stringent limit values quoted in section 3.1 for fuel phase samples reflect the possibility that if microbes exceed these values in bulk fuel phase, then spoiling microbial slimes are likely to be present somewhere in the system, ready to be passed on to an unfortunate end-user. The truth is however that no correlation can be established between numbers of microbes in water phase or at the interface and numbers in bulk fuel phase.

It is in practice frequently possible to tolerate quite high microbial contamination in the bottom of "fill and draw" storage tanks which have a high level take-off or a swing arm take-off. Eventually a progressive deterioration in fuel quality or tank bottom integrity will probably demand remedial action. Traders who rent an empty (clean?) tank are not so fortunate if they have microbial problems. Microbes precipitate progressively from the upper fuel which becomes more acceptable but at the same time the problem becomes concentrated in the lower fuel. Often the consignment is sold off in small parcels until the final purchaser is the unfortunate recipient of the lower heavily contaminated fuel.

Microbes also attach to tank surfaces in exceedingly high numbers as biofilms, where they probably play an important role in continually replenishing the populations of freely suspended microbes. Biofilms pose particular problems in that whilst they are an important part of the overall tank or system contamination, they are not easily sampled. They may also be exceedingly hard to kill. In addition to a heterogenous distribution on a macroscopic scale there are microscopic variations in microbial distribution, particularly within biofilms.

Obtaining truly representative samples is thus always going to be a difficult exercise; a single sample will never reflect the microbiological condition of fuel in the whole tank or system and hence a single numerical limit can not be meaningfully applied.

3.2.5 Temporal Changes in Microbial Populations

Numbers, types and distribution of microbes in fuel systems may change, sometimes within a relatively short time. Thus a sample analysis provides only a spot check in time and the moment results are received, usually 4 - 7 days after sampling, they will be out dated. Such is the nature of assaying living entities; microbes multiply and sometimes they die. Stringent limit values may reflect the potential for low numbers of microorganisms to proliferate to unacceptable levels, but such proliferation is not predictable, dependent largely on housekeeping procedures, particularly water drainage regimes.

3.2.6 Different Quality Requirements for Different Users and Distributors

It is largely the end user who suffers the direct consequences of microbial infection in fuel although responsibility may lie several steps back up the distribution chain; a fact of which distributors are becoming increasingly aware, conscious of several, recent, expensive litigations. It could be argued that high quality standards should be implemented for fuel in distribution to reflect the potential for future proliferation. Conversely many users may tolerate far lower standards; section 3.2.2 suggests that only when exceedingly high viable counts are obtained are filter plugging problems encountered. However, for jet fuel a no risks policy dictates the implementation of the highest quality standards. There is also a case for high quality standards in marine diesel in the light of some recent incidents of vessel's engine failure with potentially serious consequences. Fuel destined for applications employing fine filters also needs to be of higher microbiological quality. Heating Oil perhaps need not be of such a high standard but even in this application, problems have been attributed to microbial spoilage. Storage time will also be a factor in determining quality requirements. High quality standards are frequently imposed by long term storers wary of the potential for proliferation[11]. Tank and equipment corrosion will be an added risk wherever storage is anticipated and hence the presence of SRB becomes of crucial importance.

4. SAMPLING

Much information on preferred sampling points, sampling devices and transportation will shortly be available in the IP Guidelines document. Important points are summarised in the following sections 4.1 to 4.5. The importance of using correct sampling procedures and recording all relevant information about the sample, cannot be over-stressed. Such is vital if any meaningful interpretation of analysis data is to be obtained.

4.1 Sample Containers

500 ml clear glass bottles with liquid tight, and preferably gas tight, closures of a material which is not reactive with the sampled material are recommended. For bottom sludge samples wide necked jars fitted with liquid tight closures are appropriate. Sample containers and there closures can be sterilised but it is sufficient to rinse them out with material to be sampled, ideally from the top of the sampled tank, prior to use.

4.2 Sampling Devices

Preferably samples should be taken directly into the sample bottle for example using sampling cages which allow the bottle stopper to be removed at the desired level in the material being sampled. For bottom/interface samples, devices such as bottom and interface samplers can be used provided they ensure that the integrity of the sample is maintained until it is transferred to the sample bottle. Devices should be thoroughly cleaned and rinsed with material to be sampled prior to use. Our preference is to decontaminate bottom samplers with 70% Industrial Methylated Spirit; this should then be thoroughly rinsed away before taking samples.

4.3 Sampling Techniques

Sampling techniques are essentially as employed for samples for other analyses but they additionally should ensure that contamination of the sample and cross-contamination of systems being sampled is avoided. Never touch the insides of sample containers, sampling devices or their closures. Always use clean sampling equipment and sampling cord. When sampling several layers sample from top to bottom. Samples can be taken from sample outlets directly into sample bottles but it should be ensured that the outside of the sample outlet is wiped clean and the inside flushed through with material being sampled.

If possible samples should be kept cool during transportation to the laboratory. It is important that microbiological analysis is conducted as soon as possible after samples are taken, preferably within 48 hours. Microbial populations in old sealed samples containing water frequently change from a predominantly aerobic flora to a predominantly anaerobic flora; free water then often blackens due to SRB activity. Most samples would be expected to be water free. The successful detection and assay of viable microbes is then dependent on survival in the fuel. Although in "clean" jet fuel the survival of bacteria has sometimes been measured in hours, survival in gas oil is frequently much longer, possibly due to more protective extra-cellular substance. Survival of yeasts and moulds is considered to be good with a slow decay over days and weeks. The factors which influence survival in a fuel sample have not been rigorously evaluated but are believed to be presence of free water, relative humidity, storage temperature, oxygen availability, presence of protective substances (e.g. humectants) and absence of anti-microbial substances.

4.4 Sample Labelling

Samples should be clearly labelled with tie on labels with additional information recorded on separate sheets if necessary. The following information should be recorded;

- Place at which sample was drawn.
- Description of the material sampled.
- Tank number.
- Volume and depth of fuel sampled.
- Location of draw off point, if applicable.
- Ship's name, if applicable.
- Type of sample and level from where it was taken.
- Date and time of sampling.
- Name or other identifying mark of the operator who drew the sample
- Whether or not the container was sterilised or washed out with product prior to sampling.
- Appearance of sample at the time of sampling.
- Sample temperature.

The testing laboratory should record;

- Date and time the sample was received into the laboratory
- Date and time the sample was tested.

Additionally relevant information about the tank/vessel/system sample should be recorded such as tank type, roof type, description of de-watering facilities, age of tank/vessel plus details of coatings, general condition, corrosion and maintenance. Examples of forms for recording this information will be issued with the IP Guideline document.

4.5 Sampling Plans

Samples should be drawn from sufficient locations and at such a frequency that testing will provide a comprehensive view of the state of fuel in a tank or system. Obviously, practical constraints such as availability of sample points and time for sampling and not least cost will restrict these endeavours but all efforts should be made to obtain a sensible balance. Recommendations encompass two approaches to sampling;

- To sample from locations most likely to harbour microbes (usually a sample containing water phase. This sample will not represent overall condition of the fuel but will enable it to be established whether any microbial contamination is present. In our experience this type of sample is usually sufficient for simple monitoring exercises (e.g. using on-site tests) or initial surveys.

- to sample sufficient locations to provide an overall representation of microbial contamination in the tank. Such is required, as recommended below, if comprehensive information on overall microbiological quality is to be obtained.

4.5.1 Shore Tanks

It is generally accepted that in quiescent fuel tanks microbial numbers will be highest in the lower fuel layer. A knowledge of the distribution and behaviour of the microbial particulates in fuel is essential when interpreting the results of tests on fuel samples drawn from various points in storage tanks, and for planning and implementing anti-microbial strategies appropriate to the sale and use of the fuel.

When problems are suspected it may well be appropriate to sample daily or even more frequently. It is however recommended that sampling and monitoring of tanks takes place on a routine basis not just when problems are experienced. We would typically recommend monthly monitoring but this frequency may be increased or decreased with experience.

Because microbial populations may vary across a tank, particularly where tank settling has resulted in uneven distribution of water, it is advisable to sample from all available tank hatches. All efforts should be made to establish the location of the lowest part of the tank and obtain a sample containing water. The IP Guidelines will recommend duplicate samples from;

- The Upper, Middle and Lower levels using the bottle and cage technique.
- The Oil/Water Interface, if present using an interface sampler.
- The Bottom of the tank using a bottom sampler.
- Free water layer, if present using a bottle and cage or a bottom sampler.
- Sludge layer, if present using a sludge sampler.

Although testing individual layer samples is most informative, a running sample or a composite sample is often offered. The former is drawn by lowering an open bottle at a steady rate to the take-off point and withdrawing it steadily. The sample tends to be biased disproportionately towards lower fuel. A common composite sample is equal proportions of samples of upper, middle and lower fuel, each drawn from the centres of the upper third, middle third and lower third respectively. Thus running and layer composite samples are not directly comparable.

4.5.2 Ship's Cargo Tanks

The IP Guidelines will recommend duplicate samples from each ship's tank of Upper, Middle and Lower levels (a composite of these samples may be made if necessary) and the Bottom. Alternatively, as an economy, a bottom sample and/or interface sample, if present, plus a sample from 1 metre above the interface/bottom can be taken. The comments in section 4.5.1 relating to the shore tanks apply also to ship's tanks.

4.5.3 Road/Rail Cars

The IP Guidelines will recommend a Middle layer sample from each road/rail car plus if possible an outlet sample from the vehicles delivery line.

4.5.4 End User Tanks

These tanks include small permanent storage tanks for aviation, marine power generation/propulsion, industrial use, garages, and domestic heating and on-board tanks of aircraft, ships, vehicles and locomotives. The IP Guidelines will recommend samples from Middle and Bottom layers plus if possible an outlet sample from the take off line.

5. TEST METHODS

5.1 Laboratory Test Methods

Comprehensive information will usually only be obtained from analysis of samples by a competent laboratory with the relevant expertise. Laboratory tests could include not only those based on conventional microbiology, but also various methods based on newer technologies such as enzyme assays, ATP luminometer assays, gene probe technology, conductance and impedance. The latter all offer the advantage of producing rapid results but generally suffer from a lack of sensitivity. They do not have universal acceptability within the petroleum industry and because they do not directly assess the presence of microbes may suffer variability in their validation against conventional methods[12] Frequently these methods can not determine whether microbial presence is live or dead. Hence, whilst exhibiting potential for use in aqueous phase analysis in some sectors of the petroleum industry, in their current state of development these rapid technologies can not be considered for any standardisation or harmonisation programme and will not be considered further in this paper.

Laboratory methods also include non-microbiological methods which may provide insight into the consequences of contamination. Comments are included in section 5.1.5.

5.1.1 IP385/88 and its proposed update

The principle of the method is that various volumes of fuel sample are filtered through membrane filters which retain microbes on the surface. The membranes are then washed with a detergent solution and rinsed before being transferred to a layer of nutritive agar gel which is then incubated. Colonies form and are counted in order to assess numbers per unit volume of sample, subject to errors as explained in section 3.2.3. The method has been widely used but does suffer some disadvantages some of which are addressed in the modification due for publication in 1995. The method has been virtually re-written and includes more practical guidance for the user. Modifications are based on the results of trials of a number of methods by fuel testing laboratories. Typical results from these trials are given in the Table 1. Key modifications, and the rational behind them, are summarised in sections 5.1.1.1 to 5.1.1.6.

5.1.1.1 Elution of microbes from membrane.

At least one inspection company employs an in-house modification of IP385/88, whereby instead of transferring membranes directly to agar test media, membranes are agitated in an eluent to resuspend microbes. The elutent is then assayed by conventional microbiological techniques. This procedure offers advantages in the assay of heavier contamination levels and also in that the time consuming filtration step need only be conducted once. Hence, the proposed IP385 update will include an option to use an elution procedure in addition or as an alternative to a procedure where membranes are transferred directly to agar plates.

5.1.1.2 Detergent.

IP385/88 specifies the use of branded non-toxic oil spill dispersants to wash fuel through test membranes. Some of the recommended dispersants are no longer available. Tween 80 has been found to be equally as effective and hence will now be the recommended detergent. The in-house elution method described in section 5.1.1.1 omits the use of detergent, the filtration of which can take an excessively long time. However, the current proposal is that the detergent wash stage be retained in the modified IP385 as there is concern that microbes will not be reproducibly eluted into aqueous suspension from a fuel saturated membrane without the aid of a detergent. This decision could be changed if data to validate elution without the use of detergent is forthcoming. There are undoubtedly time savings if the detergent wash is omitted. Detergent wash will certainly be retained for use in the procedure where membranes are transferred directly to agar plates.

5.1.1.3 Membrane type.

IP385/88 proposes the use of 0.45 μm membranes for fungal (yeast and mould) assay and 0.22 μm membranes for bacterial assay. The 0.22 μm membranes cause filterability problems and hence because the majority of bacteria are retained by 0.45 μm membranes, this pore size is proposed for both assays in the updated IP385. Membranes made of mixed esters of cellulose have been found to present fewest filterability problems for most fuel types[13] and are recommended.

5.1.1.4 Agar Media.

Tryptone Soya Agar for bacteria and Malt Extract Agar for fungi are the test media of choice with the option of using alternative media, provided these are validated. Guidance will be given on the interpretation of results of samples where bacteria are found to have grown on the fungal medium and/or fungi have grown on the bacteria medium. The growth of yeasts on nominally bacterial media has been found to be a common cause of error in reporting results of IP385/88.

5.1.1.5 Water phase analysis.

The modified IP385 will include a recommendation that water phase in samples can be tested by conventional microbiological techniques. Procedural details will not be given but guidance will be found in the IP Guidelines document.

5.1.1.6 Sulphate Reducing Bacteria

Annexed to the modified IP385 will be a procedure for assaying Sulphate Reducing Bacteria (SRB) based on the use of Postgate's Medium as recommended in NACE Standard Method TMO194-94[14].

5.1.2 Fungal Fragment Count

This already widely used assay[15] will be issued as an IP standard method. The principle is to pass a known volume of fuel through a membrane filter which is then examined microscopically at x 250 - 400 magnification and fungal fragments counted. It is far quicker than assays for viable organisms, results usually being available within a few hours of receipt of samples, but suffers serious limitations in that it detects only one type of microbe (filamentous fungi) and is unable to distinguish viable material from dead material (see also comments in section 3.2.2). Experienced operators can however distinguish small broken fragments, probably derived from old, dying, disintegrating mycelium, from larger branching filaments which are usually viable and indicate recent detachment from an active mycelium in the tank bottom or attached to tank walls.

5.1.3 Other Microbiological Methods

In devising the updated IP385 other test methods were evaluated in trials in particular an emulsification method and a method whereby fuel is extracted into an aqueous phase. The former method is based on French AFNOR standard method M07070:1992[16] but for purposes of trials was updated to increase sensitivity; instead of testing emulsified fuel with dip-slides, the emulsion was tested by standard microbiological plate count. Dip-slides need careful recalibration if used for anything other than aqueous samples and thus the IP treated with caution the AFNOR proposal that results are interpreted directly from the manufacturers calibration chart. The extractant method was based on the use of Fuel Extractant (ECHA Microbiology Ltd.), an aqueous solution containing an inorganic flocculant; when shaken with a known volume of fuel microbes are entrained in the aqueous phase which can then be removed, mixed and tested by standard microbiological plate count. Experience has shown it is necessary to include some kind of extracting agent in the aqueous extractant as shaking fuel with water alone is prone to give incomplete and erratic extraction of microbes into the aqueous phase. When assaying moderate to highly contaminated fuels both the extractant and emulsification methods gave reasonably reproducible results which correlated well with the methods proposed for the IP385 update. However both these methods suffer from poor test sensitivity, the extractant method less so because it concentrates organisms in an aqueous phase rather than diluting them. Minimum detection levels are 250 cfu/l for the extractant method and 10,000 cfu/l for the emulsification method. Thus despite their ease of use the procedures are not appropriate for assessing lower levels of contamination and hence were not considered for the IP385 update. There are nevertheless incidences, particularly when assaying blended marine diesels when the IP385 method can not be used because of filtration problems. In such cases the emulsion or extraction procedures should be considered.

5.1.4 Expression of Results

Microbiological results are frequently quoted without reference to a test method, are sometimes quoted as numbers per litre, sometimes numbers per ml or alternatively without any reference to a unit fuel volume, a source of considerable confusion. It is proposed in the IP methods that results of analysis of fuel phase are expressed as number per litre. Water phase analysis results should be reported as numbers per ml as is standard microbiological practice for aqueous samples.

5.1.5 Non-microbiological Methods

5.1.5.1 Filterability and Particulate Contamination

There are number of standard test methods which are of use in assessing the consequences of microbiological contamination, particularly those which assess filterability and particulate contaminants. Examples of methods which assess the time taken for a known volume of fuel to pass through a membrane filter at standard vacuum and/or the weight of particulate collected are;

IP216/71(79) / ASTM D2276-89[17]
US Military Specs MIL-S-53021 and MIL-T-83133C
IP PM BH[18]

Although relatively quick, most of these tests require a large sample volume.

5.1.5.2 Filter Plugging Tendency

Other methods assess filter blocking tendency. IP387/90[19] primarily designed for marine fuels can be used. The method can be modified by changing the filter type so that it is applicable to automotive fuels.

5.1.5.3 Water Separation Characteristics

Methods which assess water separation characteristics can also be used as indicators of microbial spoilage where this has resulted in production of biosurfactants. Examples are ASTM D1094[20] and ASTM D3948[21].

5.1.5.4 Visual Examination

In heavily infected fuel there are frequently visual indications of spoilage particularly in bottom samples. Particular indications of microbial spoilage are haze and/or the presence of freely suspended soft particulate or film like material which attaches to the sides of glass bottles. Visual examination cannot be used to establish the absence of microbial contamination but it is always recommended as it provides a lot of information quickly[22].

5.2 On-site methods

There are considerable advantages in placing the ability to assess microbiological contamination in the hands of those who need the information. On-site test kits for fuel which require minimal facilities and training are available. Two are based on an extraction procedure; Bugbusters Test (SGS), Sig Fuel Test (ECHA Microbiology). Both have a sensitivity of c. 1000 cfu/l and are not strictly quantitative. The Liquicult Test (Metalworking Chemicals Services & Equipment Co.) employs the addition of 5 ml of fuel to a nutrient broth and gives semi-quantitative results but again sensitivity is poor (10,000 bacteria and 100,000 mould cfu/l). Dip-slides and related devices are widely available but their use to test fuels directly is in our opinion not to be recommended. Dip slides lack sensitivity (10^5 cfu/l or worse) for direct assays of fuels and results are highly erratic. At best they could be considered as a go/no go test for bottom samples. They can be used to assay an aqueous extractant after this has been shaken with fuel but sensitivity is still poor (about 10^4 cfu/l) and is ten times worse if used to assay a fuel emulsion (as per AFNOR M07070:1992).

To overcome sensitivity problems, an alternative to testing fuel samples is to test water phase samples and use results to decide whether to an initiate a more detailed laboratory based investigation of the fuel system. Dip-slides are suitable for such testing, the best being slides which assess bacteria, yeasts and mould cfu. On-site tests for SRB are also available and suitable for testing water phase. A disadvantage of all these on-site tests, which are based on conventional microbiology, is that they take several days to produce results. An on-site colorimetric enzymatic test for water associated with fuel, the Sig Rapid WB (ECHA Microbiology) allows semi-quantitative assessment of contamination after 1 hour.

6. SUMMARY

The standardisation of methods of sampling and testing fuels for microbiological contamination goes a long way to creating a level playing field for assessing this increasingly important fuel quality parameter, providing of course that the recommendations of the IP are adopted by the industry. Like all committee developed methods those proposed by the IP will be an amalgamation of a number of equally valid procedures and compromise the sometimes conflicting interests of the microbiologist and business. The implementation of universal limit values seems likely to remain a disputed issue, in the authors' opinion with good reason. The complexity of the problem requires expert consideration of all the factors affecting each case. The benefit of implementation of limit values *per se* is not disputed but in our opinion these should reflect the specific interests of the user or the handler of the fuel and as such should be in house values.

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(22) ASTM D4176, *Standard Test Method for Free Water and Particulate Contamination in Distillate Fuels*, ASTM.

TABLE 1. TYPICAL RESULTS OF MICROBIOLOGICAL FUEL ANALYSES USING VARIOUS METHODS.

SAMP NO.		COUNT PER LITRE BY EACH TEST METHOD				
		IP385/88	MEMBRANE ELUTION	FUNGAL FRAGMENT COUNT (MICRO-SCOPIC)*	EMULSIFIC-ATION (BASED ON AFNOR)	ECHA EXTRACT-ANT
1.	B	1 x 10^3	ND	-	ND	ND
	Y	ND	ND	-	ND	ND
	M	>10^4	4.8 x 10^4	3.1 x 10^4	2.7 x 10^4	9.5 x 10^3
2.	B	ND	ND	-	ND	ND
	Y	ND	ND	-	ND	1.7 x 10^3
	M	>10^4	1.4 x 10^6	1.5 x 10^4	1.6 x 10^6	5.5 x 10^6
3.	B	ND	ND	-	ND	ND
	Y	2.8 x 10^3	3.3 x 10^5	-	9.1 x 10^3	9.2 x 10^4
	M	ND	ND	ND	ND	ND
4.	B	100	ND	-	ND	ND
	Y	ND	ND	-	ND	ND
	M	150	5 x 10^4	ND	ND	ND
5.	B	96	ND	-	ND	ND
	Y	1.3 x 10^2	ND	-	3.3 x 10^4	ND
	M	ND	ND	3.8 x 10^3	ND	ND
6.	B	1.8 x 10^5	1.1 x 10^6	-	5.9 x 10^6	9.6 x 10^6
	Y	4.4 x 10^5	2.8 x 10^7	-	6.5 x 10^6	3.6 x 10^6
	M	ND	ND	1.5 x 10^4	ND	ND

B = BACTERIA Y = YEASTS M = MOULDS ND = NOT DETECTED

Minimum detection limits of the methods as applied are;

IP385/88; 50 l^{-1} Membrane Elution; 500 l^{-1} Fungal Fragment Count; 1500 l^{-1}

Emulsification; 10,000 l^{-1} ECHA Extractant; 250 l^{-1}

* The Fungal Fragment Count could include moulds and/or filamentous yeasts.

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CATALASE MEASUREMENT: A NEW FIELD PROCEDURE FOR RAPIDLY ESTIMATING MICROBIAL LOADS IN FUELS AND WATER-BOTTOMS

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Abstract: Low-grade microbial infections of fuel and fuel systems generally go undetected until they cause major operational problems. Three interdependent factors contribute to this: mis-diagnosis, incorrect or inadequate sampling procedures and perceived complexity of microbiological testing procedures. After discussing the first two issues, this paper describes a rapid field test for estimating microbial loads in fuels and associated water.
The test, adapted from a procedure initially developed to measure microbial loads in metalworking fluids, takes advantage of the nearly universal presence of the enzyme *catalase* in the microbes that contaminated fuel systems. Samples are reacted with a peroxide-based reagent; liberating oxygen gas. The gas generates a pressure-head in a reaction tube. At fifteen minutes, a patented, electronic pressure-sensing device is used to measure that head-space pressure.
The authors present both laboratory and field data from fuels and water-bottoms, demonstrating the excellent correlation between traditional viable test data (acquired after 48 -72 hours incubation) and catalase test data (acquired after 15 min. - 4 hours). We conclude by recommending procedures for developing a failure analysis data-base to enhance our industry's understanding of the relationship between uncontrolled microbial contamination and fuel performance problems.

Introduction. Uncontrolled microbial contamination in fuel systems has a significant adverse economic impact on operations. Participants in the fuel refining, distribution, retailing and consumption markets have only recently begun to recognize this fact. One reason for this is that research on the relationships between microbial growth and fuel performance problems rarely reaches a broad industrial audience. Additionally, many engineers and fuel chemists perceive microbiology to be an arcane science that relies on methodologies significantly different from those in which they have been trained. Moreover, most routinely used physical and chemical test methods use technologies that have been developed during the past two decades. In contrast, except for improvements in growth-medium formulation and the advent of dipslides (and other disposable media formats), the primary means for detecting and quantifying microbial contamination has remained essentially unchanged for most of this century[1,2].

Sample collection exacerbates problems in detecting and diagnosing microbial contamination. Virtually all microbial activity occurs at fuel-water boundaries, in fuel systems[3]. Not surprisingly microbiological tests, run on fuel samples suitable for fuel chemistry testing, frequently yield negative results. Fuel-water interface samples from those same systems often reveal substantial microbial contamination[4]. Unfortunately, interface samples are rarely part of routine fuel system sampling programs. Consequently, microbiological criteria do not appear in fuel specifications[5,6,7,8,9,10,11], and analysts typically exclude microbiological assays in routine fuel quality testing programs. In the absence of correlating data, microbial contamination problems are routinely misdiagnosed as cryptic, chemical incompatibilities. Plugged filters, heavy sludge deposits, high acid numbers and spot corrosion are too often attributed erroneously to factors other than uncontrolled microbial contamination. Obtaining timely accurate microbiological data remains a major obstacle to effective contamination control.

This presentation describes the test method, compares catalase activity data with traditional microbiological data and offers some strategies for testing programs to minimize microbial contamination problems in fuel oil systems.

Materials and Methods. *Sampling:* Fuel tank bottom samples were collected using a bomb-type thief[12], and transferred into previously unused high density polyethylene (HDPE) sample bottles. Separator samples were drained directly into HDPE sample bottles. Fuel filters were sealed in polyethylene bags for transport to the laboratory. All samples were shipped to the laboratory (Basic Fuel Services, Dover, NJ) where analysis was initiated within 48 hours after sample collection.

Viable Titers: Aerobic and anaerobic bacterial, and fungal (yeast/mold) titers were determined by the pour plate method[13]. BACTO™ Plate Count Agar, Anaerobic Agar and YM Agar (DIFCO Laboratories, Detroit, MI) were used as growth media for the respective microbial groups. Anerobic sulfate reducing bacterial (SRB) titers were estimated through serial dilution in BACTO Sulfate API Broth (DIFCO Laboratories, Detroit, MI), supplemented with 0.1 percent (w/w) BACTO Agar (DIFCO Laboratories, Detroit, MI). Aerobic bacteria and fungi were incubated for 5 days. Anaerobic bacteria were incubated in an anaerobe incubator for 7 days. SRB were also incubated for 7 days. All plates were incubated at 32° C.

Catalase Activity: Catalase concentrations were determined using the method of Kraft et al.[14] (modified; figure 1a - d). Precision tests were performed on catalase (Sigma Chemical, St. Louis, MO) solutions (1.0 mg catalase/L 0.01M phosphate buffer; pH 7.2). Solutions ranging from 0.1 - 1.0 mg catalase/L were used to examine the relationship between pressure data and catalase concentration. For aqueous samples, 10 mL were dispensed into each of two, 15 mL reaction tubes. One of the aliquants was treated with 1.0 mL, 0.01N sodium azide (NAZ; treating samples with 0.1 mL of NAZ per mL sample, inhibited all enzyme activity). Catalase testing was initiated approximately five minutes after NAZ pre-treatment. For samples containing less than 30 mL water, 50 mL fuel was diluted 1:1 in BACTO Bushnell-Hass Broth (DIFCO Laboratories, Detroit, MI) and shaken. After mixing, 10 mL was transferred to a dilution bottle containing 40 mL BACTO Tryptic Soy Broth (DIFCO Laboratories, Detroit, MI) and incubated at 32° C for 4 hours. To perform the catalase test, 10 mL of broth was transferred into a 15 mL reaction tube. NAZ controls were not run for pre-incubated samples. To determine catalase activity, 1.0 mL, 30 % (v/v) H_2O_2 was added. Reaction tubes were stoppered and briefly vented immediately after the H_2O_2 was added. This ensured that at time zero pressure (psig) inside the tube was zero. At 15-minutes, reaction tube head-space pressure was read using an HMB™ instrument (BioTech International, Houston, TX). Previous work[15] has demonstrated that: a) pressure build-up within the reaction tube is due to O_2 gas evolution, and b) total pressure approaches a maximum after 10 - 12 minutes; the rate of pressure-change after 12-minutes is negligible.

Biocide Testing: Two biocides, an isothiazolinone blend and a nitromorpholine blend, were tested according to ASTM E 1259[16]. Viable titers were determined using LiquiCult™ broths (MCE, Inc. Lake Placid, NY) and catalase activities were determined as described above.

Results. ***Catalase Test Precision:*** Four test series, with ten replicate analyses each were used to determine test variability. A test series was defined as a freshly prepared catalase solution. A single analyst prepared all solution and performed all analyses. The test results are presented in Table 1. A 10 mL, 0.01M phosphate buffer sample, containing 1.0 mg catalase/L produced an HMB reading of 7.9 ± 1.47 psig. One-way analysis of variance (ANOVA) demonstrate that differences among test series are not significantly different at the 95 percent confidence level (P = 5 %).

Relationship between Catalase Concentration and Test Data: Catalase was diluted in 0.01 M phosphate buffer to give stock solutions containing 0, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 0.75 and 1.0 mg catalase/L and tested. The relationship between pressure (HMB result) and catalase concentration is shown in figure 2. The HMB reading = 12.4 x catalase concentration (mg/L) + 0.01. The correlation coefficient between HMB reading and catalase concentration is 0.996 ($r_{crit;\,P=5\%;\nu=6} = 0.707$; $r_{crit;\,P=1\%;\nu=6} = 0.834$, where r = correlation coefficient, P = probability of incorrectly interpreting the correlation to be significant and ν = degrees of freedom; number of analyses - 2); demonstrating that the test effectively measures catalase in aqueous samples.

Relationship between HMB Reading and Viable Titer: Figure 3 illustrates the relationship between catalase activity and viable titer for *Pseudomonas fluorescens* (NRRL B-4200), a Gram-negative, non-spore-forming rod, typical of aerobes that contaminate fuel systems. Under axenic conditions, there is a log-linear relationship between the two parameters. The correlation coefficient is 0.93 ($r_{crit;\,P=5\%;\nu=8} = 0.632$; $r_{crit;\,P=1\%;\nu=8} = 0.765$), for the relationship described by the curve:

$$\text{Log CFU/mL} = (0.12 \times \text{HMB reading}) + 7.5$$

Catalase Activity as an Indicator of Biocide Performance: In order to determine whether catalase activity would reflect biocidal activity accurately, HMB and viable titer data were compared for two biocides used in two different fuels. Both biocides were fuel soluble, with some degree of water solubility as well. Although both fuel and water phases were analyzed, neither treated nor untreated fuel samples had significant viable titers, after 24-hours. Consequently, only water-phase data are presented in Table 2. Both biocides reduced viable titers and catalase activity during the 24-hour test period. A correlation coefficient of 0.912 was computed for the relationship between viable titer and catalase activity percent decreases ($r_{crit.;\,P=5\%[\nu=6]} = 0.707$; $r_{crit.:\,P=1°\%[\nu=6]} = 0.834$). This demonstrated that under laboratory conditions, catalase activity was a good indicator of fuel biocide performance.

Relationship between Catalase Activity and Viable Titers in Field Samples: The strong correlations demonstrated under controlled laboratory conditions suggested that catalase activity could be used to rapidly screen samples drawn from fuel systems. To test this theory, catalase activity was added to a list of four viable titer analyses that were performed on various types of fuel-system samples over a six-month period. Each sample was tested for aerobic, anaerobic and sulfate reducing bacterial titers, fungus recovery and catalase activity. A total of 195 samples were collected from diesel and gasoline tanks, diesel fuel filter housings and diesel-system coalescers/ separators.

Data for the 17 fuel samples, drawn from diesel tanks, are shown in Table 3a. Only six of the 17 fuel samples were contaminated significantly. The correlation matrix (Table 3b.) shows that catalase activity covaried significantly with all viable titer parameters. Not surprisingly, the strongest correlation (r = 0.984) was between catalase activity and CFU aerobes/mL, and the weakest (r = 0.640) was between catalase activity and SRB titers. It is noteworthy that aerobe, anaerobe and fungal titers all covaried significantly among each other.

Representative bottom samples are often difficult to obtain from smaller and underground fuel tanks. Fuel filters trap debris and microbes; providing an alternative source of information about a tank's microbial contamination. Only 20 of 64 fuel filters were free of detectable contamination (Table 4a.). Titers ≥ 1.00E+05 CFU aerobes/mL were recovered from seven filters and SRB were recovered from 22 filters. All five microbial parameters had significant correlation coefficients (Table 4b.).

Of 54 diesel-tank water-bottom samples, 37 had aerobe titers ≥ 1.0E+05 CFU/mL. SRB were recovered from 39 samples. HMB readings were ≥ 1.0 psig, for 41 samples, and ≥ 5.0 psig for 25 samples. As in the filter samples, all parameters covaried significantly (Table 5b.), once again confirming the catalase test's validity as a rapid screen for microbial contamination.

The final group of samples were those drawn from retail outlet gasoline tanks. Samples 2, 4, 6, 7, 9, 10, 12, 13, 17 - 19, 27 - 29, 32, 35, 38 - 40, 43, 44, 46, 50, 55, 56 and 60 were drawn before tanks were cleaned and biocide treated. The other samples were drawn one - two days after cleaning and treatment. Surprisingly, 26 of 31 tanks (84 percent) of the tanks tested harbored ≥ 1.0E+05 CFU aerobes/mL, in the gasoline, before servicing(Table 6a.). In the gasoline samples, aerobic bacterial and fungal titers covaried strongly between themselves and with catalase activity(Table 6b.). Again, catalase activity covaried significantly with each of the four viable titer parameters. Catalase test accuracy was further substantiated by the absence of detectable activity in any of the tanks, after servicing.

Discussion.

For generations, the primary means for estimating microbial loads in fuel systems has been viable titers. All viable titer methods share a common limitation. Microbes drawn from one ecosystem must proliferate in a different ecosystem (the growth medium), in order to be detected. ZoBell[17] discussed this problem in 1946. His concerns have since been echoed by Shmidt[18] and others[2,19]. Over the past thirty years, a variety of tests have been developed to analyze microbial activity *in situ*. Radiotracer methods[20], and chemical analysis of cell constituents[21,22,23]. In 1990, recognizing that system managers, concerned with industrial process fluid contamination control, needed alternatives to viable titers, ASTM Committee E34 introduced guidance for evaluating "non-conventional" microbiological methods[24]

Except for issues of academic curiosity, the sole purpose for monitoring microbial contamination fuel systems is to estimate the probability of current or potential biodeterioration problems. Biodeterioration in fuels systems includes microbially mediated processes whereby fuel chemistry and performance properties change, storage-tank and transfer- system structural integrity is challenged or flow is impaired. These processes are the consequences of microbial activity; enzyme activity.

Catalase, the enzyme responsible for hydrolyzing intracellular hydrogen peroxide, is virtually ubiquitous among obligately aerobic bacteria and eucaryotes[25]. It is also present in many facultative anaerobes, but is absent in obligate anaerobes. The microbes that contaminate fuels systems are predominantly catalase positive[26], although obligate anaerobes can proliferate as members of biofilm communities, where oxygen has been scavenged from the environment. Besides the genetic make-up of a contaminant population, physiological state will affect catalase activity. Dormant or moribund cells require less catalase, since they generate less hydrogen peroxide. Consequently, dormant cells, recovered from fuel samples, may yield high viable titers[27.28]. Preliminary studies, not presented here, demonstrated that four hours pre-incubation in a suitable broth medium stimulated catalase activity in cells recovered from fuel samples. This step was incorporated into the protocol for analyzing samples that contained insufficient water to run duplicate catalase tests.

Since catalase-negative microbes were unlikely to be present in fuel systems unless catalase-positive organisms were also present, the authors speculated that catalase would be a good indicator of microbial contamination. In early experiments, one of the authors (Passman, unpublished) demonstrated that catalase activity responded to biocide treatment more slowly than either viable titer or radiolabeled nutrient mineralization. Longer exposure periods and higher doses were necessary to inhibit catalase activity. Catalase activity, substrate mineralization rate and viable titers, respectively, responded to biocide treatment in decreasing order of sensitivity. Those experiments suggested that catalase activity data would provide conservative estimates of biocide performance. Moreover, earlier work had demonstrated the tests applicability in metalworking fluids[29].

The laboratory studies reported in this paper demonstrated that the catalase test is both accuracy and reasonably precise. HMB readings covaried strongly with both catalase concentration and axenic culture viable titers. Fourteen years of field experience in metalworking fluids suggested that, for contamination control purposes, low medium and high HMB results provide sufficient precision to guide action decisions. Routine preparation of catalase standards should be unnecessary, as it might lead to data over-interpretation. In metalworking fluids, samples generating < 1.0 psig do not show other symptoms of significant microbial contamination. Those generating 1.0 - 5.0 psig are typically characterized as moderately contaminated, based on other microbial, physical and chemical criteria. Samples with sufficient catalase activity to produce > 5.0 psig are heavily contaminated.

The field data presented in this paper demonstrate that the same criteria may be applied to fuel and water bottom samples. Diesel, gasoline, water bottoms and filter residues all revealed the same general relationship between catalase activity and viable titer indicators of microbial contamination. The authors are now investigating the relationship between microbiological contamination and physical-chemical changes within fuel systems.

Conclusions. The catalase test provides a rapid, reliable means for estimating microbial contamination in fuels, filter residues and fuel-system water. No test artifacts (either significant undetected microbial contamination or high HMB readings in samples yielding undetectable viable titers) were noted among the 195 varied samples analyzed. Moreover, the simplicity of the protocol and portability of the testing materials make the procedure well suited for field analysis. Since developing the methodology, the authors have been using the procedure to evaluate microbial contamination levels in tanks, within minutes after samples are drawn. When significant contamination is present, corrective action is initiated immediately and monitored as it proceeds.

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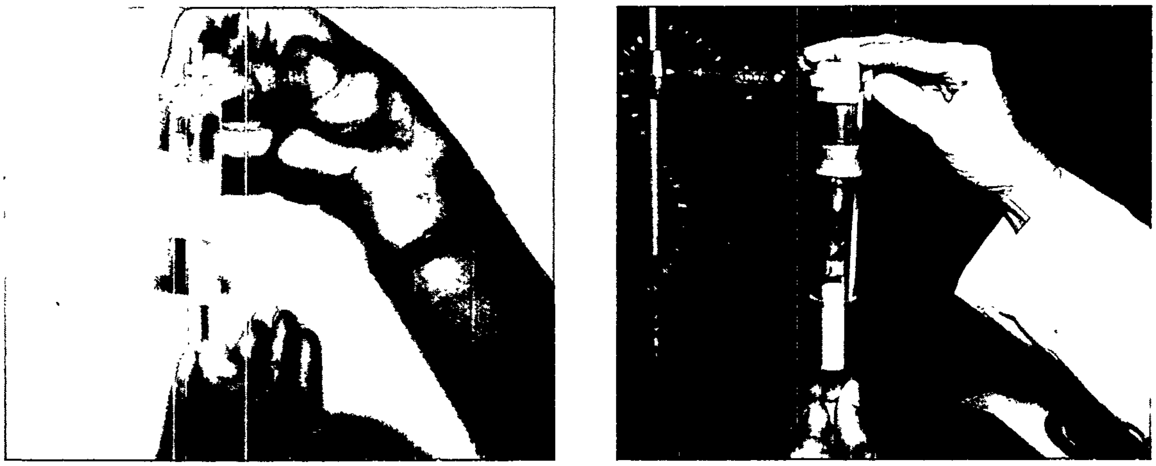
Figure 1. Catalase test protocol.

1 - a. Transfer sample to reaction tube.

1 - b. Add reagent(s) to reaction tube.



1 - c. Replace stopper and vent reaction tube. Shake tube and wait 15 min.

1 - d. Impale tube with transducer needle; read pressure (psig) on HMB instrument.

Figure 2. Relationship between catalase concentration and test data (psig)

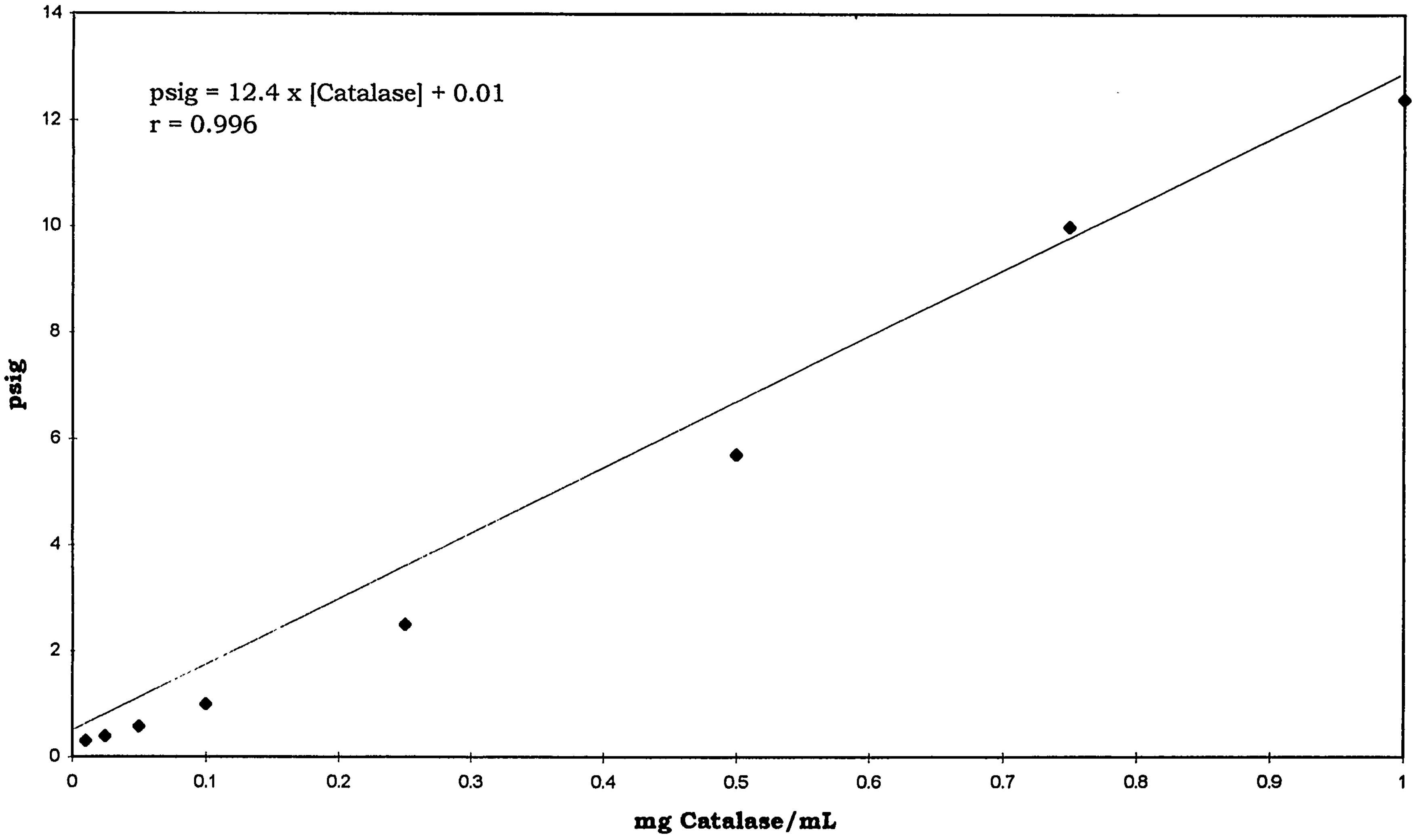


Figure 3. Relationship between viable titer and catalase activity.

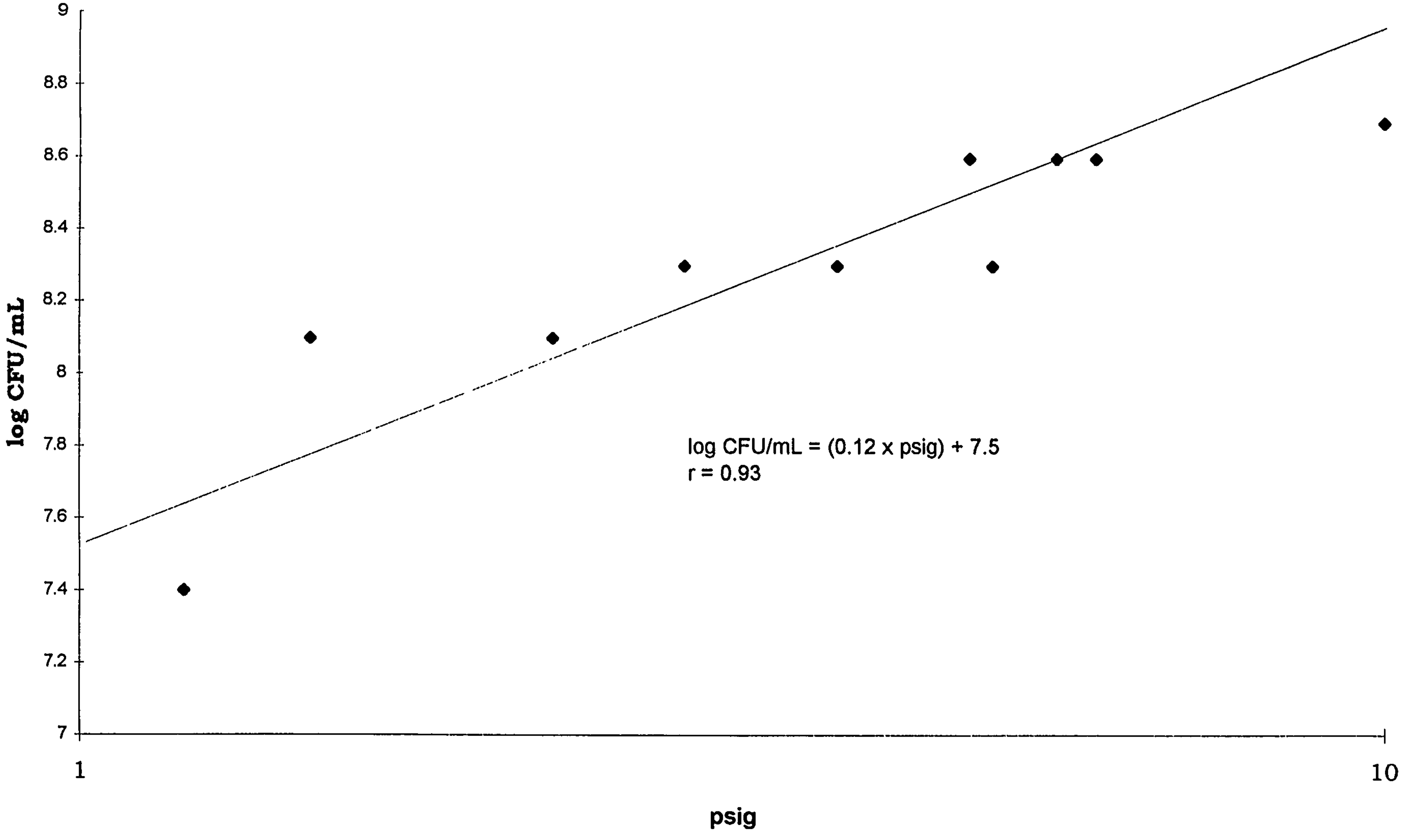


Table 1. Catalase test precision.

Replicate	Test series			
	1	2	3	4
1	6.6	5.9	7.7	8.5
2	6.9	5.1	7.6	7.3
3	7.6	6.6	7.7	7.8
4	10.1	7.9	7.0	7.5
5	8.3	8.2	7.8	7.5
6	8.0	10.7	7.6	8.1
7	7.1	11.4	7.7	8.9
8	8.4	7.3	8.1	7.9
9	7.2	7.9	8.2	6.9
10	13.9	7.2	7.6	8.0
***Average* (n = 40)**				7.9
***Standard Deviaton* (Std. Dev.)**				1.47
Coefficient of Variation				18.5%

Anova: Single Factor

SUMMARY

Series	*Count*	*Sum*	*Average*	*Variance*	*Std. Dev.*
1	10	84.1	8.4	4.77	0.69
2	10	78.3	7.8	3.84	1.96
3	10	77.0	7.7	0.09	0.31
4	10	78.3	7.8	0.34	0.58

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*F crit*
Between Groups	3.106543	3	1.035514	0.457782	2.866265
Within Groups	81.43295	36	2.262026		
Total	84.53949	39			

Table 2. Evaluation of antimicrobials in distillate fuels (ASTM E-1259).

Fuel type	Biocide	Viable titer			Catalase activity		
		Log MPN/mL		Percent decrease	psig		Percent decrease
		0 h	24 h		0 h	24 h	
Diesel	A	7.0	6.0	14%	14.0	10.5	25%
	B	7.0	2.0	71%	16.0	9.0	44%
Gasoline	A	7.0	4.0	43%	23.5	14.0	40%
	B	7.0	2.0	71%	23.5	10.0	57%

Table 3a. Relationship between catalase activity and viable titers; diesel fuel tanks.

Sample number	Parameter				
	Aerobic Bacteria (CFU/mL)	Yeast/ Mold (CFU/mL)	Anaerobic bacteria (CFU/mL)	Sulfate reducing bacteria (MPN/mL)	Catalase activity (psig)
1	0	0	0	0	0.0
2	0	0	0	0	0.0
3	0	0	0	0	0.0
4	1.00E+07	1.00E+06	1.00E+06	1.00E+04	12.3
5	0	0	0	0	0.0
6	0	0	0	0	0.2
7	1.58E+07	1.25E+07	1.35E+07	1.10E+03	16.4
8	1.42E+04	1.30E+03	1.21E+05	9.00E+00	0.5
9	0	0	0	0	0.0
10	9.08E+04	1.20E+03	1.30E+03	1.01E+01	0.9
11	1.21E+05	1.51E+05	1.02E+06	9.94E+02	1.7
12	0	0	0	0	0.0
13	0	0	0	0	0.0
14	1.90E+05	1.80E+02	1.20E+02	1.10E+01	3.1
15	0	0	0	0	0.0
16	0	0	0	0	0.0
17	0	0	0	0	0.0

Table 3b. Correlation matrix: Relationship between catalase activity and viable titers; diesel fuel tanks(1).

	Aerobes	*Y/M*	*Anaerobes*	*SRB*	*Catalase*
Aerobes	1				
Y/M	0.877	1			
Anaerobes	0.869	0.998	1		
SRB	0.581	0.121	0.117	1	
Catalase	0.984	0.824	0.820	0.640	1

Note: 1. For 17 samples: r(crit.; P=1%) = 0.606; r(crit.;P=5%) = 0.482.

Table 4a. Relationship between catalase activity and viable titers; diesel fuel filters.

Sample number	Parameter				
	Aerobic Bacteria (CFU/mL)	Yeast/ Mold (CFU/mL)	Anaerobic bacteria (CFU/mL)	Sulfate reducing bacteria (MPN/mL)	Catalase activity (psig)
1	1.02E+03	2.31E+02	1.04E+02	0	0.1
2	1.00E+04	1.60E+02	0	0	0.2
3	9.60E+05	1.20E+06	1.51E+04	1.00E+01	7.2
4	1.70E+05	8.70E+02	1.05E+04	0	3.8
5	1.10E+04	1.62E+02	965	0	0.4
6	0	0	0	0	0.0
7	1.20E+03	1.08E+02	9.00E+00	2.00E+00	0.1
8	8.20E+02	6.50E+01	8.50E+01	9.00E+00	0.0
9	0	0	0	0	0.1
10	7.89E+04	8.59E+02	1.00E+02	5.00E+00	2.3
11	0	0	0	0	0.0
12	8.40E+04	8.65E+02	6.90E+02	9.00E+00	2.3
13	0	0	0	0	0.0
14	7.80E+01	0	9.00E+00	0	0.1
15	0	0	0	0	0.0
16	8.70E+01	1.00E+01	0	0	0.1
17	0	0	0	0	0.0
18	0	0	0	0	0.0
19	7.90E+04	9.20E+02	1.09E+03	1.40E+01	2.5
20	7.30E+06	6.03E+04	7.50E+02	6.80E+01	12.3
21	9.80E+02	5.60E+01	1.20E+01	0	0.1
22	0	0	0	0	0.0
23	6.20E+04	3.90E+03	2.21E+03	2.30E+02	0.8
24	7.50E+03	2.10E+03	1.20E+03	6.00E+01	0.2
25	2.30E+03	2.50E+02	5.00E+01	0	0.1
26	7.20E+02	0	3.00E+01	0	0.0
27	6.40E+04	2.80E+02	1.00E+02	3.00E+01	0.4
28	0	0	0	0	0.0
29	0	0	0	0	0.0
30	9.20E+04	4.60E+04	2.05E+03	1.80E+02	0.9
31	6.50E+02	2.00E+01	1.00E+01	0	0.1
32	5.50E+03	3.80E+02	2.60E+02	1.00E+01	0.1
33	2.60E+03	5.00E+01	6.00E+01	0	0.1
34	3.45E+03	1.20E+02	5.50E+02	0	0.1
35	2.50E+03	1.00E+02	1.00E+01	0	0.1
36	5.00E+02	0	0	0	0.0
37	3.20E+03	9.50E+02	3.00E+02	4.00E+01	0.2
38	5.60E+04	6.40E+03	1.30E+03	8.00E+01	0.4

Table 4a. Relationship between catalase activity and viable titers; diesel fuel filters.

Sample number	Parameter				
	Aerobic Bacteria (CFU/mL)	Yeast/ Mold (CFU/mL)	Anaerobic bacteria (CFU/mL)	Sulfate reducing bacteria (MPN/mL)	Catalase activity (psig)
39	1.00E+04	0	1.65E+03	1.20E+02	0.1
40	3.20E+05	5.00E+02	2.90E+02	0	1.1
41	2.50E+03	1.00E+02	0	0	0.0
42	0	0	0	0	0.0
43	0	0	0	0	0.0
44	1.50E+03	3.00E+02	1.00E+02	1.00E+01	0.1
45	0	0	0	0	0.0
46	1.20E+03	1.00E+02	0	0	0.1
47	7.95E+07	1.48E+06	3.95E+04	4.10E+03	16.9
48	3.20E+03	6.20E+02	7.00E+01	1.00E+01	0.1
49	2.60E+04	5.00E+01	2.10E+02	2.00E+01	0.3
50	6.50E+02	2.00E+01	1.00E+01	0	0.1
51	8.00E+01	0.00E+00	0.00E+00	0.00E+00	0.0
52	0	0	0	0	0.0
53	6.70E+05	4.85E+05	1.15E+04	1.20E+03	2.5
54	0	0	0	0	0.0
55	0	0	0	0	0.1
56	0	0	0	0	0.0
57	100	0	0	0	0.0
58	3.50E+02	5.00E+01	1.00E+01	0	0.1
59	0	0	0	0	0.0
60	7.80E+03	0	0	0	0.1
61	0	0	0	0	0.0
62	0	0	0	0	0.1
63	6.40E+05	4.20E+04	1.00E+03	3.60E+02	4.0
64	0	0	0	0	0.1

Table 4b. Correlation Matrix: Relationship between catalase activity and viable titers; diesel fuel filters (1).

	Aerobes	*Y/M*	*Anaerobes*	*SRB*	*Catalase*
Aerobes	1				
Y/M	0.756	1			
Anaerobes	0.878	0.921	1		
SRB	0.954	0.782	0.909	1	
Catalase	0.779	0.769	0.807	0.739	1

Note: 1. For 64 samples: r(crit.; P=1%) = 0.320; r(crit.;P=5%) = 0.246.

Table 5a. Relationship between catalase activity and viable titers; diesel-system water samples(1).

Sample number	Parameter				
	Aerobic Bacteria (CFU/mL)	Yeast/ Mold (CFU/mL)	Anaerobic bacteria (CFU/mL)	Sulfate reducing bacteria (MPN/mL)	Catalase activity (psig)
1	9.60E+05	1.20E+06	1.51E+04	1.00E+01	7.2
2	1.70E+05	8.70E+02	1.05E+04	0	3.8
3	9.20E+05	1.04E+05	8.94E+03	0	4.2
4	8.97E+07	9.80E+04	1.09E+04	1.50E+02	16.5
5	2.23E+06	7.80E+03	6.51E+03	1.81E+02	8.5
6	6.90E+04	1.03E+03	9.80E+01	1.20E+01	2.0
7	0	0	0	0	0.0
8	1.20E+07	6.40E+04	9.01E+03	1.30E+01	13.9
9	5.90E+04	7.65E+03	7.90E+01	1.10E+01	1.1
10	0	0	0	0	0.0
11	0	0	0	0	0.0
12	9.70E+04	9.40E+02	9.00E+01	1.30E+01	3.0
13	0	0	0	0	0.0
14	4.60E+05	5.85E+04	3.95E+03	2.10E+03	2.7
15	3.60E+07	5.90E+04	5.64E+03	2.90E+02	17.1
16	6.50E+06	5.90E+04	4.85E+04	6.50E+02	10.8
17	4.85E+05	8.70E+04	9.79E+03	3.50E+02	2.8
18	5.90E+07	8.75E+05	7.20E+04	2.10E+03	14.3
19	7.15E+07	3.68E+05	6.95E+04	3.30E+03	15.4
20	1.20E+07	7.20E+04	6.50E+04	4.90E+03	11.9
21	0	0	0	0	0.0
22	8.95E+06	4.50E+05	6.40E+04	9.45E+02	12.4
23	7.99E+07	6.52E+05	1.35E+04	2.10E+03	16.4
24	4.50E+07	3.95E+04	8.50E+02	0	13.4
25	1.10E+05	4.10E+03	4.30E+02	4.00E+01	2.1
26	8.56E+04	1.20E+03	1.80E+03	6.50E+02	0.8
27	2.35E+05	5.48E+03	2.40E+02	2.00E+01	1.3
28	1.45E+06	0	1.50E+03	3.20E+02	3.9
29	5.60E+03	0	1.20E+02	8.00E+01	0.2
30	2.60E+02	0	0	0	0.1
31	0	0	0	0	0.0
32	5.60E+07	3.80E+02	5.00E+01	0	12.9
33	5.20E+07	4.05E+04	6.50E+02	2.00E+01	13.7
34	9.85E+07	5.60E+05	4.65E+04	3.20E+03	17.2
35	8.70E+05	1.50E+05	4.80E+04	6.50E+02	3.4
36	1.20E+06	9.20E+04	5.25E+04	3.20E+02	4.2
37	6.45E+07	8.75E+04	9.80E+03	1.20E+03	15.8

Table 5a. Relationship between catalase activity and viable titers; diesel-system water samples(1).

Sample number	Parameter				
	Aerobic Bacteria (CFU/mL)	Yeast/ Mold (CFU/mL)	Anaerobic bacteria (CFU/mL)	Sulfate reducing bacteria (MPN/mL)	Catalase activity (psig)
38	6.75E+07	3.60E+05	3.50E+03	1.50E+02	14.2
39	2.10E+04	5.10E+03	2.00E+02	0	0.2
40	8.15E+07	2.40E+06	3.20E+04	4.00E+03	16.7
41	0	0	0	0	0.0
42	3.80E+05	2.75E+05	6.50E+03	9.00E+02	2.3
43	9.27E+07	5.50E+06	2.80E+04	3.60E+03	18.2
44	6.50E+06	6.10E+04	1.60E+03	50	4.1
45	0	0	0	0	0.0
46	7.50E+05	1.25E+05	4.50E+03	7.50E+02	3.9
47	8.50E+02	1.20E+02	1.00E+01	0	0.2
48	7.25E+07	3.30E+06	2.70E+04	3.70E+03	16.0
49	6.20E+07	4.80E+05	1.90E+04	3.50E+03	15.9
50	5.80E+06	9.10E+04	1.60E+04	1.30E+03	7.1
51	4.90E+05	2.90E+04	1.50E+03	8.00E+01	3.4
52	5.60E+07	6.10E+06	3.10E+04	4.80E+03	17.2
53	7.25E+07	4.50E+06	4.60E+04	4.70E+03	17.5
54	9.48E+07	6.50E+06	3.30E+04	4.10E+03	18.4

Table 5b. Correlation matrix: Relationship between catalase activity and viable titers; diesel-system water samples(2).

	Aerobes	*Y/M*	*Anaerobes*	*SRB*	*Catalase*
Aerobes	1				
Y/M	0.591	1			
Anaerobes	0.407	0.348	1		
SRB	0.664	0.730	0.652	1	
Catalase	0.890	0.551	0.542	0.672	1

Notes:

1. Samples were drawn from bottoms and separators.
2. For 54 samples: r(crit.; P=1%) = 0.348; r(crit.; P=5%) = 0.268.

Table 6a. Relationship between catalase activity and viable titers; retail outlet gasoline tanks.

Sample number	Parameter				
	Aerobic Bacteria (CFU/mL)	Yeast/ Mold (CFU/mL)	Anaerobic bacteria (CFU/mL)	Sulfate reducing bacteria (MPN/mL)	Catalase activity (psig)
38	3.60E+07	2.50E+06	5.20E+04	6.10E+03	13.8
39	9.20E+07	5.40E+06	3.70E+03	3.00E+03	15.2
40	4.80E+07	2.90E+06	2.50E+03	1.80E+03	12.7
41	0	0	0	0	0
42	0	0	0	0	0
43	6.60E+06	3.00E+04	4.50E+03	4.50E+02	5.9
44	2.50E+02	0	1.00E+01	0	0.1
45	0	0	0	0	0
46	5.60E+06	6.10E+05	6.10E+04	2.10E+03	6.2
47	0	0	0	0	0
48	0	0	0	0	0
49	0	0	0	0	0
50	8.50E+04	7.80E+05	9.50E+02	5.00E+01	0.5
51	0	0	3.00E+02	0	0.0
52	0	0	0	0	0
53	0	0	0	0	0
54	0	0	0	0	0
55	2.90E+06	3.30E+03	6.00E+02	3.00E+01	4.1
56	9.30E+05	4.20E+03	3.00E+02	1.00E+01	2.9
57	0	0	0	0	0
58	0	0	0	0	0
59	0	0	0	0	0
60	9.10E+06	5.60E+04	3.70E+04	6.70E+02	10.3

Table 6b. Correlation matrix: Relationship between catalase activity and viable titers; gasoline tanks (1).

	Aerobes	*Y/M*	*Anaerobes*	*SRB*	*Catalase*
Aerobes	1				
Y/M	0.878	1			
Anaerobes	0.272	0.308	1		
SRB	0.614	0.674	0.740	1	
Catalase	0.899	0.790	0.454	0.645	1

Note: 1. For 60 samples: r(crit.; P = 1%) = 0.331; r(crit.; P = 5%) = 0.255.

Table 6a. Relationship between catalase activity and viable titers; retail outlet gasoline tanks.

	Parameter				
Sample number	Aerobic Bacteria (CFU/mL)	Yeast/ Mold (CFU/mL)	Anaerobic bacteria (CFU/mL)	Sulfate reducing bacteria (MPN/mL)	Catalase activity (psig)
1	0	0	0	0	0
2	1.20E+06	6.30E+04	8.20E+02	0	3.7
3	0	0	0	0	0
4	2.10E+02	0	1.00E+01	0	0
5	0	0	0	0	0
6	6.90E+07	3.10E+06	6.90E+03	2.10E+02	14.5
7	3.80E+07	8.76E+05	2.10E+04	6.50E+02	13.9
8	0	0	0	0	0
9	1.00E+03	0	0	0	0.1
10	1.50E+03	2.50E+02	0	0	0.1
11	0	0	0	0	0
12	9.50E+03	0	0	0	0.2
13	1.20E+06	4.90E+05	5.20E+03	0.00E+00	3.6
14	0	0	0	0	0
15	0	0	0	0	0
16	0	0	0	0	0
17	2.20E+07	2.40E+06	3.10E+03	5.00E+02	12.4
18	8.70E+03	1.00E+04	2.00E+02	1.00E+01	3.2
19	2.90E+05	3.10E+04	6.00E+02	5.00E+01	2.8
20	0	0	0	0	0
21	0	0	0	0	0
22	0	0	0	0	0
23	0	1.00E+02	0	0	0
24	0	0	0	0	0
25	0	0	0	0	0
26	0	0	0	0	0
27	5.10E+07	8.50E+05	6.50E+03	6.20E+02	14.0
28	2.30E+07	3.80E+05	5.00E+02	0	12.1
29	7.80E+07	1.60E+06	9.10E+03	2.40E+03	16.2
30	0	0	0	0	0
31	0	0	0	0	0
32	6.50E+06	1.10E+04	5.00E+03	1.20E+02	6.2
33	0	0	0	0	0
34	0	0	0	0	0
35	1.40E+06	9.10E+04	8.70E+03	3.40E+02	3.9
36	0	0	0	0	0
37	0	0	0	0	0

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BACTERIAL CONTAMINATION OF MOTOR GASOLINE

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1. Introduction

Bacterial Contamination of Motor Gasoline

Are reformulated motor fuels protected, like leaded fuels were, from microbial attack.

Microbiological growth is found frequently in the bottom of jet fuel, distillate, heavy gasoil and crude oil tanks. Experience shows that traces of water - though theoretically enough for an outbreak of growth - rarely cause problems, because the tank is most probably drained frequently. However when a water table builds up and remains untouched for some time, the likelihood for growth, leading to later operational problems, rapidly increases. Normal paraffin hydrocarbons with C_8 - C_{16} chain length appear to be especially vulnerable; in other words the kerosene/jet fuel boiling range is mainly at risk. Heavier hydrocarbon products (diesel, light heating oils and gasoils) however have increasingly seen problems over the last 15-20 years. Lighter products - mainly the gasoline boiling range appear to have been protected from microbial problems over many years. In a laboratory it was of course possible to degrade certain kinds of naphthas and finished gasolines, but those results did not mirror the findings in the field.

There are a number of reasons, why this might have been the case: Some years ago the gasolines were heavily leaded by tetramethyllead or tetraethyllead (TML/TEL) and both those substances are known to be anti-microbial. As the lead level decreased over the years from 1.0/0.8 g/liter to 0.15 g/liter, scavengers were increasingly brought in consisting of brominated or chlorinated hydrocarbons, which were even stronger biocides. Hand in hand with this the reformer severities were increased, resulting in high levels of well over 50% aromatics (10% benzene at times). Aromatic ring structures pose more difficulties than chain paraffins of virgin naphtha for biological breakdown. The need for more and more gasoline yield from a barrel of crude oil gradually saw aromatics replaced with olefins from cracking units in the gasoline blend, while benzene had to be limited to 5 vol% on health grounds. With the new lead free environment and low aromatic olefinic gasolines one would expect in some "dirty" storage situation a good chance for microbial infestation. EBV have looked intensively since 1986 for such a case to happen. A number of cases reported turned out to be military jet (naphtha/kerosene mix of straight run material) or middle distillate problems.

2. EBV-Experience

Then, in early 1992, one of the EBV-Inspectors brought home a sample from a gasoline tank with a damaged roof and about 30 cm of bottom water table. The sample showed typical interface growth down into the water phase, which lead to the suspicion of heavy contamination, later confirmed by ECHA-Microbiology Ltd.

The tank had stood untouched for almost 1 year and the water ingress was probably 6-9 months old. The general tank condition was poor in repair but general cleanliness was acceptable. The tank farm was owned and operated by a Russian trader on German soil. The gasoline was manufactured by an Italian island refiner and shipped to Hamburg on a 25000 DWT Maltese flag vessel.

The main gasoline characteristics were as follows:

Main characteristics

Grade	Euro Super unleaded
D 15	0.7512
RON	95.9
MON	85.0
RVP at 100	654 hpa

Distillation/boiling range

% evap at 70°C	20
% evap at 100°C	46
% evap at 180°C	92
final boiling point °C	208
residue vol%	1.0

other properties

sulfur wt%	0.02
copper corrosion (3h, 50°C)	1
lead g/l	< 0.001
phosphorus g/l	< 0.001

ageing indicators

existent gum (before/after nc_7 wash) mg/100ml	3/1
oxidation stability (minutes)	> 720
potential gum (4h, 100 °C, 7 bar O_2) mg/100ml	5/2

Aromatics

benzene	vol%	3.7
total aromatics	vol%	35

Oxygenates

alcohol	free
ethers	free

Analyzing the data at hand one can conclude

- the extent of the growth in the Hamburg tank was such, that with the relatively low residence time a strong contamination of the cargo fill can be suspected.

- the bacterial contamination could have been imported from Italy or from a previous cargo of the Maltese vessel. Even though the product was fresh and microbe free when manufactured, the load tank in Italy could have been contaminated. Thus a possibly contaminated cargo found perfect growth conditions in the Hamburg tank.

o the gasoline characteristics show a fuel relatively low in aromatics which must have contained crack naphtha olefins to reach the indicated octane level. The Italian refiner operates a large cat cracker. Some paraffins, though in a small percentage, also could have been contained.

o the fuel did not contain any additives or hydrocarbons known to be inhibitory to microbial growth.

Thus while the tank charge was not necessarily perfectly suited to microbial growth it was at least vulnerable. Having confirmed the presence of bacteria perfectly adapted for growth in gasoline the question arose, how would those bacteria react to modern reformulated gasoline.

Reformulated gasoline as defined in the USA by the Clean Air Act, and increasingly becoming important also in Europe, requires minimization of air pollution by:

- being low in benzene and total aromatics
- being lead and scavenger free
- having sufficient octane rating to keep engine efficiency high
- taking oxygen from the fuel as well as from the air to improve combustion and minimize unburnt hydrocarbons in the exhaust

The contaminated fuel fulfilled all the above with the exception of the last point. In order to bring oxygen into the fuel, ethers and/or alcohols must be added. The most common ones used are methanol, ethanol as alcohols and MTBE as ether. These would all migrate readily from gasoline into any contaminating water.

Alcohols - especially ethanol - are known biocides in high concentrations in water. The anti-microbial effect of MTBE is not known. All of these additives would at moderate concentrations depress the water activity (relative humidity) of an aqueous phase and thus suppress potential growth; all would probably be nutritive to specific microbes at very low concentrations. A microbiological test programme was initiated to investigate these issues relative to water contaminated gasoline.

3. Microbiological Experiments

The microbiological programme was designed to investigate tolerance to or stimulation of adapted populations of microorganisms to oxygenate in gasoline.

3.1 The first stage of the programme was to produce microbes adapted to gasoline/oxygenates. Microbes from a variety of petroleum and natural sources were dispersed in four aliquots of 200 ml water containing Bushnell Haas salts (quarter strength). Additions of;

EC1/1 2 ml methanol + 5 ml gasoline
EC2/1 1 ml ethanol + 5 ml gasoline
EC3/1 2 ml MTBE + 5 ml gasoline
EC4/1 5 ml gasoline

were made to the four flasks respectively. After two days at 25° C the presence of viable microbes was confirmed and at 5 days 2 ml of each flask were transferred to corresponding flasks of 200 ml water containing Bushnell Haas salts (quarter strength) with additions of;

EC1/2 4 ml methanol + 5 ml gasoline
EC2/2 2 ml ethanol + 5 ml gasoline
EC3/2 4 ml MTBE + 5 ml gasoline
EC4/2 5 ml gasoline

After 7 days at 25°C viable microorganisms were assayed semi-quantitatively by conventional microbiological techniques. It was found that whilst there had been prolific bacterial growth in flasks EC1/1, EC2/1, EC3/1 and EC4/1 after 2 days there was no microbial growth at the second stage except in the control flask EC4/2.

3.2 Using inocula from the first series of flasks (EC1/1 - EC4/1) an attempt was made to initiate microbial growth in three flasks containing 200 ml of gasoline containing oxygenate (1 ml methanol, 1 ml methanol, + 1 ml ethanol, 4 ml MTBE respectively) plus 10 ml aqueous Bushnell Haas salts. Is was unsuccessful; viable microbes were not recovered after 7 days except in a control flask. At this stage it was concluded that the "adapted" microbes had some tolerance to oxygenates in the aqueous phase, namely between 1.0-2.0% methanol, 0.5-1.0% ethanol and 1.0-2.0% MTBE. This probably reflected the sources of the organisms used which had probably never been contaminated with oxygenates.

3.3 At this time the new field sample of infected gasoline became available and it was decided to re-run modified experiments. The bacteria isolated from this sample (suspension AB) were added to flasks containing four 100 ml aliquots of Bushnell Haas salts (0.1% concentration) plus viable organisms from flasks EC1/1, EC2/1, EC3/1, and a composite of these three respectively.

These 100 ml aliquots were designated AB1-AB4 and 1% oxygenate was added as follows.

AB1 1 ml methanol added (inocula AB + EC1/1)
AB2 1 ml ethanol added (inocula AB + EC2/1)
AB3 1 ml MTBE added (inocula AB + EC3/1)
AB4 No oxygenate added (inocula AB + EC1/1, EC2/1, EC3/1)

After 7 days each flask was found to be heavily infected with bacteria.

3.4 Flasks were now set up containing 200 ml gasoline with added oxygenate and 10 ml of aqueous Bushnell Haas salts (0.1% concentration) plus organisms AB and also organisms from the corresponding flask AB1-AB4. This series of flasks were designated 1A-1D as follows;

1A 200 ml gasoline, 10 ml aqueous phase, inoculum AB/AB4
2A 200 ml gasoline/1 ml methanol, 10 ml aqueous phase, inoculum AB/AB1
3A 200 ml gasoline/0.5 ml methanol/0.5 ethanol, 10 ml aqueous phase, inoculum AB/AB1/AB2
4A 200 ml gasoline, 1 ml MTBE, 10 ml aqueous phase, inoculum AB/AB3.

Microbiological assays after 7 days failed to recover viable microbes from 2A and 3A but 1A and 4A aqueous phases contained >10^4 bacteria ml^{-1} .

3.5 The MTBE concentration in the gasoline in flask 4A was progressively increased to 1%, 1.5% and 2.5% at intervals of 7 days and microbiological assays of the water phase conducted immediately before an MTBE addition. The control flask 1 was tested at the same time. Gram negative bacteria were recovered and the results were as follows;

Gasoline + 0.5% MTBE: >10^4 ml^{-1}; Control: >10^4 ml^{-1}
Gasoline + 1.0% MTBE: 1.82 x 10^6 ml^{-1}; Control: 2.11 x 10^6 ml^{-1}
Gasoline + 1.5% MTBE: 4.7 x 10^6 ml^{-1}; Control: 3.4 x 10^6 ml^{-1}
Gasoline + 2.5% MTBE: 4.4 x 10^6 ml^{-1}; Control: 1.57 x 10^6 ml^{-1}

Moulds, yeasts and Sulphate Reducing Bacteria were never recovered in significant numbers. Water phase pH was always substantially neutral.

It could be concluded at this stage that Gram negative bacteria could be adapted to exhibit tolerance to gasoline containing 2.5% MTBE when the fuel:water ration was 20:1. Tolerance had not been developed to gasoline containing 0.5% methanol and 0.5% methanol/ethanol.

3.6 At this stage the gasoline in the control flask (1A) was removed and replaced with 200 ml fresh gasoline and the gasoline/MTBE from the flask 4A was removed and replaced with 200 ml gasoline/7% MTBE. After 7 days microbiological assays of the aqueous phases were conducted with the following results;

1A Control - gasoline only: 1.45×10^4 bacteria ml^{-1}
4A Gasoline/7% MTBE: 1.93×10^6 bacteria ml^{-1}

It was now apparent that a bacterial population highly tolerant of MTBE had been developed and it was decided to conduct an experiment to indicate whether this was merely tolerance to MTBE or utilisation of MTBE as an organic carbon nutrient.

3.7 A flask containing 100 ml aqueous Bushnell and Haas salts was inoculated with 0.1 ml of the water phase from the last stage of the MTBE enhancement flask 4A. This water thus contained highly adapted bacteria and MTBE which had migrated into this aqueous phase. Microbiological assays were conducted at intervals and the results were as follows;

Day	Bacterial ml^{-1}
0	1.68×10^4
3	2.88×10^5
7	8.1×10^5
16	1.14×10^6

The progressive increase in population strongly suggested that MTBE was supporting bacterial growth.

3.8 In a final experiment microbes from all of the sources available were further adapted to methanol, ethanol and methanol/ethanol and the experiment 3.4 was repeated but using much lower concentrations of oxygenate in the gasoline than in Experiments 3.2 and 3.4.

After 7 days microbiological assays were conducted and viable bacteria were recovered quantitatively. The results were as follows;

A 200 ml gasoline only, 10 ml aqueous phase: 1.83×10^6 ml^{-1}

B 200 ml gasoline/0.05% methanol,
10 ml aqueous phase: 8.5×10^5 ml^{-1}

C 200 ml gasoline/0.1% methanol,
10 ml aqueous phase: 1.74×10^5 ml^{-1}

D 200 ml gasoline/0.05% methanol/0.1% ethanol,
10 ml aqueous phase: 4.8×10^5 ml^{-1}

Thus the adapted bacteria were tolerant to low concentrations of methanol and methanol/ethanol in gasoline. The actual concentration of oxygenate in the water phase was not determined but because of preferential solubility, it was probably much greater than the concentration in the fuel phase (Experiment 3.1 is relevant).

4. Discussion and Conclusions

Experience elsewhere has established that ethanol in aqueous concentrations of 60-80% is an excellent antiseptic and that it still has some anti-microbial effect at lower concentrations, apparently by depressing water availability. Conversely one particular group of bacteria, Acetobacter spp, grow so well in dilute ethanol that they are used commercially to convert it into acetic acid (vinegar). Methanol is known to be less anti-microbial than ethanol and at low concentration is an excellent nutrient for a specific group of microorganisms, the methanotrophs. Since 1980 ICI have produced many thousand tonnes of single cell protein (Pruteen) by growing methanotrophs on methanol. There was no evidence of Acetobater or methanotroph growth in the experiments conducted but the possibility of this occuring in tank bottoms should be cause for concern. The concentration of either alcohol in a water bottom would be critical. The toxicity of methanol is well known and tank drainage water could be an environmental hazard.

MTBE probably acts like other ethers, reducing water availability and growth at high concentrations, but stimulating growth at low concentrations. These properties are exhibited by the fuel anti-icing additive, ethylene glycol mono-methyl ether.

Even though the incidents of gasoline contamination with microbes are thought to be still few and far between (since the EBV finding a few other cases have been reported) we must however expect this problem to stay with us and it may potentially increase. The real extent of it is hard to judge because gasoline manufacturers and traders do not talk about such cases. Biocide additives have in some countries been ruled illegal if they contain bromine or chlorine; others may have a hard time to be accepted by manufacturers and environmental agencies. The protective shield of lead and scavengers has been removed permanently and this study shows that it is certainly not being replaced by a new oxygenate shield; on the contrary, the latter, particularly MTBE, may even promote the problem.

The microbiological experiments were performed at ECHA-Microbilogical Laboratories in Cardiff.

5th International Conference
on Stability and Handling of Liquid Fuels
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BIOCIDAL TREATMENT AND PRESERVATION OF LIQUID FUELS

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Summary

Strict microbiological limit values are the result of damage caused by microorganisms in fuels.

With MAR 71, a biocide based on methylenebisoxazolidine, a product is available which has been tested and approved by leading car manufacturers, the mineral oil industry, and NATO.

Depending on the degree of microbiological contamination, different decontamination concepts are presented, and recommendations for the treatment of fuels which are contaminated when purchased are given.

In order to avoid recontamination, planning principles for the new design of tanks are necessary. The possibility of convenient, economical and regular drainage is a key factor here.

Introduction

As early as 1971, the Naval Research Laboratory in Washington investigated the effectiveness of various biocides for the treatment of navy distillate. With the IP Code of Practice for examination of light distillated fuel for viable microorganisms (IP 386/88), the testing of diesel fuel samples was standardised. In addition, a standard for sampling was drawn up by a work group at the Institute of Petroleum. The Fifth Draft of the working document "Guidelines for the investigation of microbial content of distillated fuels" (5.1.94) describes the sampling process in detail.

The SGS limits can be used as limit values for microbial load. The viable organisms are limited as follows: aerobes $< 10^3$ /l, S.R.B. not detected. This means that the total viable organisms are limited to $< 3 \times 10^3$/l, that is, less than the limit for drinking water, which in Germany, for example, is < 100/ml $= < 10^5$/l). However, the expert Ted Hill confirmed that even this low contamination leads to severe problems in practice.

Recognition of microbially-induced malfunctions

Although it has been known in principle for more than twenty years that microorganisms are disruption factors, often there is no information on this whatsoever in the service laboratories of the mineral oil industry.

A typical scenario was the frequent breakdown of the fire-engines at an airport. Analyses showed a filter block in the fuel system. On the basis of these results, first the fire-engine tanks, and then later the storage tanks, were cleaned. The material causing the filter block was also analysed further, and it was shown that the blocking was being caused by fibres of organic material. Based on this result, the use of paper towels was prohibited, since it was suspected that the fibres of these paper towels somehow got into the fuel system and thereby blocked the filters. However, when the problems did not cease, a microbiological control was carried out, which revealed massive microbiological contamination. Based on this knowledge, the fuel biocide MAR 71 was added to the storage tanks, and the problem was solved.

Even in 1994, in the central servicing branch of a major car manufacturer, it was not known that microorganisms can lead to filter blockages, although MAR 71 has been included on the list of approved products for years.

These examples show that microorganisms have long been known to be a disruption factor in fuels, but that this knowledge is not generally widespread. It is suspected that knowledge concerning microbial problems is intentionally not passed on, so as to avoid claims for compensation. Nobody wants to accept the responsibility for ensuring microbiologically perfect quality.

At present, microbiological purity is not a criterion of quality in mineral oil standards.

In future, knowledge about microbial problems must not be hushed up - it must be made widely known.

Microbiological tests must become standard in the event of blocked filters and unexplained sludge deposits in land vehicle engines as well as in ships' engines. The same applies to mineral oil stores, irrespective of where these come in the sales route, whether refinery or end-user filling station.

Cleaning colonised storage tanks

In storage tanks which are to be cleaned, technical difficulties are generally the reason why the measures are instituted. Microorganism counts of 10^7 organisms/l are found in the fuel and up to 10^{10} organisms/l in the water layer.

In practice, the following decision tree has proved useful when determining the measures to be taken:

A. **Base sample from the water phase is sludgy and heavily contaminated.**

➭ Empty the storage tank and clean with a suitable disinfectant system cleaner such as Grotanol SR 1, which is also able to remove and destroy the biofilms which have formed. In principle, a biocide should be added when the tank is re-filled, since experience has shown that system-cleaning never really eliminates all microorganisms. Dosing with 200 ppm MAR 71 has proved effective, and usually the fuel from the storage tank can be fed back in after the addition of 200 ppm MAR 71. However, filtering to remove particles of dirt should be an automatic part of the process. Sometimes the contaminated fuel is returned to the refinery for redistillation.

B. Base samples from the water phase are heavily contaminated, but no striking sludge formation.

↳ Clean the tank system by means of careful drainage and subsequent dosing of MAR 71. In practice, the "killing dose" use-concentration has been shown to be 1000 ppm, and that it is best to add the biocide to the tank when it is 1/3 full, before it is refilled completely. If necessary, adequate mixing is achieved by pumping the fuel round. In the first week after adding the biocide, the filters must be carefully checked because increased sludge formation can occur as a result of the microorganisms being killed.

With regard to the economic factors, the costs of biocide dosing, compared with the cleaning costs, are of lesser significance, so that in borderline cases a "killing dose" of biocide can often be used, even though there is the risk that cleaning must nevertheless be carried out later on account of the dirt load being too great.

C. Fuel and water phases are only moderately contaminated.

↳ Careful draining of the fuel systems and subsequent dosing of 50 - 100 ppm MAR 71.

Examples in practice have shown that MAR 71 can be added at the beginning of the sales route, e.g. in the refinery, so that it goes through all the trade stages into the end-user's tank. e.g. the car tank. Since a loss of biocide via the sales route must be reckoned with as a result both of killing microorganisms and of migration into the water phase of inadequately drained storage tanks, use-concentrations of 200 ppm have been used. The required minimum concentration for killing microorganisms, 50 ppm MAR 71, is thus certainly achieved in the vehicle tanks. In contrast to mineral oil stores, the good mixing that is necessary is unproblematical both in land vehicles as well as in ships.

Cleaning of fuels which are contaminated when purchased

Whereas a practically sterile fuel is produced by distillation, when buying fuel on the spot market care must be taken to ensure that one's own storage systems are not contaminated with specially adapted organisms. Sampling systems must ensure that the microbiological findings are already available when the fuel is received. Contaminated material must not be introduced into the tanks without treatment. Compared with storage tanks which have been recognised as being contaminated, the microorganism counts found here are considerably lower; although they exceed the SGS limits which I gave at the beginning, they virtually never reach the magnitude of those in storage tanks which require cleaning. When taking fuel from a tanker into the tanks, homogeneous distribution of the biocide can be ensured. Dosing can take place either via an injector or via dosing pumps. Depending on the dosing accuracy achieved, 50 - 70 ppm MAR 71 is the aim. 70 ppm provide an adequate safety margin from the necessary minimum dose in order to take account of inhomogenities and dose variations. The reliable and rapid killing of microorganisms by MAR 71 (generally within a few hours) permits the bought-in fuel to be taken directly into the tank stores. Of course, care must be taken to ensure careful draining. It should be mentioned here that modern filter/water separating systems, for example the NFV, easily achieve the necessary draining to < 60 ppm water in order to go below the growth limit for microorganisms, but microorganisms inactivate the filters by means of growth, so that filters do not replace the use of biocides for cleaning.

Properties of methylenebisoxazolidine (MAR 71)

Strict demands are made today of a modern fuel biocide. The addition of halogen compounds is generally prohibited. For example in accordance with the Federal Decree on Protection from Emissions. The efforts to use fuels with the lowest possible sulphur content has resulted in the demand for biocides which contain so sulphur. On account of the technical demands, the biocide must dissolve both in the diesel fuel and in the condensed water phase. Biodegradability and the absence of heavy metals are also demanded.

With MAR 71, a biocide based on a methylenebisoxazolidine, a product is available which has been tested and approved by leading car manufacturers, the mineral oil industry and the NATO.

MAR 71 is readily soluble in water, in organic solvents with the exception of some nonpolar systems such as petroleum ether; its solubility is good. However, low concentrations are soluble in nonpolar solvents. The determination of the distribution coefficient with diesel fuel in March 1987 showed that

$$C = \frac{\%\ \text{MAR 71 in water}}{\%\ \text{MAR 71 in diesel fuel}} = 28$$

The result shows that MAR 71 is suitable for the treatment of both the water phase and the fuel phase. The higher concentration is present in the problem zone, the water.

MAR 71 is a good biocidal compound, so that a reduction in the number of microorganisms by > 5 log steps takes place within a few hours; the detection of microorganisms is then negative, and the treated product can be sold.

In its spectrum of effect, MAR 71 covers both aerobic organisms (bacteria, yeasts, mould fungi) and anaerobic organisms. In particular, the growth of sulphate-reducing bacteria which lead to severe corrosion damage, is reliably inhibited.

On account of its excellent anti-corrosion properties, MAR 71 prevents corrosion caused by microbial breakdown products and neutralises any acids formed.

Ecological considerations

When it is used correctly, MAR 71 passes via the sales route to the vehicle fuel tank, together with the fuel. Here it is converted with the diesel fuel into normal combustion products. There is no additional environmental contamination through exhaust gases.

If MAR 71 passes into the environment - usually via a biological clarifying plant - it can be broken down biologically. According to the method OECD 209, the concentration safe for a biological clarifying plant, the EC_{50}, was determined as being 44 mg MAR 71/l. If higher concentrations of MAR 71 are passed directly into a biological clarifying plant, they can be inactivated by sodium bisulphite. The EC_{50} of MAR 71 is then greater than 100 mg/l.

With prolonged standing times, the organisms settle in the water phase, so that specific treatment of the water phase appears to be possible. Trials have shown that the diffusion of MAR 71 into the diesel fuel, even with the higher concentrations of 1000 - 1500 ppm necessary for treatment of the water phase, does not lead to any notable level of the biocide in the fuel.

Tankdesign and tank care to minimise microbial contamination

Tests have shown that a level of < 60 ppm water in diesel fuel prevents the further multiplication of organisms, since the water is then mostly present in dissolved form, and the a_w (active water) value necessary for microorganism growth is not reached. Use is also made of this fact in other industries, e.g. in the production of long-life confectionery.

Careful and regular draining of the tanks is the basic requirement. The tank design must permit complete drainage. Drainage pipes must really be fitted at the lowest point in the system. Water pockets in the piping system and in slanting filters must be avoided. The additional incorporation of filter water separating systems has proved useful, for example in the German navy.

Unnecessary contamination, such as occurs as a result of ballast water during transport by river shipping, must be avoided.

In transport via pipelines, care must also be taken to ensure that there are drainage facilities at the lowest points.

When designing tanks and transport systems, maintenance of the microbiological quality of the fuel must be included as a planning principle, and so drainage systems occupy a position of importance.

Conclusion

Even in the future, purchases of diesel fuel will show microbial contamination. Regular tests show up the risks, and require appropriate measures to be taken in order to kill these organisms.

During distillation, a diesel fuel is produced which is free of microorganisms; however, it must be carefully kept free of water during transportation and storage. If necessary, contaminated diesel fuel must be treated with a biocide. Even the break-in of cooling water during production (plate filters, for example, are never absolutely water-tight) can make this necessary. Technological defects in old systems encourage the growth of microorganisms, so that regular checking is also necessary here.

A Sample From Practice

Scenario: frequent breakdowns of the fire-brigade cars on an airport

Step 1 - analysis of the reason
    -> filter blocking in the fuel system

Step 2 - cleaning of the car tanks

Step 3 - cleaning of the storage tanks

Step 4 - analysis of the residues (fibres of organic material)

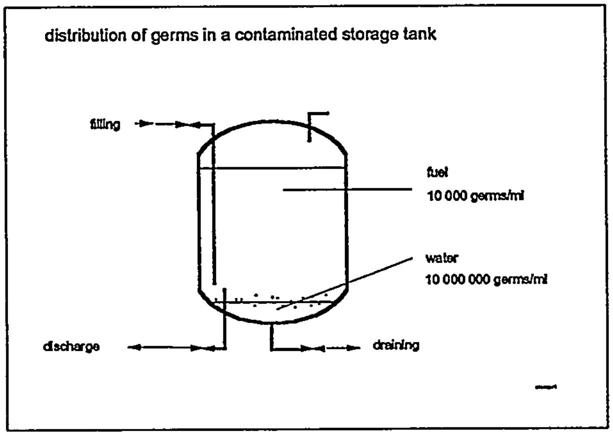
Step 5 - prohibition to use paper towels

Step 6 - first microbiological control

Step 7 - use of MAR 71 in the storage tanks

Step 8 - problem solved

WS103



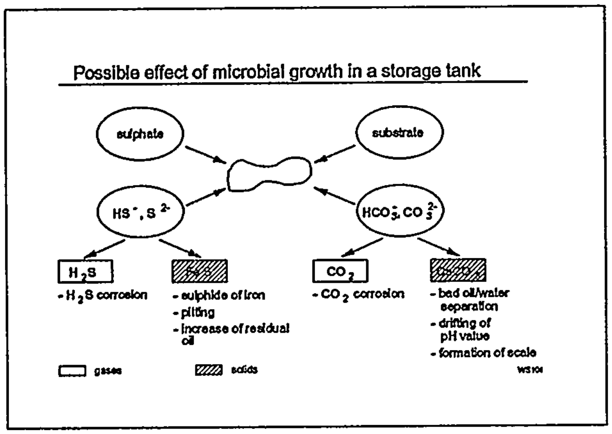
distribution of germs in a contaminated storage tank

Old Recommended Limits (S & M)

- fuel phase $< 1{,}000$ cfu/ml
- water phase $< 1{,}000{,}000$ cfu/ml
  attention: formation of biofilms possible !
- no trouble with the separation of oil/water
- no visible slime formation

Recommended Limits (SGS)

	Component	Proposed Quality Guidelines for Gas Oil
Rapid Check	Fungal Fibres (MBC)	$< 10^3$ /l
Viable Organisms	Aerobes	$< 10^3$ /l
	Filamentous Fungi (Yeasts and Moulds)	$< 10^3$ /l
	Fuel Degraders	$< 10^3$ /l
	S.R.B.	NOT DETECTED
	Total Viable Organisms	$< 3 \times 10^3$ /l



Possible effect of microbial growth in a storage tank

Cleaning of Storage Tanks

- sludge removal
- removal of biofilms
- mechanical cleaning
- cleaning with an alcaline biocidal system cleaner e.g. Grotanol SR 1 (1 - 3 % in water)
- dosage of MAR 71 to the first batch

WS101

Ecological Demands

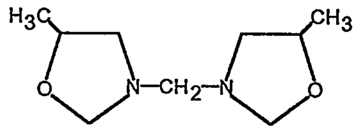
no halogen compounds
(Germany: Federal Decree on Protection from Emission)

no sulphur compounds

no heavy metals

MAR 71

Active ingredient basis



N,N'-methylene-bis-(5-methyl-oxazolidine)

MAR 71 MIC values

BACTERIA	
Alcaligenes	0.015 %
Enterobacter cloacae	0.030 %
Escherichia coli	0.030 %
Proteus vulgaris	0.030 %
Pseudomonas aeruginosa	0.030 %
Pseudomonas fluorescens	0.015 %
Pseudomonas putida	0.125 %
Staphylococcus aureus	0.030 %
YEASTS	
Candida albicans	0.125 %
Rhodutorula	0.030 %
Saccharomyces cerevisiae	0.125 %
FUNGI	
Aspergillus niger	0.030 %
Fusaria	0.030 %
Penicillium funiculosum	0.015 %
Sulphate-Reducing Bacteria	
Desulfovibrio desulfuricans	0.050 %
Microorganism from practice (isolated)	0.125 %

WS87

MAR 71

Solubility behaviour

MAR 71 is readily soluble in water. In organic solvents with the exception of some non-polar systems such as petroleum ether and benzin, its solubility is good. However, low concentrations are soluble in non-polar solvents.

MAR 71

Distribution between diesel fuel/water

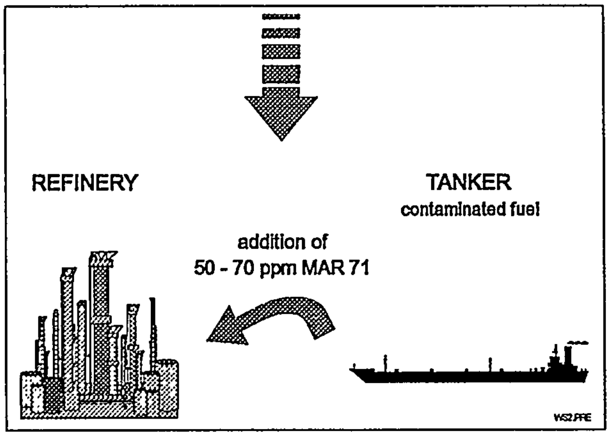
In the determination of the distribution coefficient with diesel fuel in March 1987, it was determined that

$$C = \frac{\text{\% MAR 71 in water}}{\text{\% MAR 71 in diesel fuel}} = 28$$

MAR 71

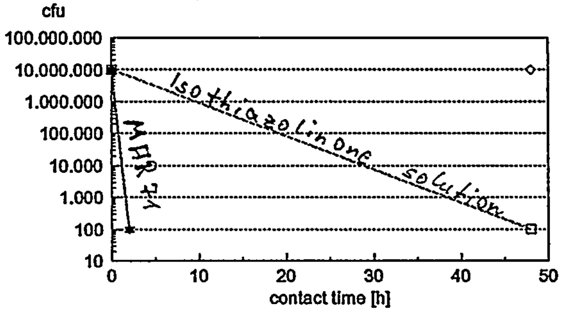
Recommended use concentration in the fuel

- ➢ 1,000 ppm - in a heavily contaminated tank system as a killing dosis
- ➢ 200 ppm - for the preservation of fuel
- ➢ 50 ppm - lowest possible use concentration



Test of reduction of micro-organism counts

(Pseudomonas aeruginosa)
0,05% use concentration

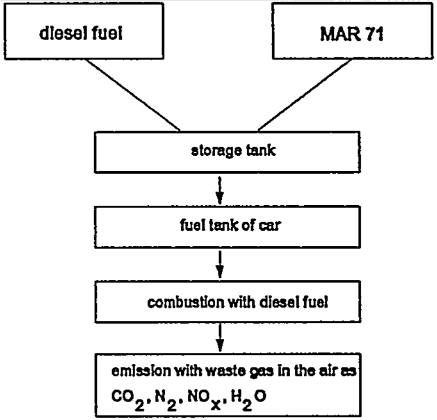


WS32

Corrosion Test

Conditions: temperature: 35°C
60 % covered
immersion time: 24 h
test material: steel

solution	contaminated water phase	MAR 71	deionized water
concentration	100 %	0.2 % in cont. water phase	100 %
pH value (before/after)	4.7/6	10.2/9.4	4 6/7.6
reduction [g/m]²	6.0	0	2.7
appearance of solution	yellow, clear layer: rust	colourless, clear	yellow, turbid layer: rust
appearance of metal gas phase interface	heavy rust	unchanged	slight rust



diesel fuel

MAR 71

storage tank

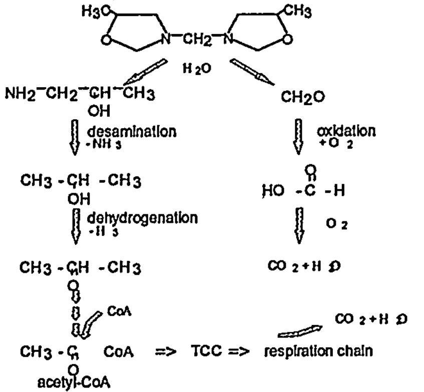
fuel tank of car

combustion with diesel fuel

emission with waste gas in the air as CO_2, N_2, NO_x, H_2O

WS93

Possible decomposition of MAR 71 in the environment



WS34

MAR 71 Inactivation

OECD 209 - Activated Sludge, Respiration Inhibition Test

EC $_{50}$: 44 mg MAR 71/l

⇨ after inactivation with sodium bisulphite

EC $_{50}$: > 1000 mg/MAR 71/l

WS37

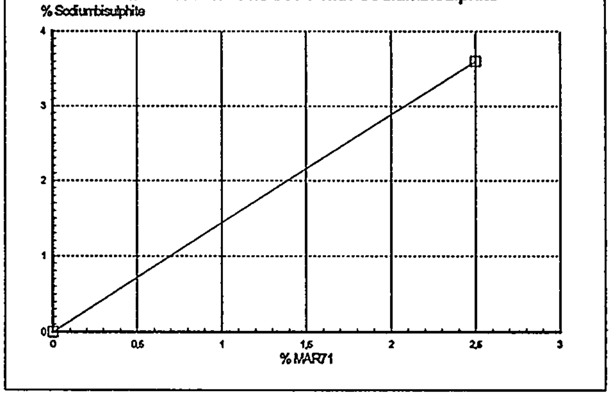
Biocidal treatment of the water phase
in a fuel tank

add MAR 71 through the draining valve
into the water phase of the tank

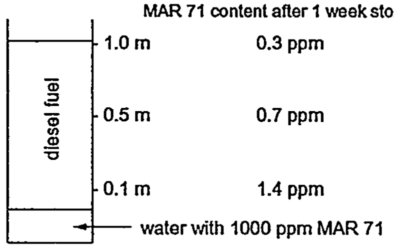
diffusion of MAR 71
in the fuel phase ?

WS119

Inactivation of MAR 71 with Sodiumbisulphite



Diffusion of MAR 71 in diesel fuel



MAR 71 content after 1 week storage time

1.0 m	0.3 ppm
0.5 m	0.7 ppm
0.1 m	1.4 ppm

water with 1000 ppm MAR 71

The amount of MAR 71 in the fuel phase after a treatment of the water phase is neglectibly low.

WS120

5th International Conference
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THE EFFECT OF COPPER, MDA, AND ACCELERATED AGING ON JET FUEL THERMAL STABILITY AS MEASURED BY THE GRAVIMETRIC JFTOT

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ABSTRACT

Thermally unstable jet fuels pose operational problems. In order to adequately identify such fuels, factors that realistically impact on thermal stability were examined. Evaluation was based on a quantitative method of measuring thermal stability, viz.,NRL's recently developed gravimetric JFTOT. This method gives a quantitative measurement of both the strip deposit and filterables formed. The pertinent factors examined, included the individual and interactive effects of: soluble copper, MDA (metal deactivator), and aging. The latter was accelerated to simulate field conditions of approximately six months aging at ambient temperature and pressure. The results indicate that the individual and interactive effects of copper, MDA, and accelerated aging appear to be fuel dependent. Based on the results, the three test fuels examined (one JP-8 and two JP-5s) were categorized as exhibiting very good, typical, and poor thermal stabilities, respectively. For both the very good and poor thermal stability fuels, the effect of copper in conjunction with accelerated aging did not significantly increase the total thermal deposits of the neat fuels. In contrast, for the typical thermal stability fuel, the combined effects of copper and accelerated aging, did. Furthermore, the addition of MDA *prior* to aging of the copper-doped, typical stability fuel significantly counteracted the adverse effect of copper and aging. A similar beneficial effect of MDA was not observed for the poor stability fuel. These results focus on the compositional differences among fuels and the need to elucidate these differences (physical and chemical) for a better understanding and prediction of their performance.

Introduction

The deposits formed from jet fuels of poor thermal stability pose operational problems. These problems, which date back to the mid-1950s include: clogging of the injector nozzles, a decrease in the efficiency of the heat exchangers, and malfunction of the fuel metering controls.[1a] However, although current commercial and military jet fuels usually exceed specification thermal stability requirements, intermittent incidents of fuels of poorer thermal stability have continued to the present.[2] This problem is further exacerbated by the higher temperatures of current production engines - a consequence of improving efficiency[2] and increasing power demands.

To adequately identify current and future fuels of marginal to poor thermal stability, it is important to: (1) evaluate factors that realistically impact on thermal stability and (2) quantify the insolubles formed. Thermal stability was determined using the Naval Research Laboratory's (NRL) recently developed Gravimetric JFTOT,[3] which gives a quantitative measurement of both the strip deposit and the filterables formed. Its operating conditions are similar to the current ASTM test method for determining the thermal oxidation stability of aviation fuels, viz.,the Jet Fuel Oxidation Tester (JFTOT: ASTM D3241). Disadvantages of ASTM D3241 include both its criteria for assessing thermal deposits. For example, the amount of heater tube thermal deposit is based on a qualitative evaluation of the discoloration of a metal tube; furthermore, efforts to quantify heater tube thermal deposits suffer drawbacks.[3] The other JFTOT criterion, a filter pressure drop limit of 3.3 kPa (25mm Hg), is not a direct measure of the amount of filterables, nor a sensitive enough measure.

The pertinent factors examined include both the individual and interactive effects of the following:

1) *soluble copper at approximately 400 ppb maximum concentration*. Dissolved copper has been found to be the most reactive of those metals that catalyze fuel oxidation,[4-6] hence its examination. Sources of copper contamination in fuels include: a) nickel-copper alloys used in the fuel piping systems of U.S. aircraft carriers and air capable ships (ships that carry helicopters);[7,8] and b) in the refinery copper sweetening process.[9] The maximum concentration employed reflects the level of contamination found in typical field samples taken from aircraft carriers at the point of aircraft fueling.

2) *MDA (metal deactivator: N,N'-disalicylidene-1,2-propane diamine) at 5.8 ppm (w/v)* concentration. Its use as a metal deactivator for counteracting the catalytic effect of copper in gasoline was reported by Pedersen[5] in 1949. Currently, this additive is approved for use in both civil and military fuels. The 5.8 ppm concentration employed is the same as the

level specified in the military specification, MIL-T-5624N, for JP-4 and JP-5 fuels (5.8 mg/L). The ASTM specification level for aviation turbine fuels is a maximum of 5.7mg/L.

3) *aging* - this was accelerated to simulate realistic field conditions, viz., approximately six months aging at ambient temperature and pressure.
Although the roles of copper and MDA on fuel thermal stability have been studied systematically and extensively,[1b,10a] adequate quantification of the data, i.e., based on the weights of the deposits (strip and filterables) has not - hence the significance of this study.

Experimental Section

Materials.

Fuels: Of the three fuels examined, fuel A is a hydrotreated Jet A-1 containing JP-8 additives; and, fuels B and C are JP-5s. Both the accelerated aged and the non-aged fuels were filtered through two nylon filters (0.8 micron porosity; 47mm diameter), before testing. Otherwise, no additional purifications were performed.

Copper II ethylacetoacetate (Eastman Kodak) was used as received without further purification. The concentrations levels employed were generally 400 ppb copper, although smaller levels (approx. 100 ppb) were also used (*see* Tables). The amount needed was generally weighed to the nearest micro gram. It was added in powder form (to obviate the introduction of a solvent to the fuel) and the solution well mixed. Addition to the fuel was made just prior to conducting the test to minimize possible losses to the walls of the container on standing.

N,N'-salicyclidene-1,2-propane diamine commonly known as *MDA* (Pfalz and Bauer) is sold under the trade name, Du Pont DMD No.2. It, likewise, was used as received without further purification and was added as a powder. Concentration levels examined include 1 and 5.8ppm (*see* Tables).

Stainless steel strips, grade 302, (approximately 7cm long and 0.5cm wide) were cut from 0.025mm thickness shimstock (Lyon industries). They were pre-cleaned by immersion in trisolvent (equi-volumes of toluene, acetone, and methanol), dried (70 °C/30 min), cooled, and weighed before use.

Filters used were MAGNA nylon membranes of 0.8 micron porosity. Depending on the amount of filterables, the filter sizes used were 13mm or 47mm diameter (*see* below). Two filters were used for each filtration, including the test and control filters.

Weighings: Both the stainless steel strips and 13mm nylon filters were weighed to the nearest micro gram using a Cahn micro balance (model 29). In cases of large amount of deposits, often noted by cloudiness of the effluent, a larger filter size (47mm) was employed and weighed to the nearest 0.1mg. For correction purposes, a control filter was also employed. Averages of 3 weighings were employed in all cases.

Aging. This was accelerated using the Low Pressure Reactor (LPR) developed at the Naval Research Laboratory (ASTM D5304-92). The conditions employed were 90 °C/24 hr/50 psig air, which simulate approximately six months aging at ambient temperature and pressure. *Note*, accelerated aging in this paper refers specifically to aging conducted in the LPR; it does not include the gravimetric JFTOT.

Gravimetric JFTOT. A detailed description of the method has been published, [3] hence only a brief outline is given. Using a reciprocating piston HPLC pump (e.g., Isco model 2350), the filtered fuel is pumped at a rate of 3 mL/min over a stainless steel strip contained in a strip holder, which is heated to a temperature of 260 °C. A backpressure of 500 psi is maintained throughout the run, via a micro valve at the fuel outlet. Duration of the run is 2.5 hr. The effluent (450 mL) is subsequently filtered using two pre-weighed 0.8 micron MAGNA nylon filters. The collected insolubles are washed with pre-filtered hexane, dried in an oven at 70 °C for 30 min, and weighed, on cooling. The control filters are treated similarly except for filtering a small amount (~50 mL) of the neat filtered fuel in lieu of the effluent.

Results and Discussion

Compared to the conventional JFTOT (ASTM D3241), the quantitative measurements of the gravimetric JFTOT were particularly valuable in examining the performance and subsequently, the roles of: copper, MDA, and simulated aging in fuels of different thermal stabilities. Differences in the thermal stabilities of the three test fuels in relation to both the individual factors examined and their interactive effects are addressed. Evaluation was based on the fuel's performance relative to the corresponding neat fuel as well as on the amount of total deposits formed. Note, data have been repeated in the Tables to facilitate comparisons.

Neat Fuels. As shown in Table 1, the neat fuels A and B formed similarly low amounts of total deposits (0.2-0.3 mg/L) and thus appear to exhibit similarly high thermal stabilities. However, differences in their thermal stabilities with respect to, copper plus accelerated aging, further differentiate these two fuels: Fuel A appears to be very good, and fuel B, typical (*see* below). In contrast, the *neat* Fuel, C, formed a significantly large amount of total deposits (7 mg/L). Thus, it has been categorized as poor. This categorization of fuel C is based on the results of an earlier study in which Hardy *et al.*[11] found that for stable fuels, the maximum total deposit was 5 mg/L.

Individual effects of copper and accelerated aging in the LPR. For the three fuels examined, neither individual effect (Tables 1 and 2, respectively) significantly increased the amount of total deposits formed relative to the corresponding neat fuel.

Interactive effect of copper with accelerated aging in the LPR. The interactive effect of copper and aging - as defined (*see* Experimental), on fuel thermal stability was found to be fuel dependent. As shown in Table 3, relative to its corresponding neat fuel, the copper-doped fuels A and C again exhibited no significant increase in total deposits, on accelerated aging. However, for fuel B, the interactive effect of copper with accelerated aging did significantly increase the total deposits (9.4 mg/L). It is this striking difference between fuels A and B that led to our categorization of fuel A, as being very good, and fuel B, as typical. Also, decreasing the copper level in fuel B from 400 ppb to 109 ppb, with accelerated aging, did not decrease the total deposits formed. This 'no concentration effect' with copper supports a copper catalysis mechanism, which is discussed later.

The effect of aging on the thermal stability of fuels has previously been found to be fuel dependent, but the copper content of these fuels was not reported.[10c] The apparent non-effect of copper in an aging fuel of very good thermal stability (Fuel A) suggests either the inherent presence of natural inhibitors or the absence of those species that are susceptible to copper catalysis, or both. The inherently poor thermal stability of fuel C, which does not appear to deteriorate further - e.g., on aging in the presence of copper, suggests the converse, i.e., either the absence of natural inhibitors, or the inherent presence of precursors/species that promote thermal instability, or both. In addition, the non-effect effect of copper and accelerated aging in fuel C suggests that the thermal deposit precursors are limiting reagents under the test conditions employed.

In the case of fuel B (typical thermal stability), the deleterious effect of copper on aging of the fuel is likely attributable to copper catalyzed autoxidation during the accelerated aging. The combined effects of aging with copper present lead to the formation of precursors that promote thermal instability in the gravimetric JFTOT (*see* below). Data supporting a catalytic role by copper, on accelerated aging of fuel B, are as follows:

a) the amount of total deposits formed from copper alone (Table 1), or fuel aging alone (Table 2) were very low (1.2-1.3 mg/L) compared to that formed (9.4 mg/L: Table 3) from the interactive effect of accelerated aging with similarly small amounts (400 ppb) of copper;

b) the total gravimetric JFTOT deposits formed on decreasing the copper concentration further from 400 ppb to 100 ppb were also similar (Table 3);

c) the small amount of insolubles formed from the copper-doped fuel on pre-addition of MDA, a reported copper chelant, [4,5,10a,12] but not on post-addition (Table 4).

Additional data also support the interactive effect of copper and aging on fuel B to be synergistic. For example, the total gravimetric JFTOT deposits formed when copper was added *before* aging was significantly higher compared to that formed when copper was added *after* aging (9.4 versus 2.4 mg/L: Table 3). Furthermore, the total deposits formed when copper was added after aging appears to be the sum of that from aging alone and copper alone (Table 3).

The catalytic role of copper in autoxidation has been reported to be twofold: [10b] 1) *at the initiation stage in autoxidation*; [12-15] an increase in the rate of initiation of free radicals by metals is illustrated in the following equation proposed by Clark: [12]

$$\text{RH (fuel)} + O_2 \xrightarrow{\textit{catalytic metals}} R\bullet,\ RO_2\bullet,\ \text{etc.}$$

2) *in the decomposition of hydroperoxides via copper catalysis*; the equations shown below are based on those proposed by Walling[18] for dissolved metal ions with multiple valence states:

$$Cu^{2+} + ROOH \longrightarrow Cu^{+} + ROO\cdot + H^{+}$$

$$Cu^{+} + ROOH \longrightarrow Cu^{2+} + RO\cdot + OH^{-}$$

Fuel thermal deposits, however, do not appear to be directly related to the concentration of hydroperoxides.[16,17] For example, in a separate study, Hardy *et al.*[16] found fuels that formed high levels of hydroperoxides were relatively thermally stable, whereas fuels that formed lower hydroperoxide levels exhibited a wide range of thermal instabilities. These results reflect the differing stabilities/reactivities of fuel hydroperoxides, since these species would vary with the composition of the fuel. Nonetheless, thermal deposits are likely produced from interactions between the precursors that are formed during autoxidation (from the reactive hydroperoxides) and the fuel polars such as nitrogen and sulfur compounds, as represented below:

$$RH + O_2 \longrightarrow \textit{reactive}\ ROOH \longrightarrow \text{precursors} \xrightarrow[\textit{polars}]{\textit{fuel}} \text{thermal deposits}$$

Clark[12] has suggested a similar pathway; but, that both autoxidation and the subsequent reactions occur during the JFTOT testing regime. As mentioned earlier, our data suggest that, for the fuels examined, copper catalyzed autoxidation leading to the formation of the precursors can also occur during accelerated aging. From a practical viewpoint, the combined tests of simulated aging with the gravimetric JFTOT are important: these tests realistically simulate the fuel pathways from the refinery to combustion in the engine as shown in the three stages below:

	Pathways	**Simulated Test**
Stage I:	*En route from the refinery to the aircraft via pipes/drums* *(ambient conditions at: t = wks)*	**Storage**
Stage II:	*Circulation within the engine: heat exchangers and filters* *via stainless steel tubing (<160°C at: t = hrs)*	**Grav JFTOT**
Stage III:	*Combustors: nozzle coking (<300°C at: t = secs)*	**JFTOT**

The above postulates and observations focus on the significance of fuel composition on thermal stability. Fuel composition is a function of not only the inherent crudes' composition but the refining processes to which it has been subjected. [10d]

Effects of MDA and its interactive effects with copper, and copper with accelerated aging in the LPR. These effects on the thermal stability of fuels B and C are given in Table 4. The effect of MDA with fuel A was not examined in view of its high thermal stability, even on aging with copper (0.41 mg/L). However, for fuels B and C, the results again indicate a fuel dependency. Thus, for typical fuel B, MDA appears to exhibit a beneficial effect on its thermal stability particularly at the recommended concentration level (5.8 ppm versus 1 ppm), but only when added prior to accelerated aging of the copper-doped fuel. In contrast, for fuel C, MDA appears to exhibit some increase in the total deposits formed versus the neat fuel in several cases; e.g., the non-accelerated aging fuel, and the copper-doped fuel without and with accelerated aging. For accelerated aging with no copper added, MDA exhibited an apparent small decrease in the total deposit relative to the aged neat fuel.

The generally beneficial effects of MDA in decreasing thermal deposits of fuels containing both defined and undefined metal content are well documented in two detailed reviews. [1c,10e] The dramatic decrease in total deposits when MDA was added *before* accelerated aging of the copper doped fuel compared to when added *after* accelerated aging supports the well acknowledged mechanism of copper chelation [4,19] to form a stable complex. Such data further indicate that the precursors of thermal deposits can also be formed during simulated aging.

A plausible explanation for the effectiveness of the MDA-copper chelate in counteracting copper's catalytic effect in autoxidation is likely related to unfavorable thermodynamics and kinetics for the redox reactions of the copper (II)-MDA complex. Though these values were not measured, this postulate is supported by the fact that depending on the ligand, both the kinetics and the oxidation potential of metal complexes/chelates in redox reactions are known to change.

With no added copper, the decrease in total deposits on MDA addition to fuel B (Table 4), both before (0.27 mg/L) and after aging (0.48 mg/L) versus the neat aged fuel (1.23 mg/L) suggests MDA possibly exhibits an additional role. In the absence of copper, its role as a surface passivator in the JFTOT has been proposed by Kendall *et al.*[20] and by Clark.[12] These authors also found the passivation mechanism to be less so, for longer tests, such as those conducted in the single-tube-heat-transfer rig (STHTR) versus the JFTOT. Additional studies by Clark *et al.*[21] indicate that more than an adsorption mechanism is operative at elevated temperatures.

Recent studies by Schreifels *et al.*[22] on the adsorption of MDA onto metal surfaces do not appear to support a passivation mechanism: very little MDA coverage (less than a monolayer) on stainless steel was found. Furthermore, the well acknowledged decrease in deposits obtained with aluminum versus stainless steel tubes in the JFTOT has been ascribed to magnesium migration. Both these factors of low MDA coverage on metal surfaces and possibly, a basicity effect by magnesium, in conjunction with - other data involving surface adsorbed acids - led Schreifels *et al.*[22] to propose that: a) MDA adsorption on a metal surface is not a prerequisite for decreasing deposition; and b) MDA's role may be an interaction with acidic sites on the metal or deposit surface.

An important inference of the overall study is that for fuels of typical thermal stability, MDA should be added before aging in order to counteract the adverse effect of copper. This result is consistent with Pedersen's recommendation in 1949, that, for gasoline, metal deactivators should be added as early as possible.[5] Also, the observed thermal stability differences among the fuels, e.g., with MDA between fuels B and C and others mentioned earlier, focus on the role of fuel compositional differences (physical and chemical).

Conclusions

In ascertaining meaningful assessments of jet fuel thermal stability, the results of this study highlight: a) the advantages of the gravimetric JFTOT in determining thermal stability, i.e., it is quantitative and much simpler than the conventional JFTOT; b) the importance of using pertinent factors such as copper, simulated aging, MDA, and their interactive effects, when evaluating jet fuel thermal stability; and c) the judicious choice of fuels, i.e., having a wide range of thermal stabilities versus mere number of fuels.

Based on the diverse thermal stability range of the three fuels examined, the results suggest that the inherent stabilities of both the very good and the poor fuel do not change when exposed to adverse factors such as copper, aging, and their interactive effects. In contrast, the typical stability fuel does deteriorate significantly when exposed to the interactive, and apparently synergistic, effects of copper and accelerated aging. However, such deleterious effects are counteracted and effectively so by MDA, but, only when present in the fuel prior to aging. Thus, early addition of MDA to fuels of typical thermal stability appears to be recommended. It is interesting to note that in 1949, Pedersen [5] made a similar recommendation for gasoline. However, MDA addition to fuels of poor thermal stability does not appear to be beneficial. These results focus on the inherent compositional differences among fuels and the need to elucidate these differences (physical and chemical) for a better understanding and prediction of their performance.

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Table 1. Effect of Copper on Fuel Thermal Stability for Three Jet Fuels

				deposits (mg/L)		
fuel	type	description		strip	filter	total
good:						
A	JP-8	neat		0.009	0.19	0.20
A	JP-8	+ ~372 ppb Cu/no LPR		0.031	0.54	0.57
		+ ~400 ppb Cu/no LPR rpt		0.042	0.52	0.56
			avg	0.037	0.53	0.57
typical:						
B	JP-5	neat		0.069	0.35	0.42
B		rpt		0.029	0.14	0.17
			avg	0.049	0.24	0.29
B	JP-5	+ 400 ppb Cu/no LPR		0.060	1.45	1.51
		rpt		0.036	1.11	1.15
			avg	0.048	1.28	1.33
poor:						
C	JP-5	neat		0.124	7.22[a]	7.34
C	JP-5	+ 94 ppb Cu/no LPR		0.052	8.22[b]	8.27

[a] black tacky residue
[b] tan colored residue

Table 2. Effect of Aging on Fuel Thermal Stability for Three Jet Fuels (No Copper Added)

fuel	type	description		deposits (mg/L) strip	filter	total
good:						
A	JP-8	neat		0.009	0.19	0.20
A	JP-8	LPR/no Cu		0.033	0.40	0.43
		rpt		0.000	0.14	0.14
			avg	0.017	0.27	0.28
typical:						
B	JP-5	neat	*avg*	0.049	0.24	0.29
B	JP-5	LPR/no Cu		0.031	1.04	1.08
		rpt		0.044	1.33	1.38
			avg	0.038	1.19	1.23
poor:						
C	JP-5	neat		0.124	7.22[a]	7.34
C	JP-5	LPR/no Cu		0.110	8.00[b]	8.11

[a] black tacky residue

[b] tan colored matte residue

Table 3. Effect of Copper and Aging on Fuel Thermal Stability for Three Jet Fuels

				deposits (mg/L)		
fuel	type	description		strip	filter	total
good:						
A	JP-8	neat		0.009	0.19	0.20
A	JP-8	+ ~372 ppb Cu/LPR		0.064	0.44	0.50
		+ ~400 ppb Cu/LPR		0.080	0.24	0.32
			avg	0.072	0.34	0.41
typical:						
B	JP-5	neat	*avg*	0.049	0.24	0.29
B	JP-5	+ 109 ppb Cu/LPR		0.086	10.54[a]	10.62
		+ 400 ppb Cu/LPR		0.107	10.22[b]	10.33
		rpt		0.087	8.44[b]	8.53
			avg	0.097	9.33	9.43
B	JP-5	+ ~400ppb Cu added post LPR (effect of Cu on aged fuel)		0.178	2.22[c]	2.40
poor:						
C	JP-5	neat		0.124	7.22[d]	7.34
C	JP-5	+ 94 ppb Cu/LPR		0.086	7.33[c]	7.42

[a] black caked residue
[b] brown glazed residue
[c] tan colored matte residue
[d] black tacky residue

Table 4. Effect of MDA and Its Interactive Effect with Copper on Fuel Thermal Stability: Without and With Aging For Two JP-5 Fuels

			deposits (mg/L)		
fuel	description		strip	filter	total
typical:	no aging/no copper:				
B	neat	avg	0.049	0.24	0.29
B	+ 1 ppm MDA/no LPR		0.024	0.10	0.13
	rpt		0.029	0.26	0.29
		avg	0.027	0.18	0.21
	no aging/ *with copper:*				
	+ ~400ppb Cu/no LPR rpt:	avg	0.048	1.28	1.33
	+ 1 ppm MDA +419 ppb Cu/no LPR		0.020	0.67	0.69
	+5.7ppm MDA +396ppb Cu/no LPR		0.016	0.15	0.17
	with aging/ *no copper:*				
B	neat/LPR	avg	0.038	1.19	1.23
B	+1 ppm MDA/LPR/no Cu		0.033	0.67	0.70
	+5.7ppm MDA/LPR/no Cu		0.022	0.25	0.27
	post LPR + 5.7 ppm MDA (no Cu)		0.044	0.43	0.48
	with aging and copper:				
B	+ 400 ppb Cu/LPR	avg	0.097	9.33	9.43
	+1 ppm MDA + 419 ppb Cu/LPR		0.191	12.22[a]	12.41
	5.7 ppm MDA + 396 ppb Cu/LPR		0.024	0.20	0.23
B	+420 ppb Cu/LPR + post LPR: + 5.7ppm MDA		0.113	7.56	7.67
poor:	no aging/no copper:				
C	neat/no LPR		0.124	7.22[b]	7.34
	+5.8ppm MDA/no LPR		0.034	11.78[c]	11.81
	no aging/ *with copper:*				
C	+94 ppb Cu/no LPR		0.052	8.22[d]	8.27
	+5.8ppm MDA +410ppb Cu/no LPR		0.010	10.42[d]	10.43
	with aging/ *no copper:*				
C	neat: LPR/no Cu		0.110	8.00[d]	8.11
	+ 5.8 ppm MDA/LPR/no Cu		0.022	6.67[c]	6.69
	with aging and copper:				
C	+ 94 ppb Cu/LPR		0.086	7.33[d]	7.42
	+410 ppb Cu + 5.8 ppm MDA/LPR		0.032	10.22[e]	10.25

[a] brown glazed residue; [b] black tacky residue; [c] light tan shiny residue with odor; [d] tan colored matte residue; [e] dark tan shiny residue.

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MECHANISM OF DEPOSIT FORMATION ON FUEL-WETTED METAL SURFACES

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Experiments were performed in a Single-Tube Heat Exchanger (STHE) apparatus and a Hot Liquid Process Simulator (HLPS) configured and operated to meet Jet Fuel Thermal Oxidation Tester (JFTOT) ASTM D 3241 requirements. The HLPS-JFTOT heater tubes used were 1018 mild steel, 316 stainless steel (SS), 304 stainless steel (SS), and 304 SS tubes coated with aluminum, magnesium, gold, and copper. A low-sulfur Jet A fuel with a breakpoint temperature of 254°C was used to create deposits on the heater tubes at temperatures of 300°C, 340°C, and 380°C. Deposit thickness was measured by dielectric breakdown voltage and Auger ion milling. Pronounced differences between the deposit thickness measuring techniques suggested that both the Auger milling rate and the dielectric strength of the deposit may be affected by deposit morphology/composition (such as metal ions that may have become included in the bulk of the deposit). Carbon burnoff data were obtained as a means of judging the validity of DMD-derived deposit evaluations. ESCA data suggest that the thinnest deposit was on the magnesium-coated test tube. The Scanning Electron Microscope (SEM) photographs showed marked variations in the deposit morphology and the results suggested that surface composition has a significant effect on the mechanism of deposition. The most dramatic effect observed was that the bulk of deposits moved to tube locations of lower temperature as the maximum temperature of the tube was increased from 300° to 380°C, also verified in a single-tube heat exchanger. The results indicate that the deposition rate and quantity at elevated temperatures is not completely temperature dependent, but is limited by the concentration of dissolved oxygen and/or reactive components in the fuel over a temperature range. Experiments were done for several fuels using the Single-Tube Heat Exchanger (STHE) apparatus to evaluate deposit formation rates with fuel at measured temperatures. The STHE test tubes were 0.64 cm O.D., 304 SS test tubes, heated at 340°, 380°, 420°, 460°, 500°, and 540°C for 4 hours with a fuel flow of 10 mL/minute. The position of the fuel deposit in the tube versus the fuel temperature at various bath set temperatures very closely approximates what was observed for HLPS heater tubes. These data support the observation based on HLPS data that the depositing position on the tube is temperature dependent. Furthermore, the magnitude of the deposit is essentially the same at all three temperatures. Oxygen measurements in both HLPS and STHE tests, indicate that oxygen is depleted at temperatures below 260°C. At higher temperatures (set temperature of 420°C) for the STHE, methane generation is observed due to pyrolysis of the fuel. At pyrolysis temperatures, surface deposit formation is fuel composition dependent.

I. INTRODUCTION AND BACKGROUND

The effect of fuel system metallurgy on fuel stability is an important concern in the development of high efficiency/advanced engine technology such as adiabatic, low-heat rejection engines. Several studies have shown that trace metals adversely affect the thermal stability of hydrocarbon fuels.[1,2] Metal concentrations as low as 15 ppb of copper, 25 ppb of iron, 100 ppb of zinc, and about 200 ppb of lead have been found to cause significant change in the thermal stability of jet

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* Underscored number in parentheses refer to references at the end of this report.

fuels. These studies suggest that the slightest metallic contamination could cause a significant change in the thermal oxidative stability of hydrocarbon fuels. In fact, the theory has been advanced that all hydrocarbon autoxidations are trace metal catalyzed.[3] Recent work,[4] in which only limited data are available, suggests that aluminum tubes with magnesium-enriched surfaces tend to have lower deposit buildups than the standard aluminum tubes. If such minor changes in surface metallurgy cause significant differences in the rate of deposit formation, major changes in surface composition could dramatically effect processes such as deposit adherence and oxidation catalysis.[5] Experiments with metal deactivator in dodecane using JFTOT equipment suggest that the effect on deposit reduction may be a consequence of interactions in the liquid-phase rather than a reduced adherence to the hot metal surface.[6]

One measure of the thermal stability of aviation fuels is the quantity of deposits formed on heated metal surfaces.[7] In accelerated stability tests conducted in accordance with the JFTOT procedure (ASTM D 3241),[8] the rating methods currently employed involve either visual comparisons or measurements of reflected light by the tube deposit rater (TDR), both of which are sensitive to deposit color and surface texture. Morris and Hazlett [7] examined deposits formed on stainless-steel JFTOT heater tubes in several ways including TDR, gravimetric carbon combustion, and two new nondestructive techniques for determining deposit volumes based on dielectric strength and optical interference. Measurements of total carbon content by combustion were used as a reference. They found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the total TDR often gave misleading results.

The rate of deposit formation in and by fuels is generally both time and temperature dependent. The hotter the fuel, the lower the time needed to form deleterious products. However, the hotter the wall (surface) used to heat the fuel, the greater are the wall (surface) deposits, as long as adequate reactants remain available or are not depleted. Deleterious Products are:

- Microparticulates: Particulates Filterable by Porous Membranes.
- Sediment: Agglomerated particulates settled to the bottom.
- Surface deposits: Insoluble fuel products formed on heated walls by one of severable mechanisms.

Mechanisms of deposit formation include:

- Autoxidation: Self catalyzed oxidation not directly involving the container surface. This is typical in long-term storage environments and accelerated tests up to around 150 degrees C.
- Thermal-Oxidative: Fuel flowing over hot surfaces as in JFTOT or HLPS or STHE with set temperatures of 200 degrees C and hotter. Relates to deposits in higher temperature surfaces of heat exchanger/fuel nozzle-injector
- Pyrolysis: Decomposition of fuel and thermal-oxidative deposits on very hot surfaces. Relates to deposits on nozzle/injector tips & combustion chamber deposits.

Typical forms of deterioration related to fuel types are:

- Gasoline:
    - Autoxidation in the storage of fuel.
    - Rapid autoxidation and thermal oxidation, ie., engine induction system depositing (ISD) in vehicle fuel system.

- Diesel:
    - Storage autoxidation, condensation, esterification, and acid-base reactions forming fuel insoluble microparticulates and sediment (agglomerated microparticulates).
    - Thermal-oxidation forming surface deposits in injectors.
    - Pyrolysis forming deposits on injector tips and combustion chamber fuel wetted surfaces.

- Jet/Gas turbine:
    - Autoxidation forming soluble gum, peroxides, and color bodies.
    - Thermal-oxidation formation of deposits on fuel wetted hot surfaces of heat exchangers, control arms, divider valves, nozzles (during operation and shut-down soak-back)

In a previous paper "Quantitation of Fuel Deposition on Hot Metal Surfaces," at the 4th International Conference on Stability and Handling of Liquid Fuels, data for a Jet A fuel was presented which led to the following conclusions:[13]

- Under JFTOT D 3241 test conditions, thickness profiles of deposits formed on a variety of surfaces including mild steel, 304 SS, Al, Mg, Cu and Au, were compared using the DMD (dielectric breakdown voltage) and Auger milling.
- Except for gold and aluminum, the deposit thicknesses measured by DMD were substantially lower than those measured by Auger milling, and the disparity in the two methods seemed to grow with increased temperature and deposit thickness. The disparities in the thicknesses measured by DMD and Auger milling were most pronounced in the copper-coated heater tubes.
- Using carbon burnoff data for quantitation, allowed an observation that the deposit magnitude essentially the same, except it seemed dramatically lower for aluminum. The highest value was 416 µg for Mg at 380°C while the lowest value at 380°C was 153 µg C for aluminum.
- Aside from variations in the thickness of deposits due to metallurgy, the most dramatic effect observed was that the bulk of deposits moved to tube locations of lower temperature as the maximum temperature of the tube was increased from 300 to 380°C. This effect was somewhat greater on the copper-coated tubes. Deposition rate is highly temperature dependent and may be quantitatively limited by the concentration of dissolved oxygen and/or reactive components in the fuel.
- Surface analysis by ESCA showed that the deposits consisted of a highly oxygenated aliphatic hydrocarbon film containing alcohol, ether, ester and carboxylic acid groups.
- The SEM photographs showed marked variations in the deposit morphology among the surface materials tested. The results suggested that surface composition has a significant effect on the mechanism of deposition. In general, it appears that insolubles coalesce in the fuel to form microspheres less than 1000 Å in diameter. The microspheres then either deposit directly onto the surface, forming a relatively smooth platelet-type structure or they agglomerate into macrospheres (1- to 3 µm in diameter) before adhering to the surface. The former is observed on aluminum and gold, while the latter is particularly evident in deposits

formed on magnesium. For copper, mild steel, and 304 SS, the deposits appear to form from several particle sizes ranging from micro to macrospheres.

- Single Tube Heat Exchanger Experiments using 304 SS tubing has confirmed the temperature dependence of fuel deposits and limited depositing capacity (with oxygen starvation) for the Jet A fuel based on HLPS data.

In this report, the earlier report is expanded by evaluating three additional fuels covering a wide range of composition from a very stable Jet A-1 to a Referee one percent No. 2 diesel fuel and emphasizes the utility of results of quantitation of fuel deposits on hot metal surfaces.

II. EXPERIMENTAL PROCEDURES

A. Hot Liquid Process Simulator: Experiments were performed in an Alcor model HLPS300 Hot Liquid Process Simulator (HLPS), which is a modular version of the JFTOT apparatus used for the ASTM D 3241 method. The HLPS was operated to give conditions equivalent to D 3241 requirements except that Triton-treated fuel prefilters were not used. Preparation of JFTOT tubes for carbon burn-off involved removing both of the tube end grips using a fine tooth jeweler's saw. Special care is taken not to handle the test section of the tube. After SEM evaluation, the test section is then placed in a pre-labeled test tube and cleaned with toluene followed by n-hexane. After descanting the solvents, the test tube is placed in a vacuum oven and dried at 75°C for approximately one hour. The specimens are now ready for carbon burn-off analysis.

B. Deposit Measuring Device: The deposit thickness measurement device (DMD) determines the thickness of a deposit on a conductive surface by applying a voltage across the deposit while measuring the dielectric breakdown of the layer at various points.[9] The DMD used in this work was first reported in Reference 10. The DMD voltage measurements were shown to relate thickness of deposits with 350 volts equal to 1 micrometer.[10] Methods for calculating deposit volume on JFTOT heater tubes were also discussed in Reference 10. This procedure was used to develop DMD data correlations to carbon burn-off values reported in Reference 7. Based on deposit density calculations, assuming that a density value of 1.0 to 1.5 g/cm^3 is reasonable, deposit volumes greater than 0.0800 mm^3 (and ranging up to 0.6365 mm^3) by DMD seemed most reliable in this work. These DMD deposit volumes correspond to carbon burn-off values of 95 µg to 877 µg of carbon, respectively.

C. Single Tube Heat Exchanger: Fig. 1 is a schematic description of the single tube heat exchanger (STHE). Fig. 2 summarizes the thermocouple measured fuel temperatures at various positions in the test tubes at the indicated bath temperatures. Prior to a run the test fuel is filtered and aerated according to the procedures outlined in ASTM D 3241, the JFTOT test. Prior to beginning a run, test fuel is pumped through the system for 15 minutes to flush the lines of all residue from the previous run or cleanup. The pumping is done with a standard HPLC pump set to deliver 10 mL/min. The pressure in the system fluctuates (due to the pulsing action of the pump) between 800 and 950 psig with the help of a back pressure regulator. A safety pressure relief valve is set at 1000 psig. The flush is performed with no heat applied to the heat exchanger tube. Once the flush is complete, the heating bath, a Techne Fluidized Bath Model SBL-2D, is raised into position around the heat exchanger tube. This point is the beginning of the 4 hour run. At this point also, a zero hour oxygen/methane analysis is made using gas chromatography. Additional oxygen/methane analyses

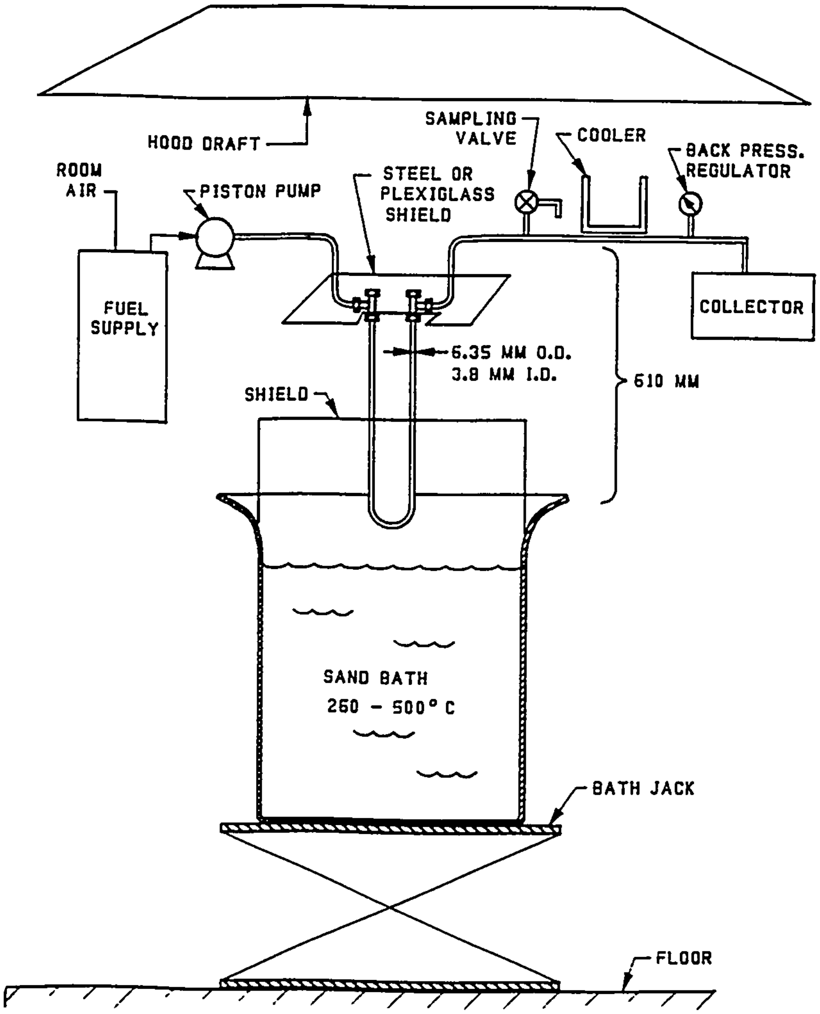


Figure 1. Schematic of Single Tube Heat Exchanger

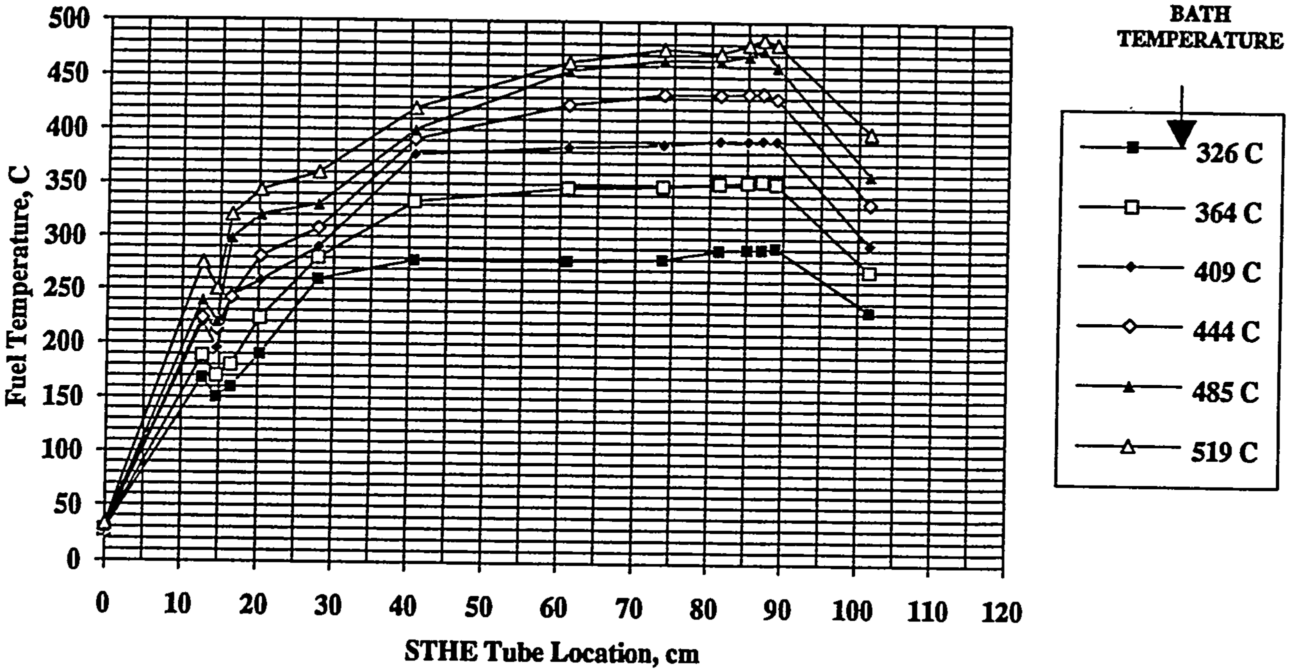


Figure 2. Fuel Temperature Versus Location in Single Tube Heat Exchanger

are conducted throughout the run, once every 10 minutes for the first hour and every 30 minutes thereafter. An end of test analysis, at ambient temperature, is also made for comparison purposes. At the end of a STHE run the heating bath is lowered away from the U-tube. Fuel is allowed to flow through the tube for approximately 10 more minutes to cool the tube. The pressure is released and the U-tube is removed from the STHE. Next the U-tube is rinsed with heptane and air dried. The tube is then clamped in a bench vise and straightened. The longitudinal center of the tube is marked. Measuring from the center point, marks are made at 3 inch (7.6 cm.) intervals along the entire length of the tube. Beginning at the inlet end of the tube, inscribe each marked-off section with a letter; starting with "A" and ending with "N." Cut the tube at each of the 3 inch scribe marks using a tubing cutter. Since the tubing cutter will tend to close the openings at each end of the 3 inch sections, use a 1/4" drill bit to open the holes to original diameter. The sections (B through M) are now ready for carbon burn-off analysis.

D. Carbon Burnoff Procedure: All analyses were conducted on Control Equipment Corporation Model 240XA Elemental Analyzer. Specially constructed quartz sample boats were used to inject the test specimen into the furnace of the analyzer. The combustion tube section of the analyzer is set at 950-975°C and the reduction tube section is set at 600-625°C. Calibration of the instrument is conducted using squalane and n-hexadecane. Analysis time is 250 seconds. Results are reported in micrograms of carbon (µg C).

E. Test Fuels: TABLE 1 provides fuel chemical and physical properties.

TABLE 1. Chemical and Physical Properties of Test Fuels

Property	Test Method	West Coast Jet A AL-19471-F	Jet A-1 AL-19546-F	Reference No. 2 (Cat 1-H) AL-19540-F	MIL-F-46162C 1% Sulfur Reference Fuel w/o Additives AL-19854-F
API Gravity	D 1298	40.8	50.4	33.6	31.1
Density, kg/L	D 1298	0.8212	0.7776	0.8566	0.8698
Flash Point, C	D 93	46	48	87	49
Cloud Point, C	D 2500	---	---	-8	<-45
Pour Point, C	D 97	---	---	-9	<-45
Freeze Point, C	D 2386	-42	-57	---	---
Kinematic Viscosity at 40 C, cSt	D 445	---	---	2.84	3.36
Distillation, C	D 86				
IBP		153	163	208	180
10 % Recovered		183	171	233	228
50 % Recovered		214	181	263	274
90 % Recovered		241	204	302	326
End Point		261	232	349	372
Residue, vol%		0.5	0.8	1.4	0.5
Ash, wt %	D 482	---	---	0.01	0.03
Carbon Residue, 10% Bottoms, wt %	D 524	---	---	0.12	0.12
Particulate Contamination, mg/L	D 2276	1.2	0.8	1.5	1.7
Accelerated Stability, mg/100 mL	D 2274	---	---	0.5	1.3
Total Acid Number,TAN, mg KOH/g	D 974	0.001	0.009	0.08	0.16
Copper Strip Corrosion	D 130	1a	1b	1a	1a
Hydrogen, wt %		13.49	---	---	12.96
Sulfur, wt %		0.04	0.008	0.39	1.02
Net Heat of Combustion, MJ/kg	D 240	42.8	43.4	42.5	42.1
BTU/lb	D 240	18406	18671	18260	18119
Aromatics, wt %	D 1319	21.7	11.8	41.1	33.1
Cetane Number	D 613	---	---	48.6	44.5
Cetane Index	D 976	---	---	44.8	43.0
Free Water and Particulate Contamination	D 4176	Sed/Bright	Clean/Bright	Sed/Bright	Sed/Bright
Mercaptan Sulfur, wt%	D 3227	0.0004	---	---	0.2086

III. DISCUSSION

Data in Fig. 3 obtained using the Hot Liquid Process Simulator (HLPS) at 380°C compares the Jet A fuel with three additional fuels; a very stable Jet A-1, a Reference No. 2 D diesel, and a referee 1 % Sulfur diesel No. 2. The test tube metallurgy included 316 SS, 304 SS aluminum plated on 304 SS, and magnesium plated on 304 SS. Note that for all the fuels except the Jet A, lower deposit levels were observed on the hot magnesium surface. Deposit levels are known to vary with fuel type and surface metallurgy.[14]

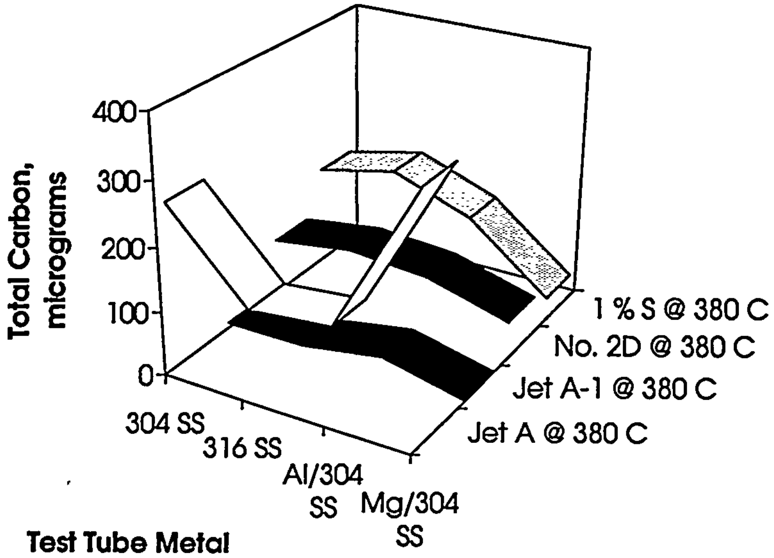


Figure 3. Carbon Data for Four Fuels on Various HLPS Metal Test Tubes

At both 300°C and 380°C as shown in Fig. 4, deposit formation is dramatically reduced to essentially no deposit when the 1 % Sulfur diesel fuel was purged with nitrogen as opposed to air, which showed significant deposit carbon burnoff values also in Fig. 4.

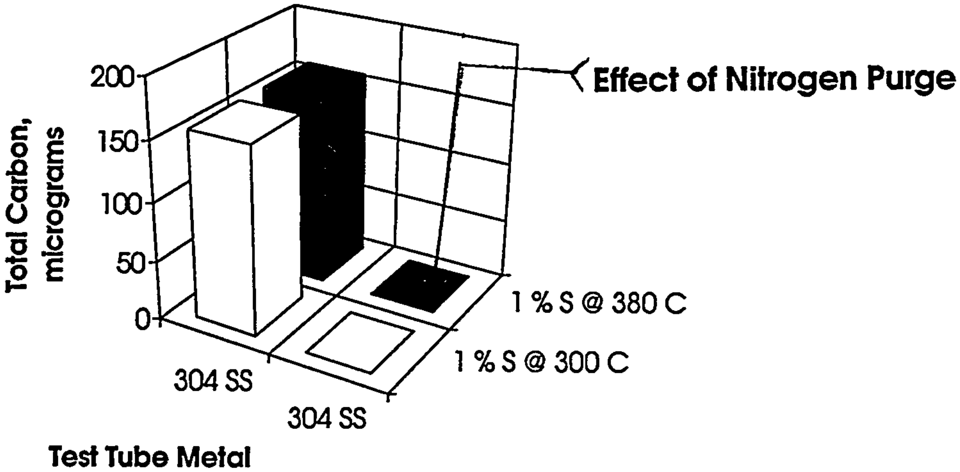


Figure 4. Fuel Nitrogen Purge Effect on Deposit Level on HLPS Metal Tubes

By measuring oxygen and methane in the test fuel, sampled as it exits the reactor, oxygen was depleted at 300-340°C and methane generation (indicative of pyrolysis) generally started at about 380°C depending on the fuel type as shown in Fig. 5. No methane was observed for the Reference No. 2 D fuel even at the upper test temperature of 460°C.

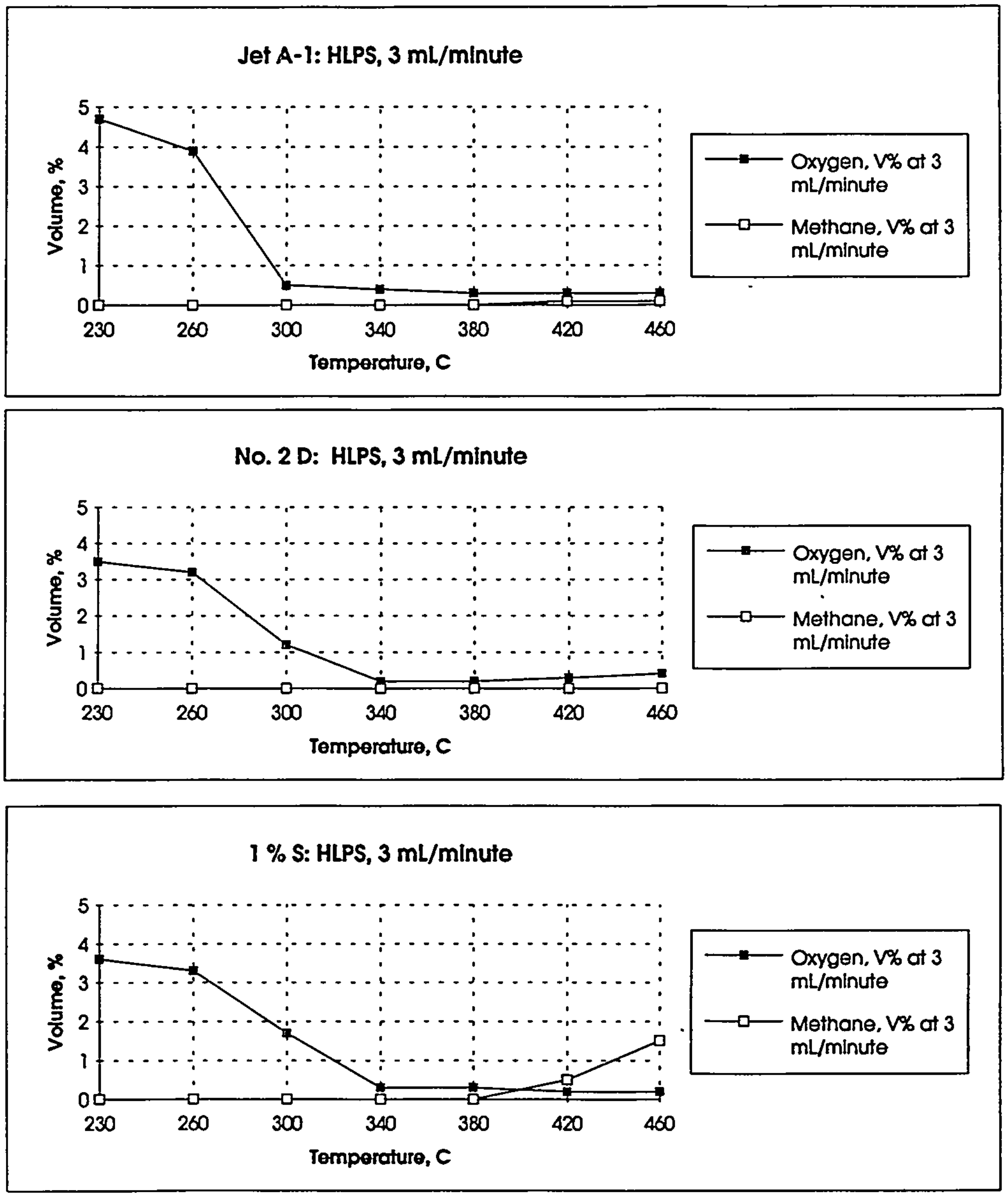


Figure 5. HLPS: Temperature Effects on Oxygen and Methane

The Single Tube Heat Exchanger (STHE) gave more consistent and definitive results in that the three reacted with all the available oxygen below a 260°C bath temperature, and formed methane in the temperature of 400-445°C, as shown in Fig. 6.

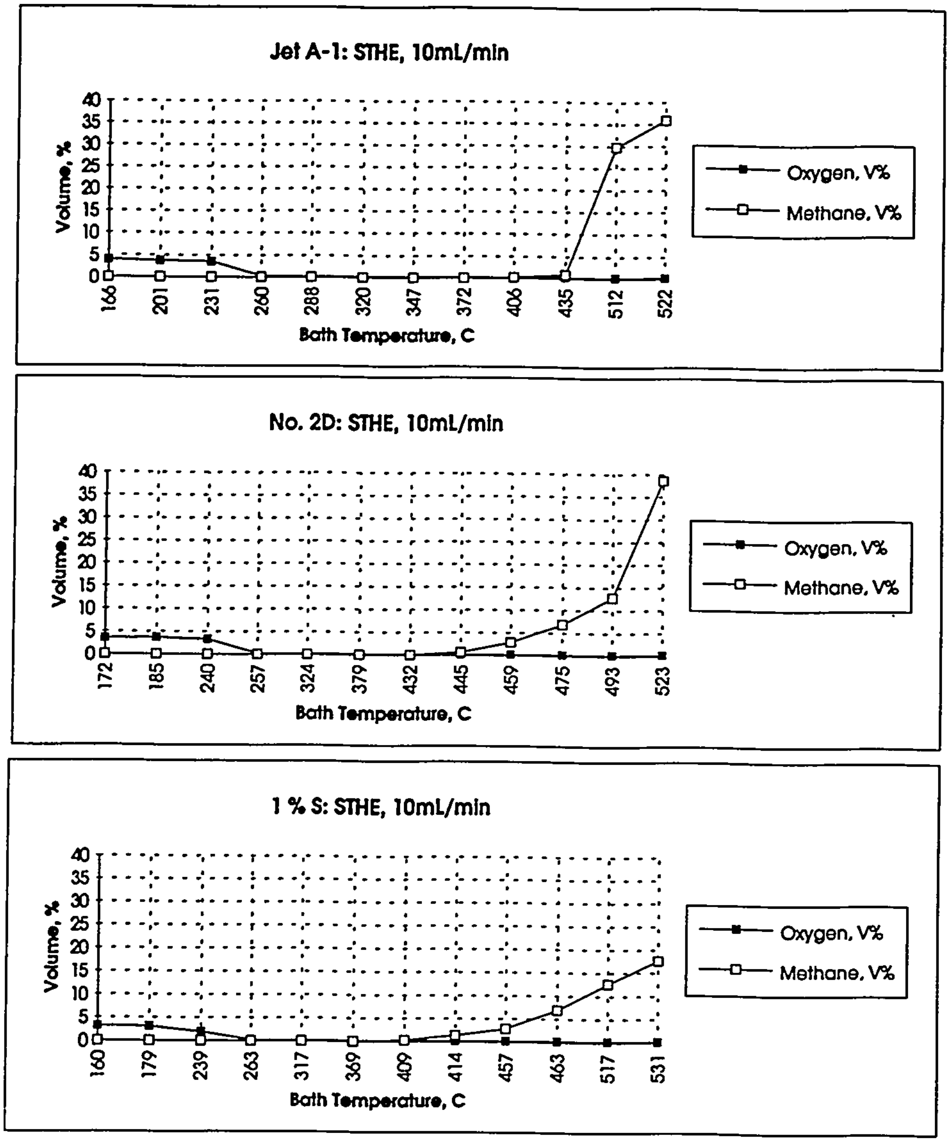


Figure 6. STHE: Temperature Effects on Oxygen and Methane

Deposit levels were measured as carbon burn-off values for both 304 SS and 316 SS test tubes in the STHE apparatus. This data is summarized in Fig. 7:

- Higher deposit levels were observed for Reference No. 2D on 304 SS compared to 316 SS.
- Deposits formed by the 1 % Sulfur fuel at pyrolysis temperatures on both 316 SS and 304 SS, but at higher tube locations. Deposits observed at lower tube locations in lower bath temperature experiments, were not present at the higher test temperatures.
- Deposits from the Jet A-1 were significantly higher on 316 SS, especially at the higher test temperatures.

Data for particulates, summarized in Fig. 8, were measured by filtering reacted test fuel (at room temperature) through porous membrane filters having a nominal pore size of 0.8 micrometer. The particulate level tended to be lower at the higher pyrolysis temperatures, and were not formed at all for the very stable Jet A-1.

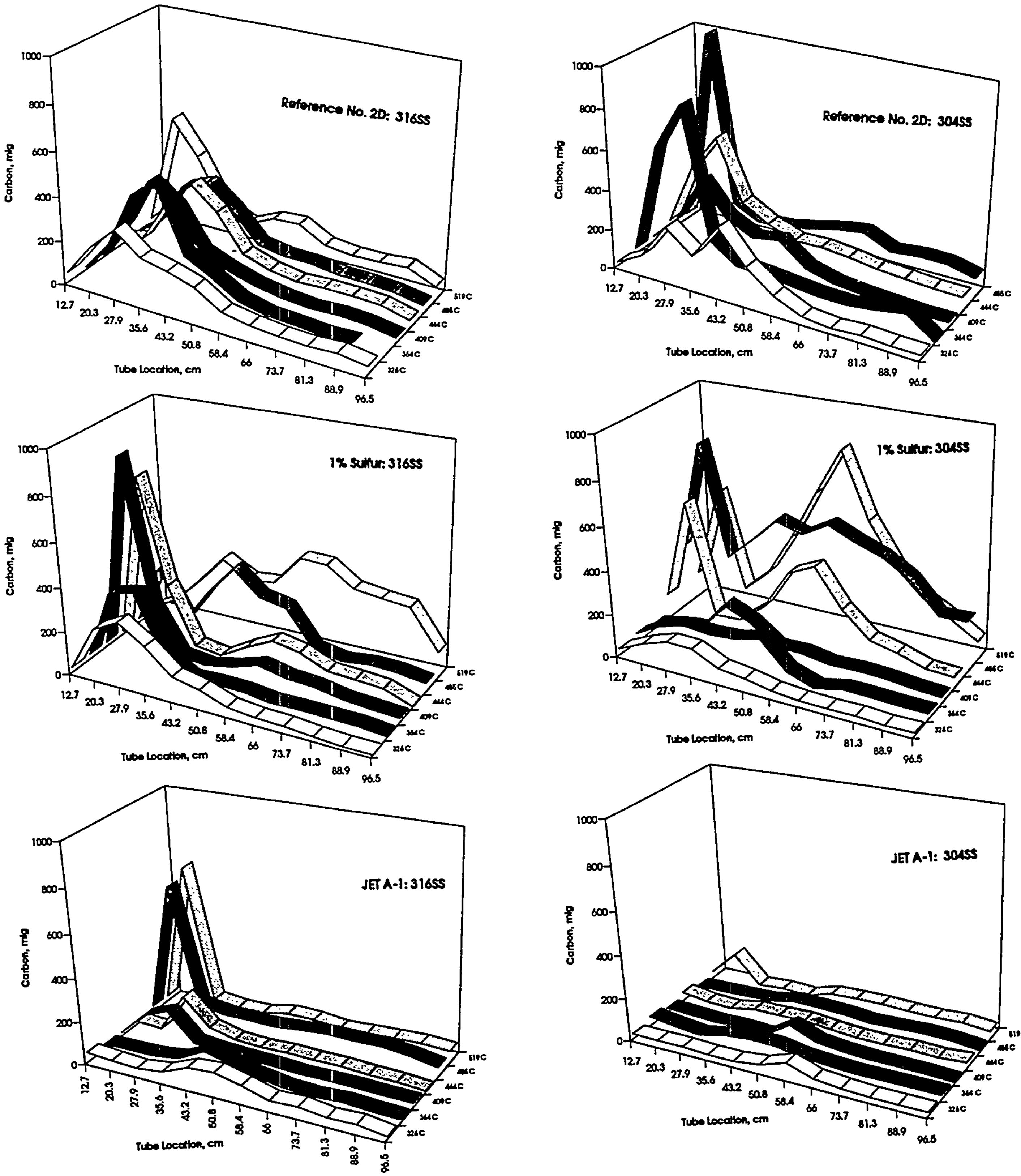


Figure 7. Carbon Data for Three Fuels at Various STHE Bath Temperatures

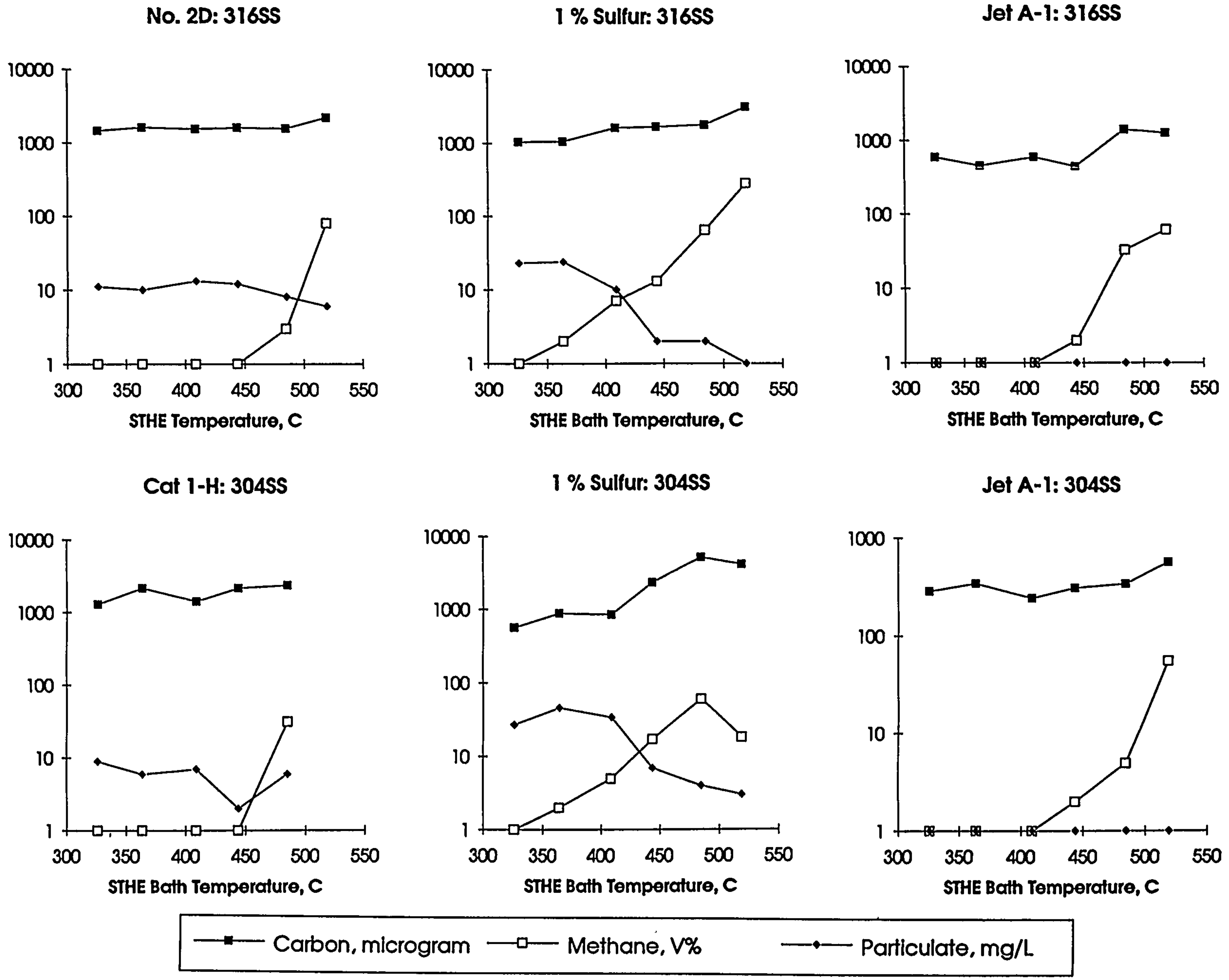


Figure 8. Fuel Microparticulate Levels after STHE Stressing at Various Temperatures Using 304 SS and 316 SS Test Tubes

When the 1 % Sulfur test fuel was passed through filters of various pore sizes, as the hot fuel exited the test tube, the data in Fig. 9 was obtained using a 17 micrometer stainless steel filter, a 5 micrometer silver filter and a 1.2 micrometer silver filter in separate tests. While no deposits were found on the 17 micrometer filter, significant quantities were observed on both the 5 and 1.2 micrometer filters. Removal of the particulates during high temperature filtration was not reflected in the room temperature particulate values. Small size particulates formed in the fuel at high temperatures may not cause equipment distress (compared to large particals which would both plug injector filters and closely rubbing, highly loaded surfaces.

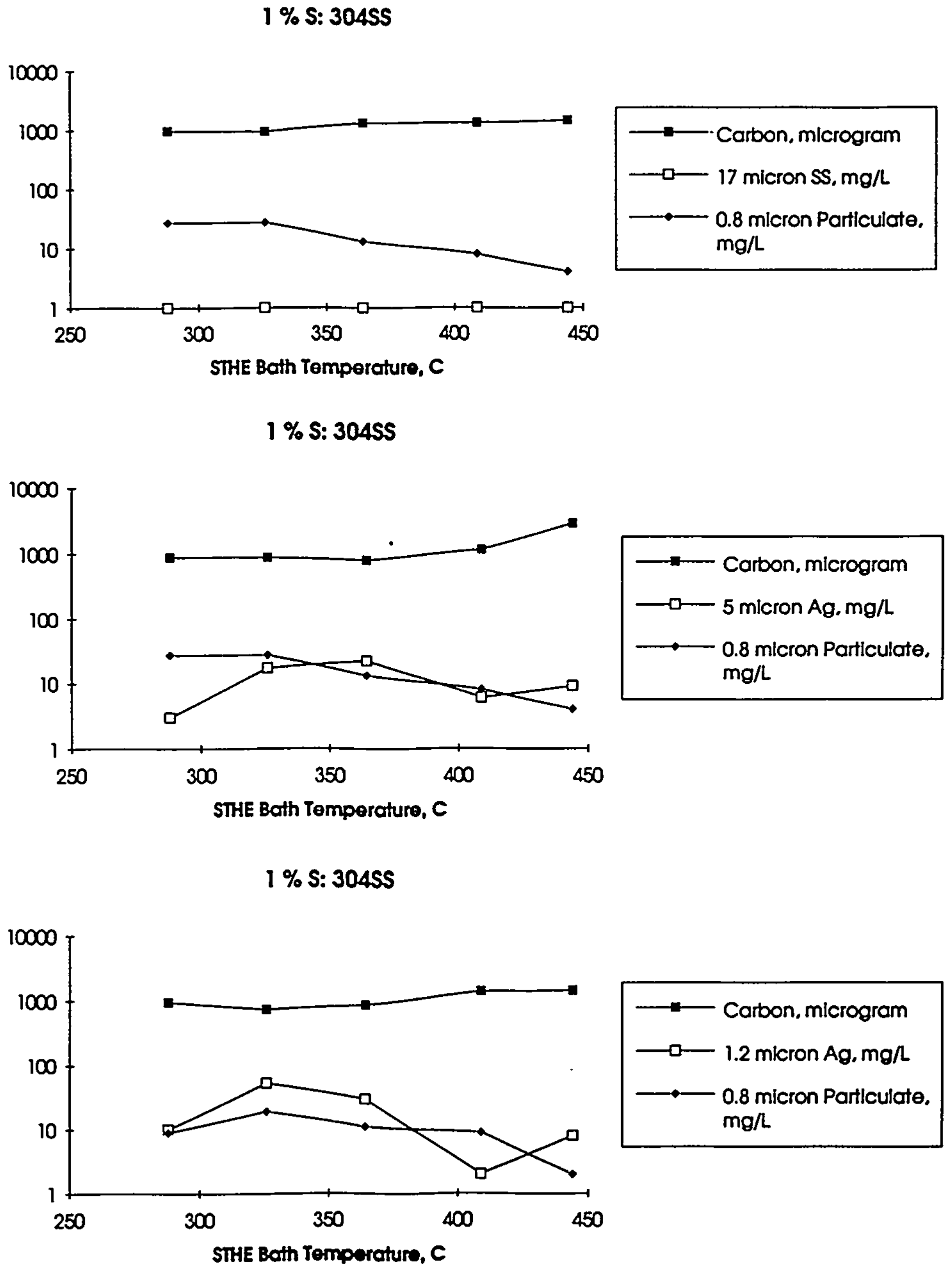


Figure 9. 1 % S Fuel Microparticulate Levels at Room Temperature after STHE Stressing at Various Temperatures and Flowing Through In-Line Metal Filters

When the 1 % Sulfur fuel was purged with nitrogen, deposit levels in Fig. 10 were significantly reduced from the aerated sample deposit level at 364°C.

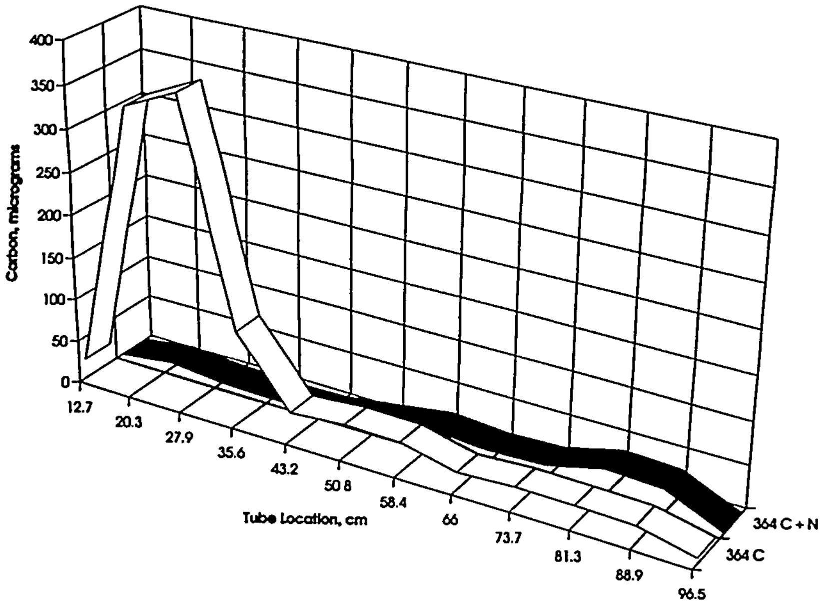


Figure 10. Nitrogen Purge Effect on 1 % S Fuel Deposit Level in STHE 316 SS Metal Tubes at 364 Degrees C

When two test tubes were used in series, very low deposit levels were observed on the second tube using the 1 % Sulfur and the Reference No. 2 D fuels. Figure 11 provides comparative data for the Reference No. 2 D fuel in both 316 SS and 304 SS test tubes, at 364 °C.

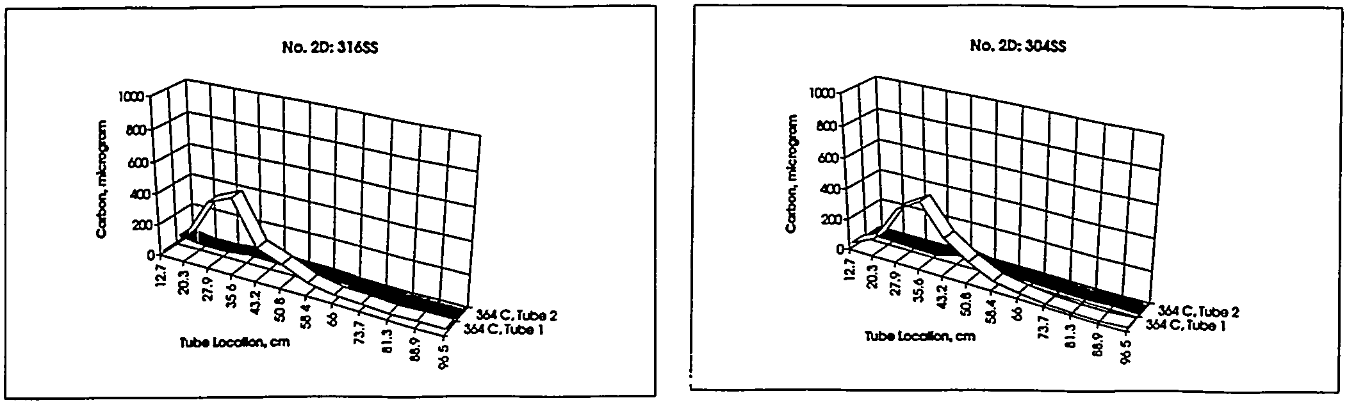
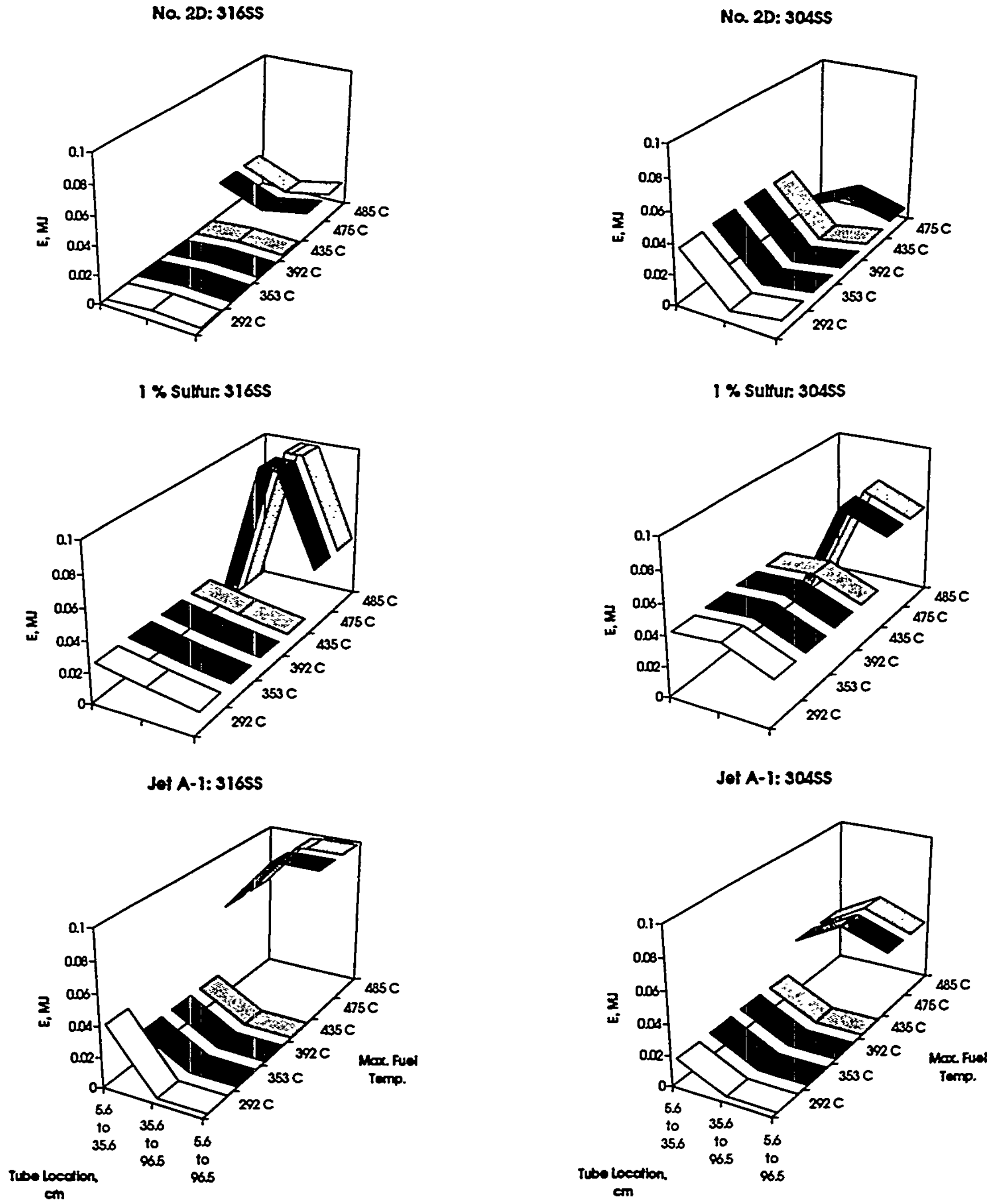


Figure 11. Reference No. 2D Fuel Deposit Level on STHE 316 SS and 304 SS Serial Metal Tubes at 364 Degrees C

Arrhenius activation energy values are summarized for the three fuels in Fig. 12 (for different sections of the test tubes covering the 5.6 to 35.6 cm, 35.6 to 96.5 cm, and 5.6 to 95.6 cm which was the whole tube). As would be expected, the values generally reflected the change in deposit quantity with temperature. Knowing that the oxygen was depleted at about 260°C, increases in deposit level with increase in temperature would not be expected to in crease until pyrolysis temperatures were reached, and even then deposit levels would probably be lower as any deposit formed on the surface may subsequently pyrolyze.


No. 2D: 316SS

No. 2D: 304SS

1 % Sulfur: 316SS

1 % Sulfur: 304SS

Jet A-1: 316SS

Jet A-1: 304SS

Figure 12. Arrhenius Energies of Activation For Three Fuels on 304 SS and 316 SS STHE Metal Tubes Using Carbon Levels for the Whole Tube and Two Sections of the Tube

IV. Conclusions

- The mechanism of deposit formation on fuel-wetted hot metal surfaces involves thermal-oxidation reactions which are limited by the available oxygen. Different fuels contain different amounts of reactive species capable of oxidizing and subsequently agglomerating to form fuel insolubles which attach to the hot surfaces. Formation of non-deleterious thermal-oxidative products can effectively deplete the available oxygen, thus preventing deleterious oxidation. Metal surface composition effects the quantity of surface deposition, depending on fuel composition and depending on whether the temperature is high enough for pyrolysis to occur.

- At higher pyrolysis temperatures, deposit levels are influenced by both the fuel composition and the surface composition.

- The STHE is a viable procedure for evaluating deposit formation from fuels at high temperatures.

- While the HLPS is a viable tool for evaluating the relative stability of fuels, the temperatures of the test tube are less effective than the bath temperature of the STHE, which more accurately reflects the bulk fuel temperature as it passes out of the heated section of the test tube. This is particularly true at STHE temperatures which caused fuel formation of methane, but no methane was observed at similar tube temperatures in the HLPS for at least one of the test fuels.

- Reduction of deposit can be accomplished by reducing oxygen or heat-pretreating the fuel.

V. Recommendations

- The Army Fuel System Design Guide in The Standard Army Refueling System[15] should address reducing the replenishment of Oxygen in the fuel as this relates to the design of the tank venting system.

- An expanded test matrix, including both tube size and test time, should be evaluated to support conclusions reached in this report related to the mechanism of deposit formation in hot-fuel flowing systems. Test fuels should include additives, especially deposit modifiers, oxidation inhibitors, and detergent/dispersants.

- Fuel prestressing/cleanup systems and oxygen-reduction additives should be evaluated for eliminating thermal-oxidative deposits in hot fuel systems.

VI. Acknowledgement

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EFFECT OF HIGH SURFACE AREA ACTIVATED CARBON ON THERMAL DEGRADATION OF JET FUEL

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Different solid carbons added to jet fuel during thermal stressing cause substantial changes in pyrolytic degradation reactions. Activated carbons, especially high surface area activated carbons were found to be very effective in suppressing solid deposition on metal reactor walls during stressing at high temperatures (425 and 450°C). The high surface area activated carbon PX-21 prevented solid deposition on reactor walls even after 5h at 450°C. The differences seen in the liquid product composition when activated carbon is added indicated that the carbon surfaces affect the degradation reactions. Thermal stressing experiments were carried out on commercial petroleum-derived JPTS jet fuel. We also used *n*-octane and *n*-dodecane as model compounds in order to simplify the study of the chemical changes which take place upon activated carbon addition. In separate experiments, the presence of a hydrogen donor, decalin, together with PX-21 was also studied.

Introduction

Jet fuel degradation occurs under long-term low-temperature (oxidative) storage conditions as well as short-term high-temperature (pyrolytic) stress. During both storage and exposure to high temperatures jet fuel decomposes, forming insoluble materials which could deposit in fuel lines or on other surfaces. The higher temperature that jet fuels may be exposed in the future, possibly in the range of 400–500°C, as a result of increased demands for "thermal management" on aircraft complicates the problem even further. Many chemicals have been used as additives, antioxidants, metal deactivators, dispersants and passivators for fuel applications in the oxidative regime. They should be used with caution in fuels taken into the pyrolytic region, since at high temperatures the oxygen plays very complex role and participates in many side reactions[1]. Recently, Coleman et al.[2] reported the promising news that benzyl alcohol and 1,4-benzenedimethanol could retard the formation of carbonaceous solids in Jet A-1 fuel at 425°C in nitrogen and air atmosphere. The performance of an additive depends on factors, such as type of fuel, fuel composition, additive concentration, and temperature of stressing. It is well known that a fuel that shows the highest degree of instability also has the highest free radical concentration[3]. Alfelli et al.[4] reported that solid adsorbents, which they called "Fuel stability foam," produced from polyurethane were found to be effective in greatly improving diesel fuel stability.

We have studied the changes in degradation reactions when different carbons were added to JP-8 jet fuel during thermal stressing at 450°C (ref. 5). The solid carbons with the most disordered structure and the highest surface reactivity (*i.e.*, activated carbons) produced the most significant effect on in preventing solid deposition on reactor surfaces. The addition of carbon black also prevented solid deposition, but the effect was not as evident as that seen with the activated carbon addition. The most ordered and the least reactive solid (SP-1 graphite) used did not have a significant influence on thermal reactions.

We assumed that the activated carbons added during thermal stressing of jet fuels promoted a variety of surface reactions because of their active surfaces. The reactivity of an activated carbon depends on the nature of the carbon surface, the presence of carbon-oxygen surface structures, the availability of the active sites and the surface area. Spiro[6] studied the catalytic effect of carbons on reactions in solution and reported that the surface area played an important role on carbon catalytic activity. In our previous studies, we showed that the activated carbon surface area is an important parameter which determines to a high degree the effectiveness in suppressing solid deposition during thermal stressing at high temperatures[7]. For better understanding the role of activated carbon during thermal stressing, we used model compounds *n*-dodecane and *n*-octane. Using model compounds simplifies the study of the chemical changes upon activated carbon addition[8].

The main objective of our work reported in the present paper was to study the thermal degradation of commercial petroleum- derived JPTS jet fuel (as well as model compounds *n*-dodecane and *n*-octane) in the presence of high surface area activated carbon PX-21.

Experimental Section

Thermal stressing experiments were carried out on 10 mL samples of a commercial petroleum-derived JPTS jet fuel at 425 and 450°C for 1 and 5h. The JPTS fuel is a thermally stable jet fuel, containing a proprietary additive JFA-5[9]. The experiments were carried out in microautoclave reactors purged with ultra-high purity (UHP) grade nitrogen five times to minimize the presence of dissolved oxygen and finally pressurized to 0.7 MPa with nitrogen or air. The *n*-dodecane, *n*-octane, and *cis/trans*-decalin used as model compounds were purchased from Aldrich and used without further purification. In some experiments, 5 or 50% decalin was added to the alkane model compounds. The experimental method for stressing and analyzing the model compounds was the same as used for the authentic fuel. The high surface area activated carbon PX-21 was obtained from Amoco Oil Company. The influence of the amount of PX-21 carbon was studied by adding different quantities (50, 150, and 250 mg) during thermal stressing of the model compounds or the fuel.

Gas chromatography (GC) of liquid samples was conducted using a Perkin-Elmer 8500 GC with a fused silica capillary column. Quantitative analysis of the liquid products was performed based on the calibration curves obtained from external standards. Compounds in the liquid products were identified by capillary gas chromatography–mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with HP 5971A mass selective detector.

The gaseous products obtained after stressing were analyzed using a Perkin-Elmer AutoSystem gas chromatograph equipped with two different columns and detectors for quantifying the components. The gaseous products were identified by comparing their retention times with those of standard gases (Supelco), and quantified by using external standards.

The activated carbon PX-21 was characterized before and after stressing experiments by N_2 adsorption at 77K using a Quantachrome automated adsorption apparatus, Autosorb-1, model ASIT and the BET surface areas were calculated[10]. The activated carbon PX-21 and the deposits obtained after thermal stressing were examined using a polarized-light microscope, Nikon-Microphot FXA and a scanning electron microscope (SEM), ISI ABT, model SX-40A.

Results and Discussion

Thermal stressing of JPTS jet fuel with PX-21 activated carbon at 425 and 450°C in N_2 and air atmosphere. The thermal stressing experiments on JPTS jet fuel in the presence of high surface area activated carbon PX-21 were carried out at 425 and 450°C for 5h in nitrogen and air. Initially, the fuel is a clear, colorless liquid which became dark brown after 5h at 450°C. The liquid obtained after thermal stressing of 10 ml JPTS mixed with 100 mg PX-21 is much lighter and does not differ very much in color from the unstressed JPTS.

Tables I and II present the results for thermal stressing of JPTS with and without PX-21 at 425 and 450°C for 5h in nitrogen and air. When PX-21 is added, generally, higher liquid products yields and lower final reactor pressure are obtained with no solid deposition. The trends observed from thermal stressing at 450 and 425°C are essentially the same, except for lower liquid yields and higher reactor pressures with more solid deposition in the absence of PX-21 at higher temperature (Table II). The presence of oxygen (air) during stressing causes more degradation of jet fuel (Tables I and II).

Figures 1 and 2 show the yields of alkanes in the liquid products after stressing. The C_8 and C_{14} alkanes are not shown because they are coeluted with other compounds. It is clear from the figures that adding PX-21 gives lower concentrations of shorter chain alkanes (C_5-C_9) and C_1-, C_2-, and C_3-benzenes, and higher concentrations of longer chain alkanes (C_{10}-C_{15}), compared to the composition of the liquids produced without PX-21. Overall, addition of PX-21 appears to preserve the alkanes present in JPTS. A more extensive degradation in the presence of air is also noted from the lower concentrations of longer chain alkanes (Figure 2).

The differences seen in the liquid product compositions shows the active role of PX-21 in the degradation reactions. One possible explanation for the apparent increase in the stability provided by the activated carbon could be the stabilization of nascent free radicals on carbon surfaces. It is also apparent that the presence of oxygen limits the stabilizing effect of the added carbon upon stressing the fuel under the same conditions.

There are substantial differences also in the head-space gas yield and composition obtained after thermal stressing of JPTS with and without PX-21 in nitrogen, as shown in Table III. The major compounds in the gas sample obtained after thermal stressing of JPTS alone are methane, ethane coeluted with ethylene, and propane. Except for propylene and butene, the other C_3-C_6 gas species are in negligible concentrations. Lower methane and propylene and much higher propane and butene yields in the presence of PX-21 suggest significantly different reaction mechanisms of thermal degradation upon activated carbon addition.

The BET surface area of PX-21 is 2090 m^2/g. It shows anisotropic microstructures (an unusual characteristic for activated carbons), since it is derived from a petroleum coke. Table IV shows the BET N_2 surface area of PX-21 after thermal stressing at 425 and 450°C in nitrogen and air atmosphere. The initial surface area of PX-21 activated carbon decreases substantially. The surface areas of PX-21 after thermal stressing at 450°C decrease more than after thermal stressing at 425°C. Most probably, the higher temperature contributes to more extensive interaction of carbon surface with jet fuel. It should be also noted that the surface area of PX-21 after thermal stressing in air is lower than in nitrogen. Clearly, oxygen also contributes to the adsorption/deposition processes. The scanning electron micrographs of PX-21 after stressing at 450°C show a thin layer of carbonaceous solid covering the activated carbon surface as well as a few discrete particles deposited on the surface. The PX-21 has a very microporous structure (2090 m^2/g), and it is not possible to observe the micropores with scanning electron microscopy. Most probably, activated carbon micropores are also filled with liquid products or solid deposits.

Thermal stressing of *n*-octane mixed with 5% decalin and PX-21 activated carbon at 450°C for 1h in N_2 atmosphere. Song at al.[7] reported that adding hydrogen donors, such as tetralin or decalin, to jet fuel reduced formation of solid deposit at 450°C and decreased the extent of fuel decomposition and gas formation. The increased stability of jet fuel in the presence of H-donors is attributed to the stabilization of the reactive radicals, which contributes to inhibiting radical decomposition, cyclization, aromatization, and condensation reactions. When the activated carbon is present during thermal stressing of *n*-octane+decalin one might expect that the hydrogen-transferring pyrolysis mechanism to be different. Adding PX-21 considerably reduced the pressure increase during stressing of *n*-octane as well as the formation of lighter compounds, such as C_4 and C_5 alkanes. The final product of H-transfer from decalin when it acts as a hydrogen donor is naphthalene. The higher amount naphthalene and the lower amount of decalin identified in the liquid stressed with PX-21 indicates that PX-21 affects the H-transfer reactions. Figure 3 shows the naphthalene and tetralin concentrations in the stressed liquids upon adding different amounts of PX-21, indicating significant increases upon adding as little as 50 mg of PX-21 with the effect leveling off at 150 mg PX-21 addition. It is possible that most of the hydrogen is abstracted by the carbon surface and redonated to stabilize the free radicals arriving on the surface.

The specific structure of activated carbons can explain their role as a hydrogen carrier during thermal stressing of *n*-octane+decalin and *n*-dodecane+decalin at 450°C. Activated carbons have a structure consisting of sheets of aromatic condensed ring systems stacked in nonpolar layers. These sheets have edges, defects, dislocations and discontinuities. The carbon atoms at these places have unpaired electrons and residual valencies and are richer in potential energy. These carbon atoms are highly reactive and constitute active sites or active centers.

Considerable research has been dedicated to understand the nature of these active sites in the surface and catalytic reactions of carbons. Puri and Bansal[11,12] studied the chlorination of coconut charcoals and observed that the chemisorbed hydrogen was eliminated in a number of steps, depending on the temperature of the treatment. This was attributed to the fact that hydrogen in charcoals was bonded at different types of sites associated with various energies of activation. The activation energy of adsorption at relatively more active sites is 7.4 kcal/mol. Sherman and Eyring[13] made theoretical calculations of the energy of activation for dissociative chemisorption of hydrogen from a carbon surface and found the values to vary with carbon-carbon spacing.

Thermal stressing of *n*-dodecane mixed with 5% decalin and PX-21 activated carbon at 450°C for 1h in N_2 atmosphere. Figure 4 shows the variations of naphthalene, *cis* -decalin and *trans*-decalin concentrations of the liquids obtained after stressing of *n*-dodecane alone and with 50, 150 and 250 mg PX-21. The naphthalene concentration sharply increases when activated carbon is added. The concentration of naphthalene in the stressed liquids shows a linear dependence on the amount of activated carbon mixed with dodecane, and increases with the increasing carbon concentration from 50 to 250 mg. The amount of *cis*- and *trans*-decalin in the stressed liquids shows the opposite trend, *i.e.*, decreasing with the added PX-21 concentration. The decrease in decalin concentration is not as sharp as the increase in the concentration of naphthalene, suggesting that part of the naphthalene comes from the pyrolytic degradation that takes place during thermal stressing, Dodecane →Alkylcyclohexenes →Alkylbenzenes → Naphthalene .

Figure 5 shows the changes in the concentrations of shorter chain alkanes and alkenes as a function of the amount of PX-21 added. The alkanes *n*-butane, *n*-pentane and *n*-hexane coelute with the corresponding alkenes and their area percents can not be calculated separately. There is a sharp drop in the percent area of *n*-butane+butene and *n*-pentane+pentene when activated carbon is added, as well as in the concentration of *n*-hexane+hexene and *n*-heptane. The amount of carbon does not seem to affect the concentration of shorter chain alkanes and alkenes, but it does affect the stability of dodecane, as can be seen from Figure 6. The area percent of dodecane stressed without carbon is 10% lower than with PX-21. There is an additional stabilization of dodecane when the amount of carbon increases from 50 to 250 mg. However, dodecane concentration does not differ very much in the stressed liquids, being 62.80% in the liquid with 50 mg PX-21 and 65.15% in the liquid with 250 mg PX-21.

Thermal stressing of *n*-dodecane mixed with 50% decalin and PX-21 at 450°C for 1h in N_2 atmosphere. Table V compares the experimental results obtained after stressing dodecane with 50% decalin and with 5% decalin. It was seen that the color of stressed liquid is darker and there is less liquid left after stressing of dodecane with 5% decalin than with 50% decalin. There is no deposit formation on the reactor walls when activated carbon is added in both cases, but there is a larger increase in the activated carbon weight when the decalin concentration is 5%. These results suggest that the degree of thermal degradation of dodecane depends on both the amounts of decalin and the activated carbon added. Most probably, activated carbon added to dodecane mixed with 5% decalin adsorbed more of the intermediates/or accumulated more deposits from the degradation reactions.

Table VI shows the main compounds identified in the liquids after thermal stressing of *n*-dodecane+decalin (50%) mixed with 50, 150 and 250 mg PX-21. The rest of the compounds identified are in negligible concentrations and are not listed in Table VI. From Table VI, the area percents of dodecane, decalin, naphthalene, and tetralin in the liquids obtained from thermal stressing of dodecane+50% decalin follow the same trends as those obtained after stressing of dodecane with 5% decalin. The concentrations of dodecane, naphthalene, and decalin increase with adding activated carbon. The increase depends slightly on the amount of carbon added. In accordance with the increase in naphthalene and tetralin concentration, the *cis*- and *trans*-decalin concentration decreases.

The data in Table VI for alkane concentration in the stressed liquids with and without PX-21 lead to the following speculations: The variation of product distribution with PX-21 is mainly due to distinction between different radicals. The lower concentration of light compounds C_4-C_8

and higher concentration of C_9-C_{11} alkanes obtained from stressing of dodecane+decalin+50 (or 150) mg PX-21 suggest that the primary radicals were more stable than the secondary. However, with the increasing amount of PX-21, the alkane concentration increases, and, in the liquid stressed with 250 mg PX-21, the concentration of C_6-C_{11} alkanes is even higher than the alkanes concentration from dodecane+decalin stressed without carbon. These results are in contradiction with the higher percent of dodecane preserved with increasing amount of PX-21 added. Most probably, the active sites of PX-21 carbon promote certain cracking reactions in addition to stabilizing the free radicals.

Conclusions

The high surface area activated carbon PX-21 during thermal stressing at high temperatures (425 and 450°C) suppressed solid deposition from jet fuel and model compounds *n*-dodecane and *n*-octane on the metal reactor walls. Higher concentrations of longer chain alkanes and lower concentration of alkylated aromatics were identified in the liquid products obtained from thermal stressing of JPTS in the presence of activated carbon. The activated carbon surfaces appear to be effective in stabilizing the free radicals or catalyzing recombination reactions. The presence of oxygen limits the stabilizing effect of the added carbon upon stressing the fuel under the same conditions.

Adding decalin as H-donor additionally reduced the extent of decomposition of *n*-dodecane and *n*-octane. The activated carbon addition also appears to promote H-transfer reactions during thermal treatment. The structure of the activated carbon PX-21 consists of sheets of aromatic condensed rings with edges and defects where the carbon atoms are highly reactive. Most probably, the active sites of PX-21 carbon act to stabilize the pyrolysis products, enhance the H-transfer reactions and to promote some cracking reactions.

Acknowledgments

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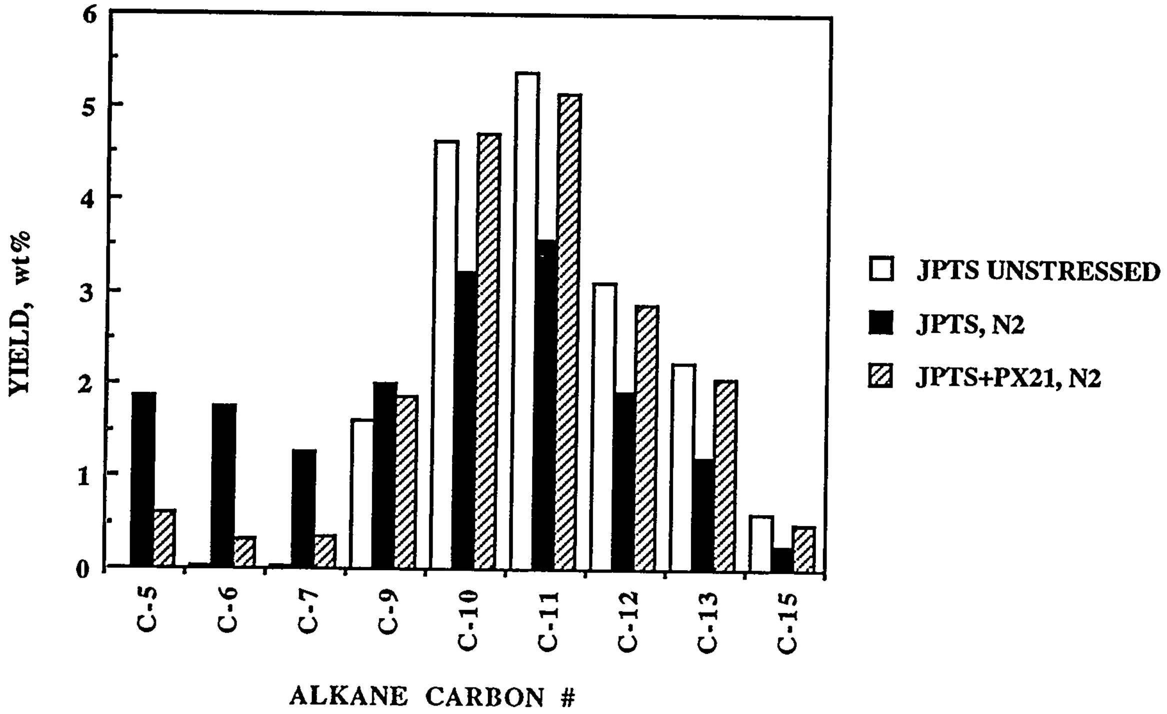

Figure 1. Yields of n-Alkanes from Thermal Stressing of JPTS Jet Fuel at 425°C for 5h in Nitrogen.

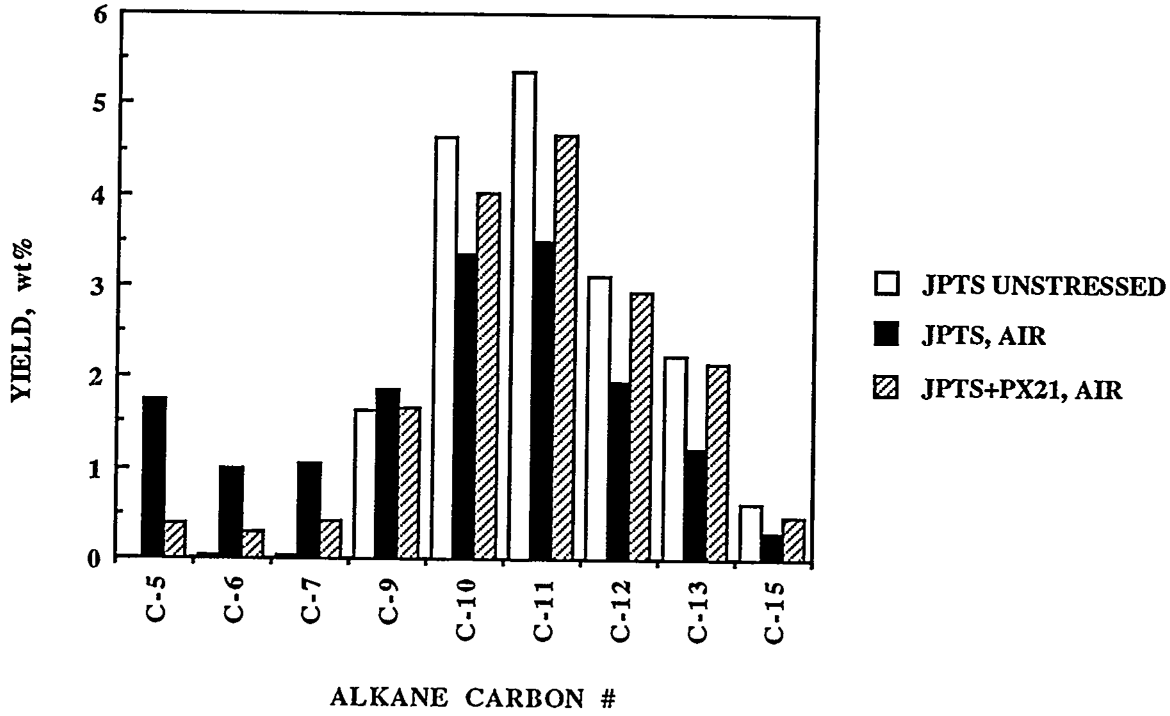

Figure 2. Yields of n-Alkanes from Thermal Stressing of JPTS Jet Fuel at 425°C for 5h in Air.

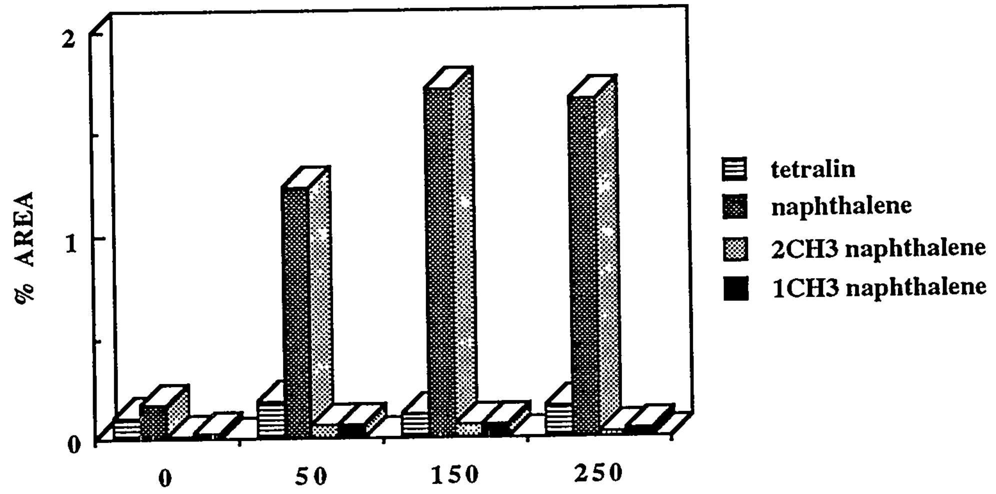

Figure 3. Effect of PX-21 Concentration on the Naphthalene and Tetralin Concentrations in the Liquids Obtained from Thermal Stressing of n-Octane with Decalin.

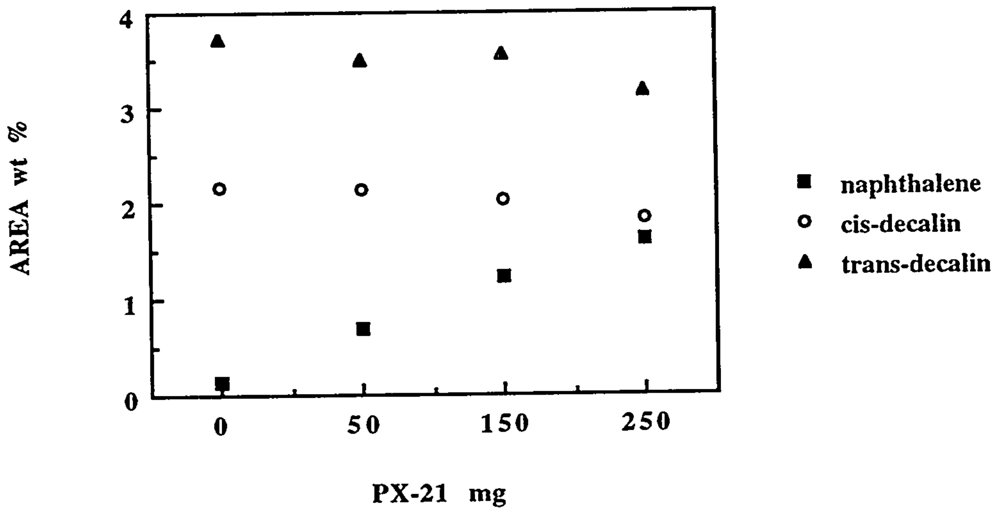

Figure 4. Effect of PX-21 Concentration on the Naphthalene and Decalin Concentrations in the Liquids Obtained from Thermal Stressing of n-Octane with Decalin.

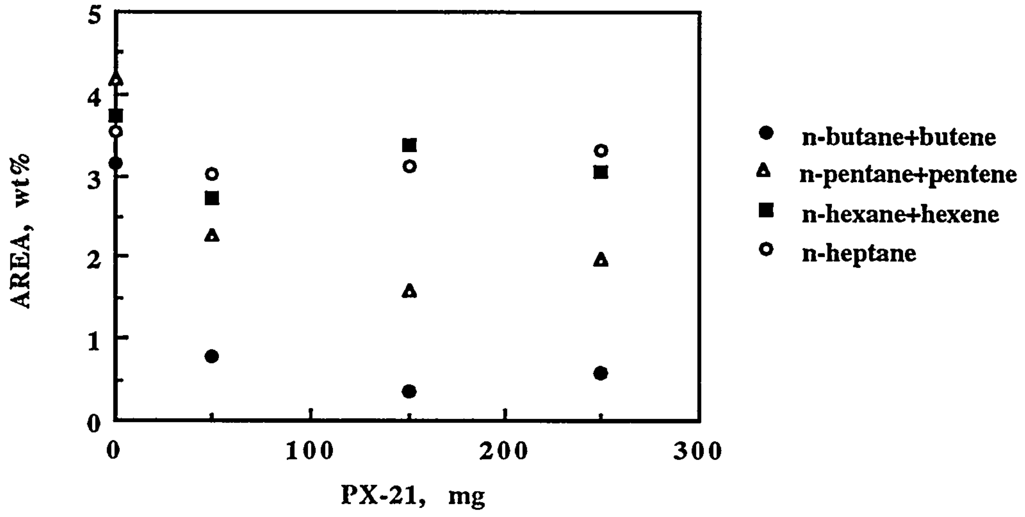

Figure 5. The Relative Concentrations of Shorter Chain Alkanes and Alkenes as a Function of the Amount of PX-21 Added.

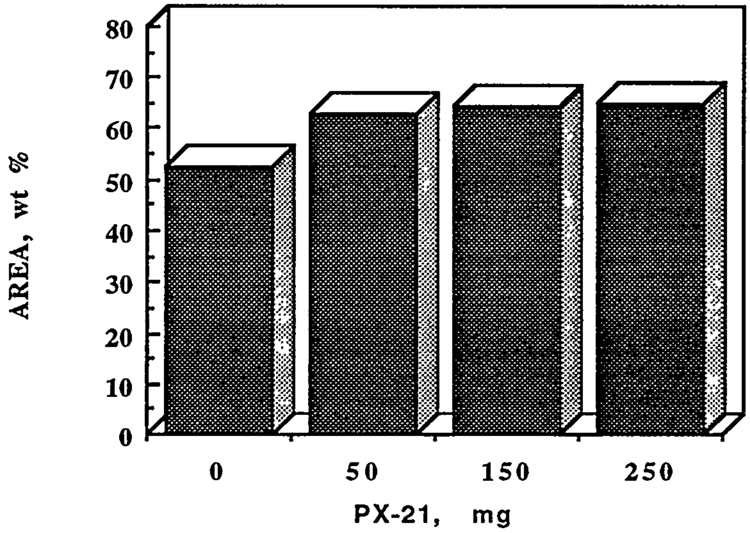

Figure 6. The Relative Concentration of Dodecane in the Liquids Obtained from Stressing with and without Added PX-21.

Table I. Yield of Liquid and Solid Products and Reactor Pressure after Thermal Stressing of JPTS with and without PX-21 at 425°C for 5 h.

Sample JPTS: 10 ml (PX-21: 50 mg)	Solid on reactor walls, mg, ± 10 mg	Liquid yield, ml ± 0.3 ml	Final gas pressure (cold), psi ± 100 psi	Increase of weight of solid, %
JPTS in N_2	20	9.0	200	-
JPTS+PX-21 in N_2	-	9.5	100	32
JPTS in air	30	8.2	200	-
JPTS+PX-21 in air	-	8.8	100	34

Table II. Yield of Liquid and Solid Products and Reactor Pressure after Thermal Stressing of JPTS with and without PX-21 at 450°C for 5 h.

Sample JPTS:10 ml PX-21:100 mg	Solid on reactor walls, mg ± 10 mg	Liquid yield, ml ± 0.3 ml	Final gas pressure (cold), psi ± 100 psi	Increase of weight of solid, %
JPTS in N_2	60	5.1	550	-
JPTS+PX-21 in N_2	-	5.5	300	35
JPTS in air	83	4.5	500	-
JPTS+PX-21 in air	-	5.0	300	50

Table III. Percent by Volume of Gases Obtained from Thermal Stressing Experiments of JPTS with and without PX-21 at 425°C for 5h in Nitrogen.

Compounds identified	JPTS stressed alone, %	JPTS stressed with 100 mg PX-21, %
methane	37.58	34.55
ethane+ethylene	34.06	34.73
propane	14.20	20.99
propylene	9.67	0.00
i-butane	0.94	1.07
butane	0.56	0.00
butene	1.67	8.66
pentane	1.14	0.00
pentene	0.10	0.00
hexane	0.08	0.00

Table IV. Surface Area of PX-21 Activated Carbon after Thermal Stressing with JPTS.

Stressing conditions	BET N_2 surface area, m^2/g
unstressed JPTS	2090
425°C, 5h, in nitrogen	785
425°C, 5h, in air	630
450°C, 5h, in nitrogen	550
450°C, 5h, in air	320

Table V. Some Experimental Results from Stressing of Dodecane with 5 and 50% Decalin and 50, 150 and 250 mg PX-21 at 450°C for 1h.

	Dodecane + 5% Decalin				Dodecane + Decalin 50%			
	0 mg PX-21	50 mg PX-21	150 mg PX-21	250 mg PX-21	O mg PX-21	50 mg PX-21	150 mg PX-21	250 mg PX-21
Color	yellow	yellow	yellowish	yellowish	yellowish	colorless	colorless	colorless
Liquid, ml	7.6	5.6	5.0	4.6	9.6	9.5	9.0	7.0
Deposit, mg	45	-	-	-	20	-	-	-
Increase of solid weight,%	-	75	75	80	-	55	65	70

Table VI. The Main Compounds Identified in the Liquids Obtained after Thermal Stressing of Dodecane+Decalin 50% Mixed with 50, 150 and 250 mg PX-21 at 450°C for 1h.

Compounds identified	Dodecane+ Decalin 50%	Dodecane+ Decalin 50% + 50 mg PX-21	Dodecane+ Decalin 50% + 150 mg PX-21	Dodecane+ Decalin 50% + 250 mg PX-21
n butane+butene	1.05	0.13	0.36	0.49
n pentane+pentene	1.51	0.48	0.83	1.27
n hexane	1.33	0.84	1.25	2.02
n heptane	1.27	1.04	1.17	1.54
n octane	1.41	1.26	1.26	1.58
n nonane	1.24	1.23	1.29	1.63
n decane	0.46	0.63	0.73	1.05
n undecane	0.56	0.53	0.51	0.31
n dodecane	28.68	35.11	35.39	36.50
cis decalin	20.78	20.11	18.14	14.17
trans decalin	30.96	29.35	29.55	27.78
naphthalene	0.09	0.70	1.17	1.99
tetralin	0.40	0.92	1.30	1.99

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DEVELOPMENT OF OXYGEN SCAVENGER ADDITIVES FOR JET FUELS

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Abstract

Our current research program is in response to the U. S. Air Force's FY93 New Initiative entitled "Advanced Fuel Composition and Use." The critical goal of this initiative is to develop aircraft fuels which can operate at supercritical conditions. This is a vital objective since future aircraft designs will transfer much higher heat loads into the fuel as compared with current heat loads. In this paper it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient in flight removal of a fuel's dissolved oxygen. It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. It is envisioned that a thermally activated reaction will occur, between the oxygen scavenging additive and dissolved oxygen , in a controlled and directed manner. Consequently formation of insoluble thermal degradation products will be limited. It is believed that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient thermal stability to function in significantly higher temperature regimes. In addition, it is postulated that the successful development of thermally activated oxygen scavengers will also provide the sub-critical thermal stability necessary for future development of endothermic fuels.

1. Introduction

Currently, aircraft fuels have a practical temperature limit (325°F, 150°C) which cannot be exceeded without causing serious problems in the fuel system. If this temperature threshold is exceeded, the fuel chemically decomposes to form gums and solids which adversely affect the fuel system. Conventional wisdom posits that these fuel deposits are the end result of a sequence of complex chemical reactions that are thermally promoted between oxygen dissolved in the fuel and certain "reactive" fuel molecules.[1] If this paradigm(i.e. conventional wisdom) is correct then efficient removal of oxygen from the fuel would limit the oxidative break down of the fuel. Consistent with this view is the general observation that purging a jet fuel of dissolved oxygen usually will result in a tremendous improvement in the thermal stability of that fuel.[2]

Recent studies have revealed that most of a fuel's dissolved oxygen is consumed by chemical reactions which initially produce peroxides at temperatures between 150-260°C.[3] In addition, the following experimental observations provide very significant clues as to the nature of the chemical reactions between oxygen and trace fuel components at these temperatures:

> (i) Jones et al. have recently reported how different concentrations of dissolved oxygen affect the formation of insolubles in jet fuels at 185°C. Of the two Jet A's examined, one was found to produce insolubles at a rate which exhibited a zero order dependency in oxygen, while the other fuel produced insolubles at a rate which exhibits a first order dependence in oxygen.[4, 5]
>
> (ii) Classical chain - breaking donor antioxidants (i.e. substituted phenols and phenylene diamines) usually do not inhibit deposit formation when a fuel is stressed at temperatures of 150-250°C.[6,7]

Based upon observation (ii) it should be clear that the sub-critical oxidative stability of jet fuels is currently problematic. Consequently, it is imperative that this problem be rectified in order that future aircraft fuels possess adequate thermal stability to enable them to achieve supercritical conditions with minimal degradation within the fuel system. It is proposed herein that the efficient removal of dissolved oxygen from jet fuels during flight might provide the necessary improvement in sub-critical fuel stability. If this line of reasoning is correct, then the fundamental problem can be reduced to the problem of removal of a fuel's dissolved oxygen before it contributes to the thermal degradation of the fuel.

There are two fundamentally different approaches to the removal of dissolved oxygen from a jet fuel during flight. One approach would be to utilize a technological solution (on board purging), while another approach would be to effect a chemical solution. We envision the chemical solution to entail adding a specifically designed fuel additive (concentration 200-400 ppm) to the jet fuel. Theoretically, this additive would chemically react (as the temperature of the fuel increases) with the dissolved oxygen and thus remove it, in an innocuous manner, from the fuel during flight. In this manner the jet engine would receive its fuel with minimal dissolved oxygen (hence the fuel will have high thermal stability), and there would not be any "unnecessary" (i.e. purging technology) payload added to the aircraft.

The focus of our research program is to explore the fundamental chemistry necessary to develop potential fuel additives (candidates) that will function as thermally activated oxygen scavengers. It is envisioned that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient thermal stability to function as " JP-900" fuels. In addition, it is postulated that the successful development of thermally activated oxygen scavengers will also provide the sub-critical thermal stability necessary for future endothermic fuels. This is a **vitally important objective** since it is now clear that most of a jet fuels thermal oxidative degradation occurs at sub-critical temperatures, *Vide supra.* Therefore, all of our current efforts in additive development are directed at solving the sub-critical oxidation problem. It is anticipated that future work will examine the chemistry of all successfully developed sub-critical additive candidates under supercritical conditions.

In order to logically articulate an approach to the development of thermally activated oxygen scavengers the fundamental reactivity of molecular oxygen with organic molecules needs to be reviewed.

IA. The Reaction of Organic Molecules with Molecular Oxygen

Recently we have published an in depth "state of the art" discussion of the various (low temperature) reaction mechanisms potentially involved in the oxidative phase of the degradation of petroleum products. [8,9] Consequently, only a brief summary of the pertinent details of autoxidation with respect to this proposal will be addressed.

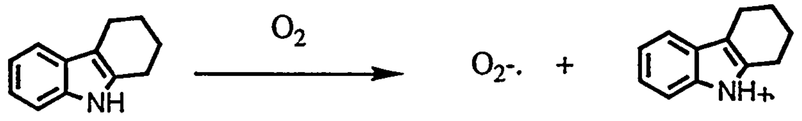
The most common type of reaction between organic molecules and molecular oxygen is a peroxyl radical-chain oxidation. For this mechanism the observed initial rates of oxygen absorption are found to be (i) independent of oxygen concentration when the partial pressure of oxygen above the solution exceeds 100 torr (i.e. zero order in oxygen), (ii) one half order with respect to the initiator concentration, (iii) first order with respect to the concentration of RH, and (iv) inhibited in the presence of phenolic antioxidants.

We have recently proposed a second, less common type of reaction between electron rich (i.e. readily oxidizable) organic molecules and molecular oxygen as being important in the oxidative degradation of various fuels. [8, 10] We have designated this reaction as electron transfer initiated oxygenation (ETIO), and define such a reaction as:

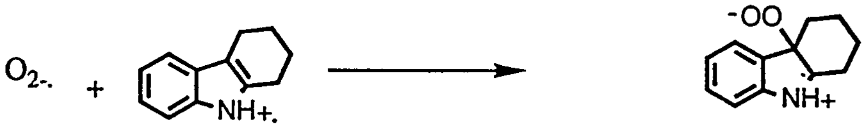
> Any oxygenation reaction in which the rate limiting step involves an electron transfer from the substrate to molecular oxygen (or its reduction products).

The ETIO concept should be thought of as an entire family of oxidation mechanisms (not just one mechanism) in which the common feature is rate limiting electron transfer. The ETIO concept provides a rational explanation for the previously mentioned Jet A O_2 order dependency noted by Jones et al. [4] Most currently used petroleum antioxidants are designed to suppress the classical peroxyl radical-chain oxidation. Since the ETIO concept represents an alternative oxidation pathway it might provide a rational explanation for the oxidative degradation of fuel products in the presence of chain breaking antioxidants (hence, observation (ii) in the introduction can be rationalized). [11]

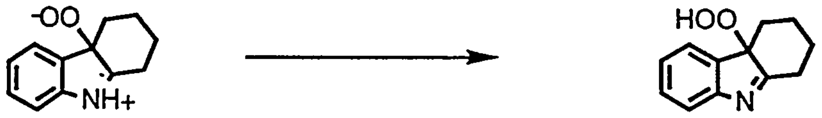
Below is depicted the simplest possible description of an ETIO mechanism using tetrahydrocarbazole (THC) as a model substrate. In this mechanism reaction (5) is the rate limiting step with steps (6) and (7) being fast:



(5)



(6)



(7)

Invoking the standard steady state approximations and deriving the corresponding rate law yields: [8]

$$-d[THC]/dt = k[THC][O_2]$$

Thus the rate law from the most simple depiction of an ETIO reaction is second order overall (first order in both $[O_2]$ and [THC]). Consequently, the presence of a first order dependency in oxygen, for an autoxidation, is consistent with the ETIO concept and inconsistent with the operation of the simplest depiction of a peroxyl radical chain. In addition, it is important to note that both mechanisms form the same initial oxidation product (RO_2H). Therefore the peroxyl radical chain mechanism and the ETIO mechanism are linked by a common intermediate (an organic hydroperoxide). Therefore, an autoxidation in which an ETIO mechanism provides initiators (from hydroperoxide decomposition) for a peroxyl radical chain, would be expected to exhibit a small fractional order dependency in oxygen, *Vide infra.*

The validity of the above mentioned idea that both ETIO and peroxyl radical-chain oxidation can contribute to the oxidative degradation of various petroleum products is supported by an interpretation of recently published studies. It is important to realize that each mechanism can operate either independently or simultaneously. Fodor et. al [12] have measured the rates of peroxide formation in jet fuels at temperatures from 43-120°C with oxygen partial pressures ranging from 2-165 psi. The rate of peroxide formation was found to be independent of the oxygen partial pressure. In addition, Black et al. [13] have recently reported that peroxide formation upon stressing several jet fuels(low pressure reactor (LPR) method, 100°C, 100 psi oxygen) could be significantly suppressed by use of phenolic antioxidants. Both of these reports are consistent with a peroxyl radical chain mechanism for peroxide formation during simulated aging of the studied jet fuels.

Hardy et al. [14] have stressed (LPR, 80°C, 25-100 psi O_2) straight run diesel fuels that contained 30% catalytic cracked LCO (light cycle oil) and measured insoluble formation as a function of oxygen partial pressure. For those fuels which were oxidatively reactive, the amount of insolubles produced were found to be a function of the oxygen partial pressure. Data presented for one diesel fuel/LCO blend indicates that initial insolubles formation for this fuel exhibits an approximate first order dependency in oxygen. However, the other reactive diesel fuel blends exhibited oxygen order dependencies of less than one. The one diesel/LCO blend in which insoluble formation was found to exhibit first order dependency in oxygen is consistent with the operation of a simple ETIO type pathway for deposit formation. In addition, Hardy et al. [15] and Bernasconi et al. [16] have shown that standard antioxidants (substituted phenols, and phenylene diamines) are generally not effective in limiting insoluble formation for oxidatively reactive diesel fuels. Thus, all of these observations are inconsistent with a simple peroxyl radical-chain mechanism for the observed diesel/LCO blend oxidative degradation.

II. Experimental Section

All experimental details have been previously described.[17a]

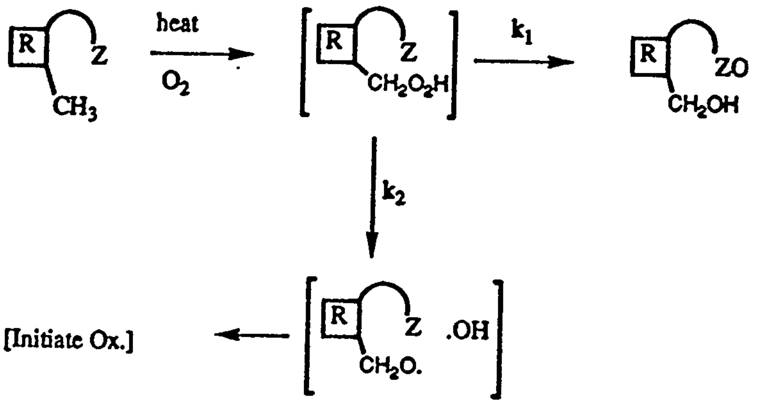
III. Development of Oxygen Scavenger Additives

Contained in this section is a logical articulation of our approach to the development of oxygen scavenger additives. For clarity this section is divided into 2 parts; with part A developing and establishing the necessary presuppositions and the overall thinking. Presented in part B is our preliminary results to date.

IIIA. Conceptualization of Idea

The idea conceptualized in Scheme 1 is predicated upon the following observations concerning jet fuel degradation, as indicated by both peroxide and insolubles formation:

Scheme 1



(i) insoluble formation increases with temperature and at < 300°C, tends to involve reactions of trace indigenous heteroatom containing molecules (S,N, and probably O) with dissolved oxygen.[1, 17b,18]

(ii) most of the oxygen consumption by the bulk fuel and concomitant peroxide formation occurs at temperatures between 150-260°C. [3,5]

(iii) under the pressure regimes typically found in current jet engines(or simulating devices), somewhere between 300-450°C a jet fuel experiences the physical transition from a liquid into a supercritical fluid. This phenomenon usually results in a sharp decrease in the rate of autoxidative deposit formation . [2]

(iv) at temperatures >400°C, most fuel insolubles tend to be produced by pyrolysis reactions. [19, 20]

If the above stated observations and interpretations are correct, and if it is possible to extrapolate aspects of low temperature chemistry (i.e. 50-100°C) into the temperature regime of 160-300°C, then in Scheme 1 is wedded a logical approach to significantly enhance sub-critical jet fuel stability. Inherent in the design of Scheme 1 is the presupposition that the *primordial* fuel degradation reactions reported in the introduction, (i-ii), are ETIO in nature (except the one jet A mentioned in (i)). Consequently, in the absence of oxygen the extent of these reactions will be greatly limited. The additives represented in Scheme 1 will be designed to undergo the ETIO reaction at a lower temperature than the fuel's indigenous ETIO "bad actors". Although this approach does not directly address supercritical fuel stability, it is believed that significant thermal stability improvement will be achieved for the following reasons:

(v) Taylor [18] has reported in his 1974 study, at least for the two jet fuels examined, that reduction of the dissolved oxygen content from air-saturated values (~60ppm) to less than 15ppm, decreased deposit formation produced under supercritical conditions by greater than 50% (when compared to similar deposit levels produced without oxygen removal).

(vi) we envision the oxidized additives structurally containing both, a polar head group and a hydrocarbon tail which may enhance the "solubility capacity" of the supercritical fluid (i.e. the oxidized additive may be able to peptize insolubles).

In Scheme 1 is articulated a logical formulation of how an oxygen scavenger additive would perform its function. The sequence of events begins with the thermally promoted reaction between a portion of the additive molecule [R] and dissolved oxygen to form the initial REDOX product (i.e.. on a gross level, the additive is oxidized while oxygen is reduced to produce the "generic hydroperoxide" shown in Scheme 1. The actual details of these events are complex, and currently are speculative. However, we here postulate that the ideal additive will react with oxygen by ETIO, and not by a peroxyl radical chain mechanism. [8] Therefore we set the following experimental criteria for a successful additive candidate:

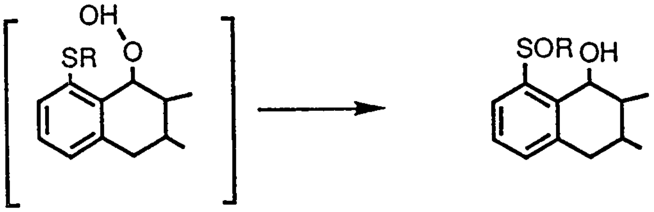
a) a potential additive candidate must have a rate law that exhibits a first order dependency in both oxygen and the substrate.

b) a potential additive candidate must exhibit a significant rate of oxygenation in the presence of a high concentration of a phenolic antioxidant.

As indicated in Scheme 1 the fate of the "generic hydroperoxide" is dependent on the relative magnitude of the rate constants k_1 and k_2. Ideally a pendent nucleophile (Z) is appropriately poised for facile intramolecular hydroperoxide reduction (k_1) to produce the corresponding secondary REDOX product. In Scheme 1 it is assumed that all REDOX products are soluble in the liquid fuel. Competitive with the "k_1" process is the thermally promoted homolysis of the weak O-O peroxide bond to produce the reactive hydroxyl and alkoxyl radicals. The rate constant for this process is designated k_2 and to the extent that k_2 is competitive with k_1, the fuel will be subjected to general autoxidative degradation (by these radicals initiating peroxyl radical chains). To limit this scenario at least two criteria will be employed to maximize the "k_1" process at the expense of the "k_2" process:

(vii) the molecular structure of the primary REDOX product needs to promote the facile intramolecular formation of the appropriate transition state for its rapid conversion into the secondary REDOX product. This can be accomplished by positioning the Z atom exactly five or six atoms removed from the terminal oxygen of the hydroperoxide (see Scheme 2).[21]

Scheme 2



(viii) for certain additive molecular designs, the molecular structure of the primary REDOX product will be so unstable, that spontaneous conversion into secondary REDOX products will occur(consequently the presence of a Z group is not necessary).

IIIB. Preliminary Data

In table 1 is compiled preliminary results of the initial screen of various potential additive candidates. The note worthy feature is that our first three additive candidates, fluorene, 2,5-dimethylpyrrole (DMP) and 1,2,5-trimethylpyrrole (TMP), were deemed as non viable additive candidates. This is based upon the candidates not meeting the previously discussed order and additive criteria. Most importantly, however, is that one compound, candidate 1, met our preliminary criteria.

In figure 1 is presented a more detailed analysis of the oxidation of candidate 1 in dodecane. In plot A is shown a GC analysis of the consumption of candidate 1 at 120°C. A linear plot with much scatter in the data is revealed. In plot B is shown an anologous plot at 150°C, the important features being the linearity of the consumption curve and the apparent lack of an induction period. Finally, in plot C is revealed a linear curve for the rate of formation of the oxidation product of candidate 1.

In table 2 is presented a preliminary initial rate study for the oxygenation of candidate 1 under different experimental conditions. Two experimental observations are pertinent: First, while candidate 1 is consumed most rapidly in the absence of BHT, in the presence of 1, 2, or 3 equivalents of BHT a significant rate of oxygenation is obsevered. Second, changing the solvent from nonpolar hydrocarbons (dodecane and decalin) to a more polar solvent (1,2,5-

trichlorobenzene) results in an increase in the rate of oxygenation for candidate 1. This result is consistent with a transition state for the oxygenation of candidate 1 being polar.

Conclusion

In this paper it is argued that the thermal stability of most jet fuels would be dramatically improved by the efficient removal of a fuel's dissolved oxygen (in flight). It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. Consequently, it is envisioned that a thermally activated reaction between the oxygen scavenging additive and dissolved oxygen will occur, in a controlled and directed manner, such that formation of insoluble thermal degradation products will be limited.

To date our data has identified one potential additive candidate which meets our preliminary specifications. Work is in progress to examine and tailor appropriate solubility characteristics for this additive candidate.

Acknowledgment. We thank the Air Force Office of Scientific Research (AFOSR) for their gracious and generous support of this work.

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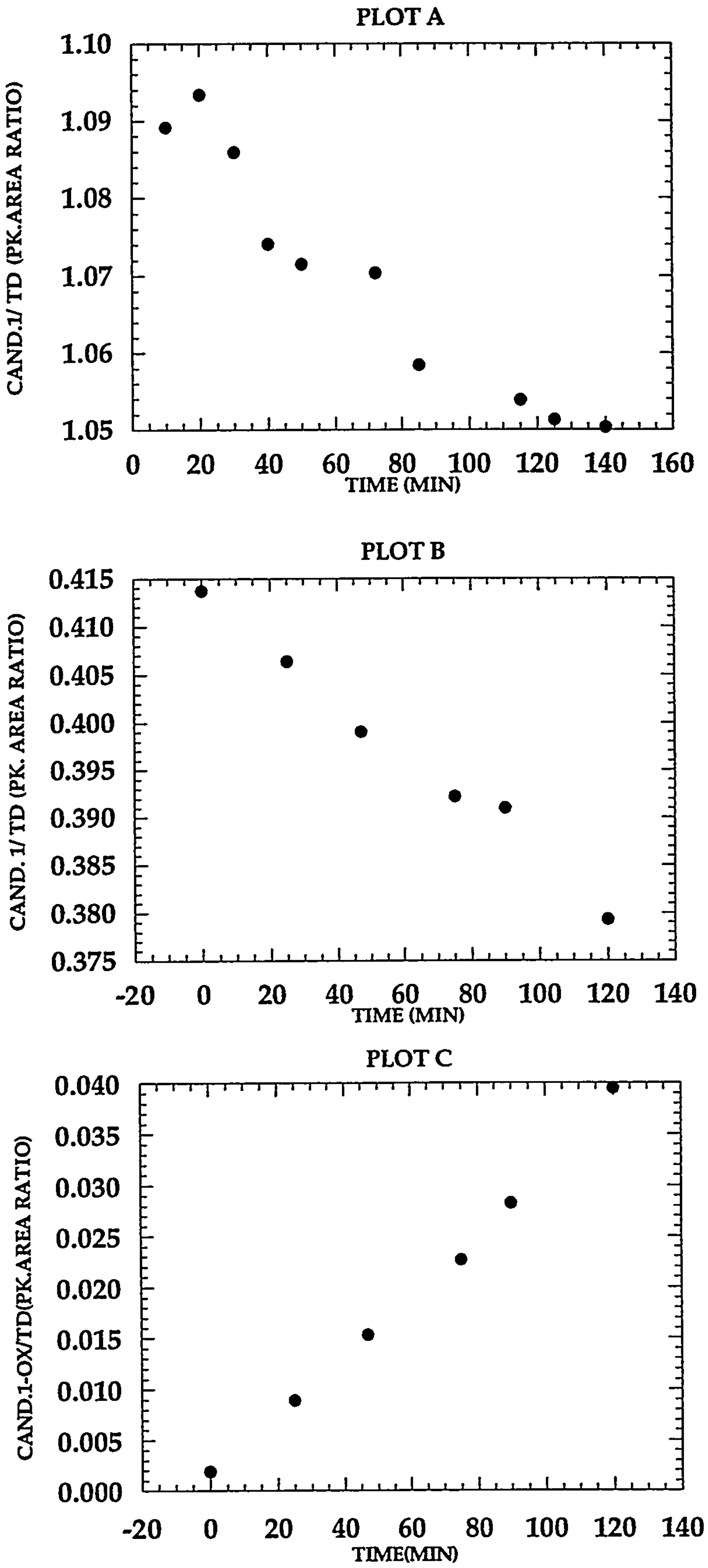

Figure 1. Change in substrate concentration as a function of time, in dodecane.

Table 1

Reaction Order Data for Additive Candidates

Substrate	Additive(s)	Solvent	Temp. ^{o}C	Subs. order	O_2 order
fluorene	none	dodecane	165	not det.	0.8
fluorene	BHT	dodecane	165	no Rx.	no Rx.
DMP	amine	dodecane	120	1.1	0.8
DMP	amine/BHT	dodecane	120	not det.	approx. 0
TMP	none	dodecane	100	not det.	approx. 0
Candidate 1	BHT	dodecane	150	1.1	1.2
Candidate 1	BHT	decalin	150	1.0	1.3

Table 2

Initial Rate of Consumption for Candidate 1 at 150^{o}C

Solvent	Additive (eqs.)	Int. rate of loss
dodecane	none	1.24×10^{-4}
dodecane	1 x BHT	1.36×10^{-5}
dodecane	2 x BHT	1.70×10^{-5}
dodecane	3 x BHT	1.57×10^{-5}
trichlorobenz.	1 x BHT	3.24×10^{-5}
decalin	1 x BHT	1.03×10^{-5}

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DEVELOPMENT OF THERMAL STABILITY ADDITIVE PACKAGES FOR JP-8

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Advanced military aircraft use fuel as the primary heat sink to cool engine and airframe components. As the fuel is thermally stressed, thermal oxidative reactions take place that result in the formation of deposits. These deposits degrade aircraft performance and ultimately lead to premature servicing of the affected components. The frequency of these incidents, coupled with the projected cooling requirements for future systems, demonstrates that current thermal stability limits are inadequate. In response to this situation, the United States Air Force (USAF) has embarked on a program to improve thermal stability using specially formulated additive packages. Results indicate that additives offer significant thermal stability improvement. This paper describes the USAF program to develop and deploy an improved JP-8 for fleet-wide use by 1998.

Introduction

Jet fuel is used as the primary heat sink in advanced military aircraft to cool engine and airframe components in addition to providing the propulsive energy for flight. The heat dissipated into the fuel causes thermal degradation leading to the formation of insoluble materials. These materials foul critical fuel system components affecting the efficient and safe operation of the aircraft. Thermal stability limits have been established to assure fuel quality and to control the severity and incidence of fouling problems. However, actual field experience indicates that fuel degradation and deposition is a current problem that adversely affects fleet operations and costs millions of dollars each year to correct. Heat loads in future systems are projected to increase placing even more emphasis on the fuel as the cooling medium.[1] The status quo for thermal stability is untenable if the operability and performance goals of advanced military aircraft are to be achieved and maintained.

The causes and effects of thermal instability have been studied and documented by many researchers over the years.[2] Thermal stability in this case refers to the tendency of a fuel to form bulk and surface deposits under thermal oxidative stress. In simple terms, heat promotes the autoxidation of the fuel via a free radical mechanism forming a variety of oxidized species. Subsequent reactions involving these intermediates results in the formation of soluble and insoluble products. Reactions between trace polar compounds (e.g. sulfur, nitrogen and oxygen containing molecules) and the oxidized intermediates produce the deleterious fuel system deposits. Any technique that interferes with or inhibits these reactions or removes the polar contaminants from the fuel should benefit thermal stability.

The degree of improvement required over conventional JP-8 was based on heat load projections for advanced aircraft. The stability of conventional fuel restricts the maximum bulk temperature to 325°F (163°C) at the inlet to the main burner nozzle and to a wetted-wall temperature of 400°F (204°C) inside the nozzle passages. These limits were established based on field experience to minimize deposition and extend service life. Under certain flight conditions these temperatures are exceeded which increases deposition rates substantially. The enormous throughput of fuel magnifies the problem and results in considerable deposition. The primary concern with thermal stability in advanced aircraft is not related to large temperature increases, but the time-at-temperature and fuel recirculation after thermal stressing. More advanced concepts under development (Integrated High Performance Turbine Engine Technology Program) will subject the fuel to considerably higher temperatures, exacerbating any thermal stability problems. Based on the current state of affairs along with the knowledge of future requirements, the USAF set a goal of increasing thermal stability limits 100°F (56°C). This translates into allowing the bulk temperature to reach 425°F (218°C) and the wetted-wall temperature to reach 500°F (260°C), providing a 50% increase in available heat sink. The improved stability fuel is referred to as JP-8+100.

There are a variety of techniques that can be used to improve thermal stability. Some of the options include hydro-refining, clay filtration, removal of dissolved molecular oxygen, metal surface treatments and additives. Each technique has advantages and disadvantages related to cost, practicality and efficacy. After considering the available options and the ramifications associated with each, the USAF selected the additive approach to improve the thermal stability of JP-8.

Additive Development

Additives are used extensively in petroleum products to enhance a variety of properties including thermal stability. Motor gasoline, diesel fuel and lubricating oils all contain additives designed to improve performance. The tremendous demand for these products encouraged vigorous investment in additive development. The situation with jet fuel is very different. The comparatively low demand, high degree of specification and fungible nature detracts from the incentive to pursue costly additive development and approval efforts. As a result, very few additives are available specifically designed to enhance thermal stability . Metal deactivator additive (MDA) is the only such additive permitted in both civil and military fuels. JFA-5 is an additive package consisting of an antioxidant, a dispersant and MDA and is used exclusively in

JPTS, a highly refined kerosine used in the U-2/TR-1 aircraft. Testing was performed in a variety of fuels and the results showed that our thermal stability goals could not be achieved with MDA or JFA-5. Consequently, petroleum companies and additive manufacturers were contacted and requested to submit additive candidates for our evaluation. Most of the candidates submitted are used in products other than jet fuel, the remaining candidates are experimental. Over 200 additives have been submitted to date, with two showing particular promise. The additives discussed in this paper include an antioxidant, a metal deactivator, a dispersant and a detergent/dispersant. A description of these additives can be found in Table 1.

A great deal of effort was spent in determining how best to screen a large number of additives in a short period of time. The approach follows a hierarchical structure starting with simple screening tests and culminating in full-scale component and engine tests (Figure 1). The strategy is to use the screening tests to identify the promising additives quickly, reject the others and move forward with a small set of candidates. A variety of fuels are used to assure that additive performance is not restricted to a single fuel. The most promising additives are promoted for evaluation in more complex test devices that attempt to simulate some portion of the fuel system. If positive results are obtained here, material and additive compatibility, storage stability, specification conformance and combustion performance testing is initiated. The final step in the process is evaluation of JP-8+100 in the reduced scale fuel system simulator (RSFSS). The RSFSS is a 1/72 scale model of the F-22 fuel system and is designed to closely simulate all aspects of the fuel system. Successful testing in the RSFSS is followed by full-scale component and engine tests.

Screening Tests

Three different screening tests are used to perform the initial evaluations on every additive submitted for the JP-8+100 program. These tests are not designed to simulate any particular part of the fuel system or environment. The test temperature and/or the availability of dissolved oxygen is elevated to accelerate the deposition process. Dose levels used for the additives are based on the recommendations of the manufacturer. Packaging, reformulation and optimization is carried out only if the additive performs well in each screening test and in each reference fuel. The "optimized" additive or additive package is used for all subsequent testing.

Additive performance and acceptance is based on the ability of an additive to reduce deposition to a level similar to JPTS. Each test device establishes a thermal stability baseline with JPTS and all JP-8+100 formulations are then compared to that baseline to determine additive efficacy. The reference fuels used in the screening tests are listed in Table 2.

Hot Liquid Process Simulator (HLPS): The HLPS is a derivative of the well known Jet Fuel Thermal Oxidation Tester (JFTOT), ASTM D 3241, a device long in use as a jet fuel qualification test. The test conditions selected to evaluate additive performance are similar to those used to qualify JPTS. Tests are performed at 335°C for 5 hours at a flow rate of 3 mL/min. Series 316 stainless steel tubes are substituted for the conventional aluminum tubes to permit quantitation of the deposit by carbon burnoff using a LECO RC-412 Carbon Analyzer.

Test results obtained with the HLPS are shown in Figures 2, 3 and 4. Figure 2 shows the performance of the two most promising additive packages in our primary reference fuels. Significant reduction in surface carbon is obtained as well as elimination of any increase in differential pressure on the 17 μm stainless steel filter. Figure 3 shows the effect of combining the individual components of the additive package on surface deposition. In fuel 2926 and 2980, the addition of BHT reduces surface carbon, however, in fuel 2827 BHT increases deposits slightly. These results are consistent with other experiments that show fuel 2926 consumes oxygen quite rapidly, 2980 consumes oxygen at an intermediate rate, whereas fuel 2827 consumes oxygen slowly. Antioxidants are most effective in those fuels that oxidize readily and have little or no effect in fuels that oxidize slowly.[3] The effect of MDA on surface carbon in the HLPS is quite predictable. In each case, the addition of MDA reduces surface carbon. Clark[4] has attributed the beneficial results seen in the JFTOT or HLPS to a passivating action of the MDA on a clean metal surface. The short duration of the test exaggerates the benefits of MDA and can make poor quality fuels appear better than the best hydrotreated fuels. A complete metals assay has not been performed on these reference fuels to determine the presence and level of transition metals. The line superimposed over the plots indicates the deposit level for JPTS.

The potential of MDA to cause an increase in deposition rate at longer test times was evaluated in the HLPS using the additive package with and without MDA. Figure 4 shows the effect of MDA on surface deposition in tests performed up to 30 hours. The MDA did not cause any increase in surface carbon in these extended tests, however, other test devices are more suited to investigate this phenomenon. Indiscriminate use of MDA is not recommended as a panacea for thermal stability problems. When thermal stability is off-specification due to dissolved catalytic metals, the use of MDA is appropriate and advisable. Its use as a permanent part of any additive package for JP-8 is still to be determined.

Isothermal Corrosion/Oxidation Test (ICOT): The ICOT apparatus used for additive screening is described in ASTM D4871. In the ICOT, 100 mL of fuel is placed in a glass test tube and inserted into an aluminum block heater at 185°C. A water-cooled condenser (20°C) is fitted to the test tube and a glass blower tube inserted through the condenser into the fuel. Air is sparged into the fuel at 1.3 L/hr. The fuel is stressed for 5 hours, removed from the heater and allowed to stabilize overnight. The bulk insolubles are measured gravimetrically by filtering the entire sample through a 1 µm glass fiber filter. Surface insolubles formed on the blower tube were evaluated visually.

The ICOT results for the reference fuels and the two additive packages are shown in Figure 5. In all three fuels, both additive packages reduce bulk insolubles to zero. The surface deposits on the blower tube were also dramatically reduced. The neat fuels formed a deposit band of 5 - 8 mm in width, the additized fuels were 1 mm or less. Figure 6 shows the results of adding MDA to 8Q405 and BHT. The positive response to MDA was unexpected because the entire system is composed of glass. Similar results have been obtained with other fuels even though dissolved catalytic metals were not present. Although we feel this is a very valuable screening tool, a caveat must be mentioned when using tests such as the ICOT to evaluate thermal stability or additive efficacy. Any test that is accelerated by the addition of excess oxygen may give misleading results. For example, hydrotreated fuels of high thermal stability oxidize readily producing copious amounts of insoluble material because autoxidation reactions are driven far beyond what would occur in actual aircraft systems. Any effect of an additive is quickly overwhelmed by the extent of oxidation.

Quartz Crystal Microbalance (QCM): The QCM apparatus has been described in detail previously and will only be discussed briefly here [5,6]. The fuel is stressed in a 100 mL Parr bomb reactor which has been modified with an rf feedthrough for the QCM. A pressure transducer is used to monitor the pressure decay in the reactor that results from oxygen reaction. The reactor is heated with a clamp-on band heater which is controlled by a PID temperature controller via a thermocouple immersed in the fuel. The reactor is filled with 60 mL of fuel leaving ~40 mL of headspace. The fuel and headspace are sparged with air for 1 hour at room temperature prior to each run. After sparging, the reactor is sealed at atmospheric pressure and the heater is turned on. A computer monitors the quartz crystal frequency, the crystal damping voltage, the temperature and the headspace pressure at 1 minute intervals. A typical run is 15 hours at a temperature of 140°C. QCM deposition data are only valid for the relatively constant (± 0.3°C) period of the run after the ~45 minute heat-up time.

The change in the quartz crystal frequency with time at constant temperature is used to monitor deposition. The total mass accumulation after 15 hours for the reference fuels with and without the additives is plotted in Figure 7. In each case, the additive packages reduce surface deposits to levels similar to JPTS. The effect on deposition by adding BHT and MDA to 8Q405 is shown in Figure 8. These results demonstrate the effect of BHT on a fuel that oxidizes readily versus one that consumes oxygen slowly. Fuel 2926 benefits significantly when BHT is added to 8Q405 contrary to the effect in fuel 2827. The MDA adversely affects fuels 2827 and 2980 when added to the 8Q405 and BHT. The deposition curves for these runs show a positive change in slope towards the end of the 15 hour test. The explanation for this behavior is not clear, but is likely related to the continued stressing of the fuel over the duration of the experiment.

Simulation Tests

The next step in the additive development process is testing in fuel system simulation test rigs. Only additives that have met the criteria established in the above screening tests are evaluated. These devices have been designed to simulate different parts of an aircraft fuel system.

Augmentor Fouling Simulator: Details of the augmentor simulator have been described previously and will only be discussed briefly here.[7] This device consists of a tube heated to ~620°C in which fuel flowing at a low rate (1.5 mL/min) is vaporized at 1 atm. This low flow simulates leaking or residual fuel in the augmentor injection system. Periodically, a short surge of fuel at a much higher flow rate (3000 mL/min) is sent through the tube, simulating augmentor use. After the test period, the tube is sectioned and the deposition determined by carbon burnoff. The majority of deposit is located where the fuel changes phase from liquid to gas. This behavior is consistent with field observations.

Results of augmentor tests under both surge and non-surge conditions for the reference fuels and 8Q405 are shown in Figure 9. The quantity of deposits is consistently reduced under surge conditions. This is most likely due to a mechanical "scraping" of the deposit by the high fuel flow. 8Q405 adds to the deposit under non-surge conditions, but is seen to reduce deposits with the surge flow. The improvement may be related to a change in the physical characteristics of the deposit, e.g., the density, which facilitates removal under the high flow condition. The benefit of 8Q405 predominates at short test times (~7 hours) essentially extending the induction period. As the surface becomes coated, the deposition rate increases and parallels the neat fuel. The excellent performance of fuel 2926 in this test remains to be explained.

Extended Duration Thermal Stability Test (EDTST): The EDTST was designed to evaluate the most promising additive candidates under conditions that closely simulate the fuel system on advanced military aircraft. The test rig consists of a 60 gallon feed tank, a gear pump, two clam-shell heaters and a collection tank. The first heater or preheater is used to establish the desired bulk fuel temperature before entering the second heater. Bulk fuel temperatures selected are representative of the fuel temperatures encountered due to airframe and engine heat loads. The second heater is used to establish wetted-wall temperatures associated with main burner injection nozzles. Emphasis is placed on bulk fuel and wetted-wall temperatures because they are used to define limits for engine fuel system design.[8]

EDTST results for fuel 2980 with the two additive packages are shown in Figures 10 and 11. Section number refers to the relative distance along the stainless steel tube. A bulk fuel temperature of 177°C and a wetted-wall temperature of 260°C were used for these tests. These temperatures are considerably higher than the design limits imposed on current aircraft (163°C and 204°C). Both additive packages reduced surface deposits to levels slightly higher than JPTS. Analysis of the filterable deposits showed substantial reduction here as well. Full realization of the 218°C bulk temperature has not yet been demonstrated, however, even JPTS (our thermal stability benchmark) breaks down at this bulk temperature and forms deposits in the preheater.

Material and Additive Compatibility, Specification Conformance, Storage Stability and Combustion

Material and Additive Compatibility, Specification Conformance: The next phase of the program is to perform compatibility and specification conformance testing with the JP-8+100 additive candidates per ASTM D4054. A comprehensive material list has been prepared that includes over 150 metallic and non-metallic materials. Airframe materials are immersed in the test fuel and placed in an oven at 93°C for 28 days. Every seven days the fuel is exchanged with fresh fuel. Test fuels include JP-8, JP-8+100 and four times the maximum recommended concentration of the JP-8+100 additives. The procedure for evaluating the engine materials is similar, but the test temperature is raised to 163°C and 218°C. Testing is currently underway and preliminary results do not indicate any unusual problems with the JP-8+100 additives.

Additive compatibility testing has been completed with the JP-8+100 candidates and all approved military specification additives. The additives included corrosion inhibitors per QPL-25017 revision 17, fuel system icing inhibitor (diethylene glycol monomethyl ether), MDA and static dissipater additive. No evidence of incompatibility was noted following the guidelines in Procedure B of ASTM D4054.

Specification conformance of JP-8+100 was evaluated using Procedure A of ASTM D4054. All JP-8 (MIL-T-83133D) specification tests were run on the base JP-8 and the JP-8+100 candidates. Both JP-8+100 fuel candidates failed ASTM D3948, Standard Test Method for Determining Water Separation Characteristics of Aviation Turbine Fuels by Portable Separometer. 8Q405 and MCP-147B both function as surfactants to prevent agglomeration and surface adhesion of insoluble materials. The effect of surfactants on coalescence is well known and the results were not unexpected. Several efforts have been initiated to further evaluate the extent and severity of the water shed problem. Another property affected by the addition of 8Q405 was electrical conductivity. At a concentration of 100 mg/L, 8Q405 increased conductivity an average of 140 pS/m in our three reference fuels. This effect on conductivity must be taken into account in order to assure that current conductivity requirements for JP-8 (150 - 600 pS/m) are not exceeded.

Storage Stability: An accelerated storage stability test has been developed for use as a tool to predict the long-term storage characteristics of JP-8+100 formulations. The procedure is a modified version of the storage stability test developed by the Naval Research Laboratory and Naval Air Warfare Center.[9] Four fuels which exhibit widely different thermal oxidative stabilities have been selected for testing. These fuels represent fast and slow oxidizers and high and low deposit producers. Briefly, 250 mL aliquots of each fuel is placed in 300 mL capacity Parr reactors. The reactors are pressurized with 50 psi air and placed in a convection oven at 100°C. One reactor is removed every 24 hours, cooled to room temperature in a water bath and depressurized. 200 mL of the stressed fuel is filtered through preweighed 0.8 μm filters and the particulates determined gravimetrically. The remaining 50 mL is analyzed for peroxides, phenols, conductivity and total acid number. Testing of the fuels has recently been initiated and results are unavailable at this time.

Combustion Characteristics: Combustion experiments were conducted with fuel 2980 and 2980 plus 8Q405/BHT/MDA to investigate the effects of the additive package on combustion performance. The concentration of the additive package was varied from normal concentration to 100 times normal strength to exaggerate any possible effects. Performance parameters investigated included combustion efficiency (emissions) and stability (lean blow-out).

The combustor used in these experiments was a single-cup General Electric CFM56 swirl-cup and dome configuration. The combustor was operated at atmospheric pressure with inlet air temperatures of 260°C. The air flow rates delivered to the dome varied from 2 - 6% dome pressure drop. Emissions data is presented in Figure 12 and was obtained with a water-cooled sampling probe. The plot shows the combustion efficiency as a function of equivalence ratio for the different additive concentrations in the fuel. The results indicate that even at 100 times the recommended additive concentration, no loss in combustion efficiency was apparent. Figure 13 shows lean blow-out data as a function of combustor loading. The additive package had no detrimental effect on combustor stability at any of the concentrations investigated.

A single stationary turbine blade was placed in the exhaust stream of the combustor to determine if the combustion products would attack the thermal barrier coating or the metal surface with the additives present. The blade was air-cooled to simulate temperatures in this area of the engine. A visual inspection of the blade did not reveal any coking or erosion of the surface. A more in-depth analysis of the blade will be performed using scanning electron microscopy.

Reduced Scale Fuel System Simulator (RSFSS)

Testing in the RSFSS is the last step in the additive evaluation process before full-scale component and engine tests are accomplished. The RSFSS was configured to accurately simulate the thermal management system in the F-22. Actual engine and airframe hardware was modified to scale and incorporated into the simulator to evaluate performance degradation due to fouling. A generic mission cycle was devised to closely simulate heat loads, fuel flows, time at temperature, transients and fuel recirculation at different flight points. A complete test consists of 75 missions at ~2.5 hours each. The 75 missions are run consecutively, consuming ~700 gallons of fuel.

At the end of the test, the burner feed arm is removed from the rig, sectioned and surface deposits measured by carbon burnoff. Figure 14 is a plot of burner feed arm deposition with fuel 2980 and 2980 plus 8Q405/BHT/MDA. At a wetted-wall temperature of ~218°C, significant deposition occurred with 2980. The JP-8+100 additives were able to reduce the surface deposits to near background levels.

The servo valves and the flow divider valve were calibrated before each test to establish baseline performance characteristics. Hysteresis increased significantly in each valve after fuel 2980 was run. The hysteresis check after JP-8+100 showed no deviation from the initial calibration. The valves were disassembled after each run to visually inspect for deposition. The internal components of the servo valves and the flow divider valve were coated with a brown stain or lacquer after fuel 2980 was run, but appeared clean after JP-8+100 was run.

Full-scale component and engine testing follows successful testing in the RSFSS. Plans are in place to run JP-8+100 in full-scale nozzle tests, combustor rigs, fuel control systems and in a variety of military engines. The benefits of JP-8+100 will be demonstrated in these tests and validated for fleet wide use by 1998.

Conclusions

The work presented in this paper demonstrates that additives are a viable approach to improving thermal stability. By combining the appropriate constituents into an additive "package", i.e., an antioxidant, a metal deactivator and a dispersant, fuels of varying quality can be significantly improved. The efficacy of the additives tested here is fuel dependent and it is doubtful that any additive or group of additives will be universally effective. The requisite improvement in thermal stability for advanced military aircraft can be realized by the judicious selection of additives.

The detergent and dispersant type additives facilitate water entrainment and interfere with efficient water separation. This problem was expected and plans are in place to investigate the scope and severity of the problem and remedy the situation.

The ability of any single bench-scale test to accurately predict in-service thermal stability has yet to be demonstrated. The approach of screening in accelerated tests and validation in simulators may eventually lead to the development of relationships between simple laboratory tests and fuel performance in the field. Testing to be completed in the next two years will validate this premise. At a minimum, the screening tests have the potential to become standardized techniques for the measurement of thermal stability.

Acknowledgments

The authors would like to acknowledge the contributions of the many people responsible for generating the data presented in this paper. Tedd Biddle and Bill Edwards of Pratt & Whitney, Becky Grinstead, Steve Zabarnick, Ed Binns, Gordon Dieterle and Jim Shardo of the University of Dayton Research Institute and Mike Burns of WL/POSC. The authors also acknowledge valuable discussions with Mel Roquemore of WL/POSC and Grant Jones of Systems Research Laboratory.

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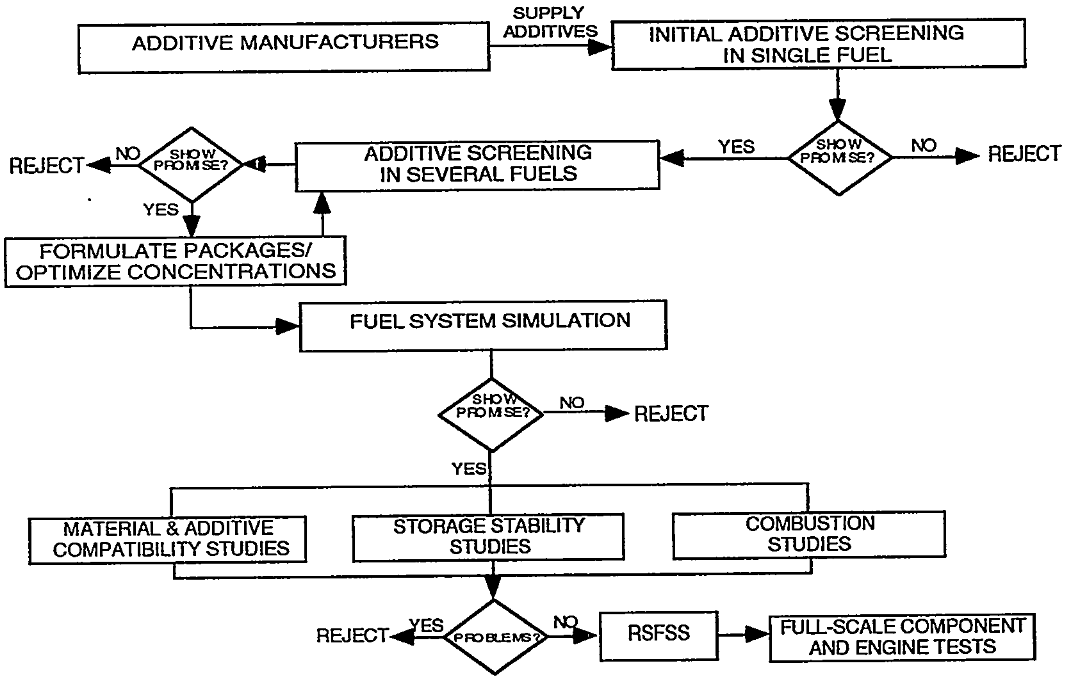

Figure 1. Additive Development Process

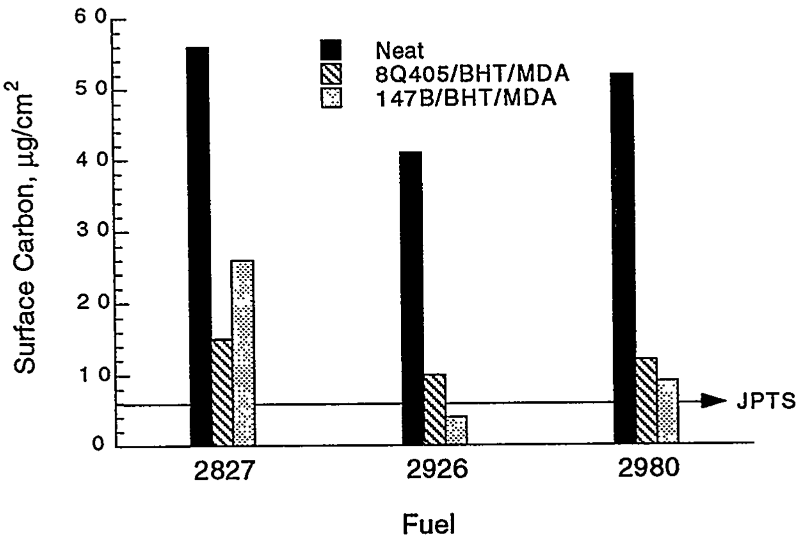

Figure 2. HLPS Results for JP-8+100 Candidates

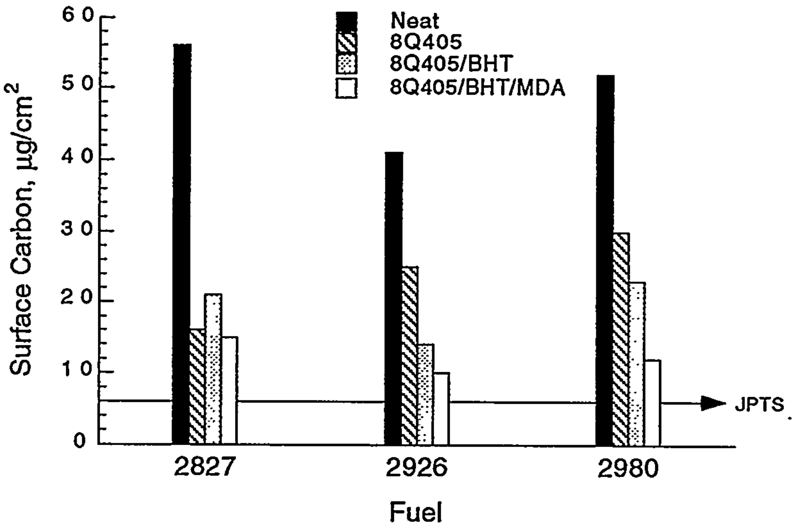

Figure 3. Effect of Individual Additives on Deposition

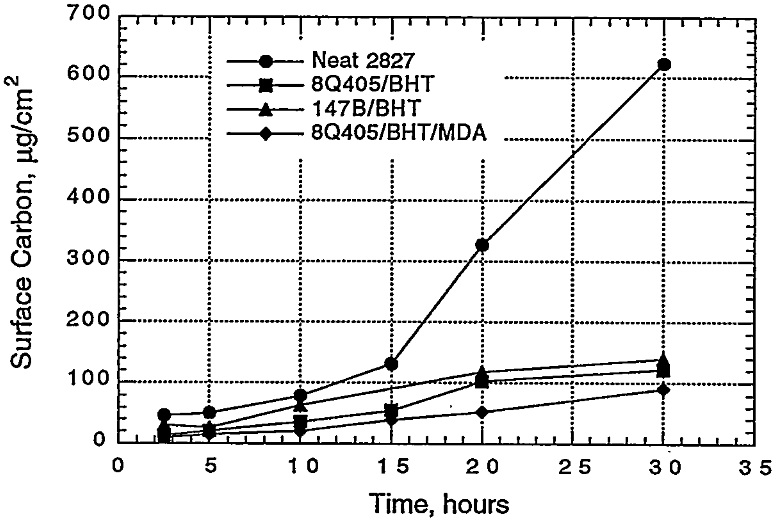

Figure 4. Extended Duration Testing in HLPS

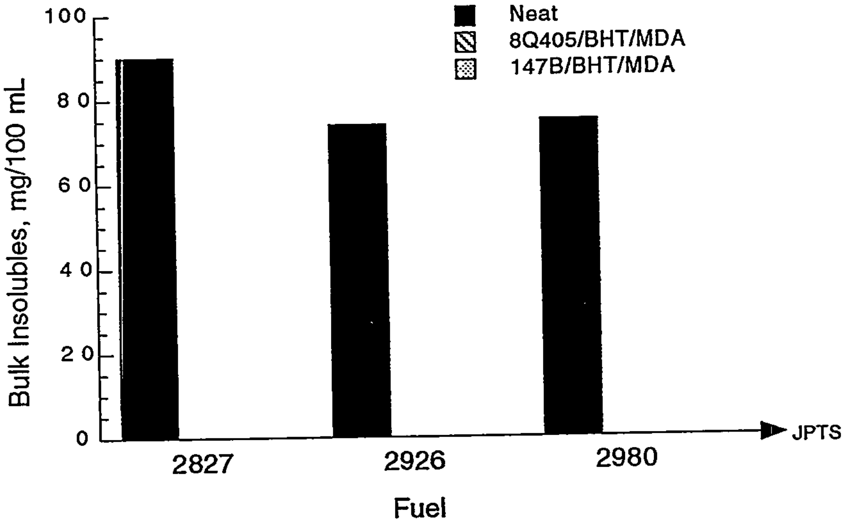

Figure 5. ICOT Results for JP-8+100 Candidates

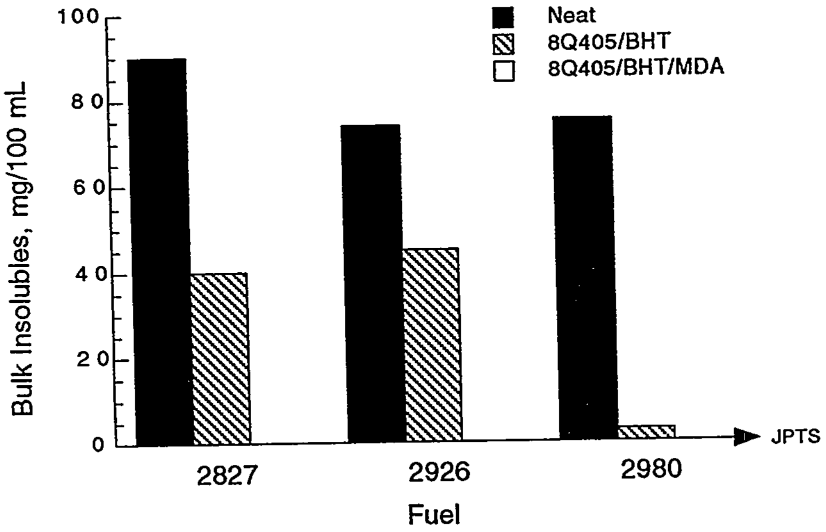

Figure 6. Effect of MDA on Bulk Insolubles

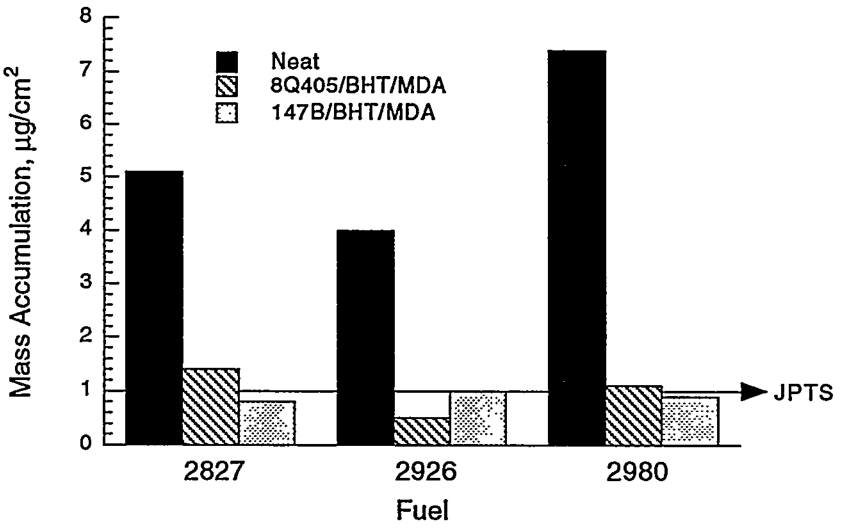

Figure 7. QCM Results for JP-8+100 Candidates

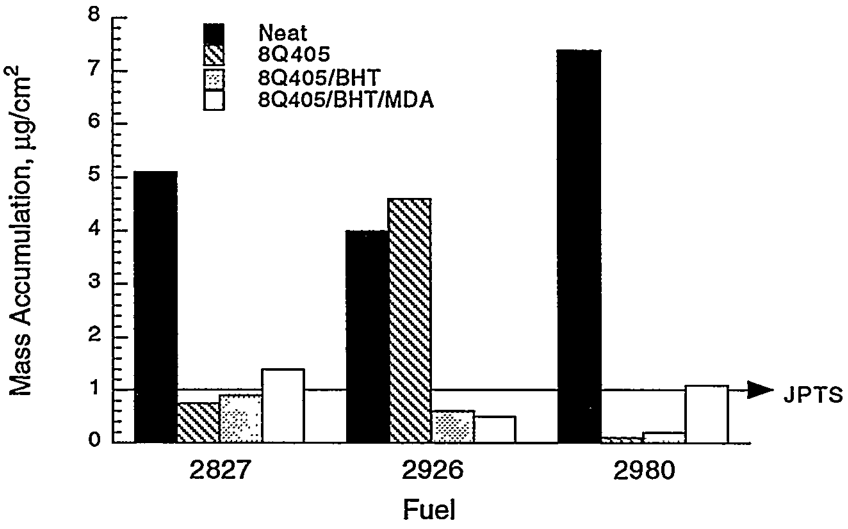

Figure 8. Effect of BHT and MDA on Mass Accumulation

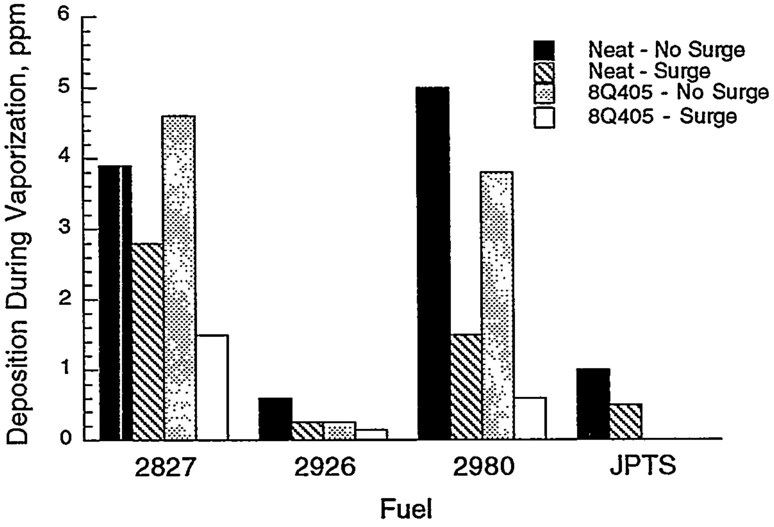

Figure 9. Augmentor Deposition Results for 7 Hour Tests

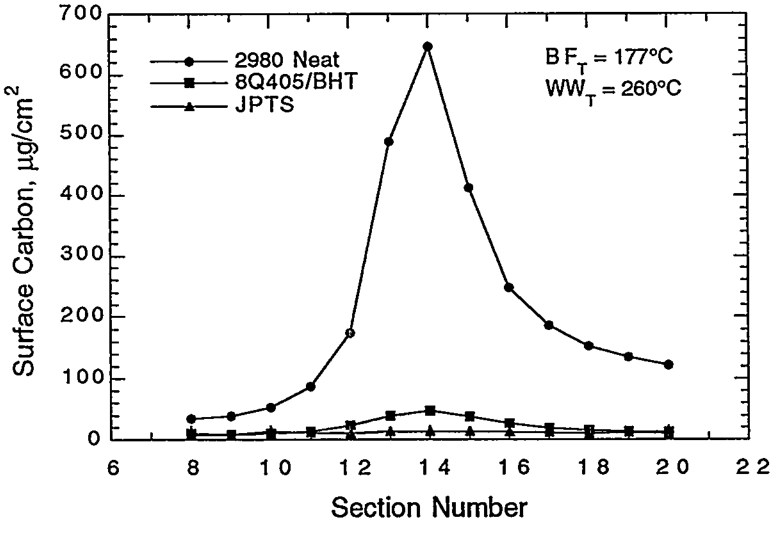

Figure 10. EDTST Results for Fuel 2980 and JPTS

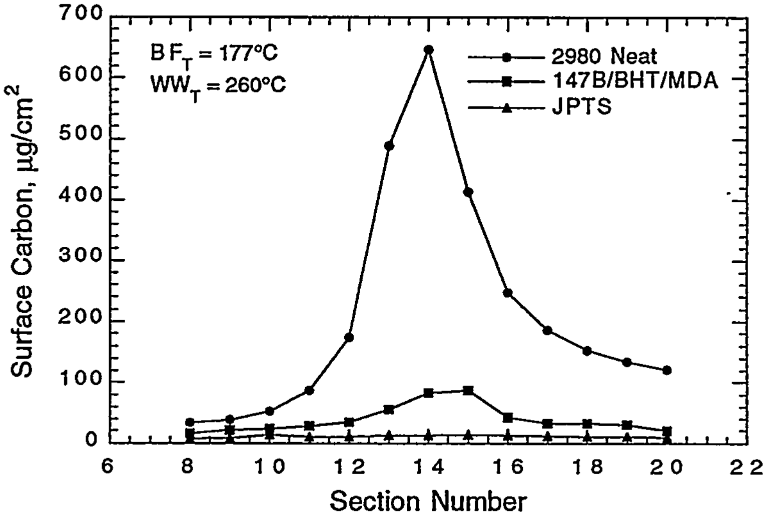

Figure 11. EDTST Results for Fuel 2980 and JPTS

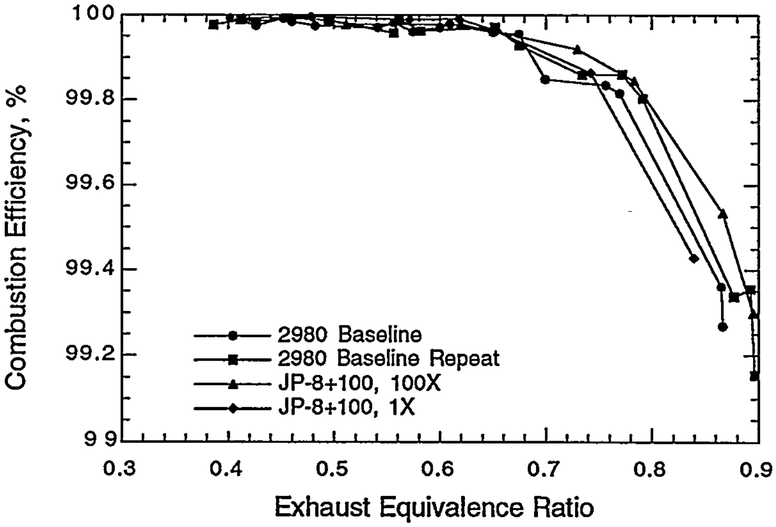

Figure 12. GE CFM56 Combustor Efficiency

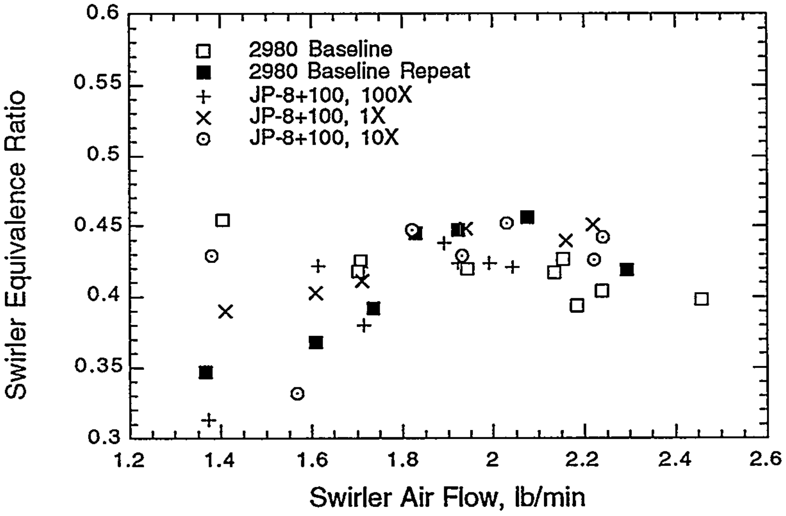

Figure 13. GE CFM56 Combustor Stability

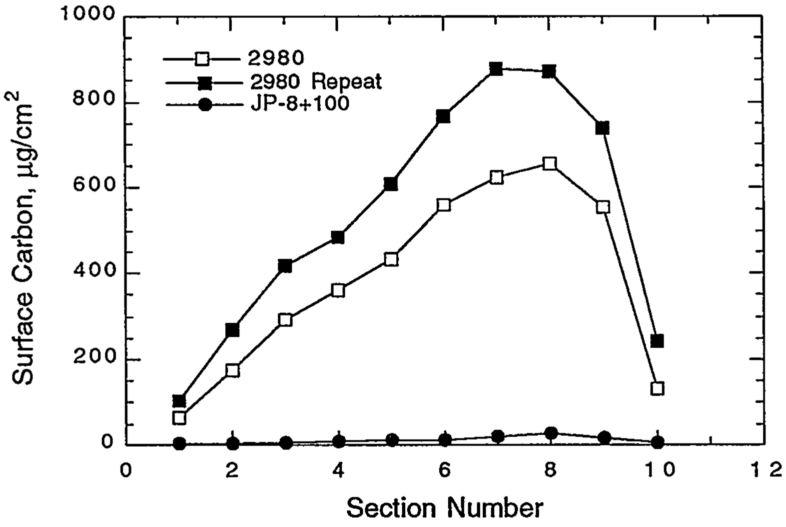

Figure 14. RSFSS Burner Feed Arm Deposition Results

Additive	Function	Formula	Concentration, mg/L
BHT	Antioxidant	2,6-Di-t-butyl-4-methylphenol	25
MDA	Metal Chelator	N,N'-Disalicylidene-1,2-propane diamine	10 (7.5 active)
8Q405	Dispersant	Proprietary	100
MCP-147B	Detergent/Dispersant	Proprietary	300

Table 1. Additive Descriptions

Fuel Code	Fuel Description	HLPS Breakpoint °C	HLPS Surface Carbon μg/cm^2	HLPS ΔP mm Hg/min	ICOT Insolubles mg/100 mL	QCM Surface Dep μg/cm^2
2799	JPTS	398	6	1/300	0	1.0
2827	Jet A St. Run	266	56	300/240	90	5.1
2926	Jet A H. Treat	288	41	70/300	74	4.0
2980	Jet A Merox	288	52	12/300	75	7.4

Table 2. Reference Fuels

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
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STUDIES OF JET FUEL ADDITIVES USING THE QUARTZ CRYSTAL MICROBALANCE AND PRESSURE MONITORING AT 140 C

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The quartz crystal microbalance (QCM) and pressure monitoring are used for the evaluation of jet fuel additives for the improvement of jet fuel thermal stability. The mechanisms of additive behavior are determined by measuring the time dependent deposition with the QCM and oxidation by pressure measurements. Studies at various additive concentrations permits the determination of optimum additive concentrations. Additive packages made of mixtures of antioxidants, detergent/dispersants, and metal deactivators are shown to yield good improvements in thermal stability over a wide range of jet fuel types.

Introduction

Recent advances in jet aircraft and engine technology have placed an ever increasing heat load on the aircraft. The bulk of this excess heat is absorbed by the aircraft fuel, as jet fuel is used as the primary coolant for the numerous heat sources. This hot fuel reacts with dissolved oxygen to form oxidized products and deposits. The formation of deposits results in the fouling of fuel lines, valves, actuators, nozzles, and various other aircraft components with the potential to result in catastrophic failure. Jet fuel additives are added to fuel in small quantities to improve its oxidation and deposition characteristics.

In this paper we present results on the study of four classes of jet fuel additives: antioxidants, dispersants, detergents, and metal deactivators. Other additives used in jet fuels are: lubricity enhancers, static dissipaters, and corrosion inhibitors. Antioxidants interfere with the fuel autoxidation chain mechanism by intercepting peroxy radicals, which are the primary radicals responsible for continuing the chain.[1] These antioxidants molecules have an easily abstractable hydrogen atom which encourages reaction with peroxy radicals. Dispersants and detergents usually consist of molecules with a polar "head" attached to long non-polar hydrocarbon chain. In a non-polar fuel the hydrocarbon chain is attracted to the bulk fuel, and the polar head is attracted to any polar compounds or groups of compounds present in the fuel. Dispersants work by surrounding these polar compounds forming a micelle-like structure around the polar compound. Thus, the polar compounds present are not able to aggregate and form larger groups of polar compounds that would result in formation of insoluble deposits and gums.

Detergents act in a similar manner but the polar head actually binds to the surface while the hydrocarbon chain extends into the fuel. Detergents are able to remove polar species from surfaces. Metal deactivators are species that can bind to metal atoms that may be present as atomic or molecular species in the bulk fuel or by binding to metal surfaces. The interaction of these metal deactivator species with the bulk and/or surface metal atoms discourages the well known catalysis of chemical reactions by metals.

The present work is part of the Air Force JP-8 + 100 program, in which an additive package is being developed to extend the thermal stability of JP-8 jet fuel by 100 degrees F ("Thermal stability" refers to the deposit forming tendency of a fuel). This program involves the evaluation of proprietary and non-proprietary additives from many manufacturers. Table I lists the additives studied in this work, their additive classification (as stated by the manufacturer), and the type of compound, if known. In this work, a quartz crystal microbalance (QCM) is used for the real-time, *in situ* monitoring of the surface deposition. Also, a pressure transducer is used to monitor the pressure decay in the reactor that results from oxygen reaction. The combination of a very sensitive technique for monitoring deposition (QCM), along with a method for directly monitoring oxidation (pressure measurements) allows us to not only evaluate additives but also to study and classify additives based upon their deposition/oxidation characteristics.

Experimental

The experimental apparatus has been described in detail previously, and will only be discussed briefly here.[2,3] The fuel is stressed in a 100 ml Parr bomb reactor which has been modified with an RF feedthrough for the quartz crystal microbalance. It is heated with a clamp-on band heater which is controlled by a PID temperature controller via a thermocouple which is immersed in the fuel. The reactor is filled with 60 ml of fuel and thus contains a ≈40 ml headspace. The fuel and headspace are sparged with air for one hour at room temperature prior to each run. At the end of the sparge period the reactor is sealed at atmospheric pressure and the heater is turned on. At this point the computer data acquisition is initiated. The computer monitors the quartz crystal frequency, the crystal damping voltage, the temperature, and the headspace pressure at one minute intervals. A typical run is performed for 15 hours at a temperature of 140 °C. QCM deposition data is only valid during the relatively constant (±0.3 °C) period of the run after the ≈45 minute heat-up time. The Parr reactor is cleaned thoroughly between runs and a new quartz crystal is used for each run.

The change in the quartz crystal frequency in time at constant temperature is used to monitor the deposition. The quartz crystals used were 5 MHz, 2.54 cm diameter, 0.33 mm thick, AT-cut wafers. These crystals, obtained from Maxtek Inc., were manufactured with gold electrodes and overtone polished. The quartz crystal resonator is driven at 5 MHz by an oscillator circuit that was developed at Sandia National Labs.[3] This circuit tracks the impedance variations of the crystal in order to determine the resonant frequency of the device. The oscillator circuit also provides an amplitude output that indicates crystal damping. The reactor was also fitted with a Sensotec 0-50 psia absolute pressure transducer.

The theory that relates the measured frequency changes to surface mass has been presented in detail elsewhere,[4] and will only be discussed briefly. When a crystal is excited at its resonant frequency it undergoes a shear deformation with displacement maxima at the crystal faces. Mass accumulation on the crystal surface moves synchronously with the surface, resulting in a decrease in the resonant frequency. Also, a thin layer of liquid can be entrained by the surface, also resulting in a decrease in the resonant frequency. The decrease in resonant frequency is described by

$$\Delta f_0 \approx -\frac{2f_0^2}{N(\mu_q\rho_q)^{1/2}}\left[\rho_s + \left(\frac{\rho\eta}{4\pi f_0}\right)^{1/2}\right] \qquad 1)$$

where f_0 is the unperturbed resonant frequency, N is the harmonic number, μ_q is the quartz shear stiffness, ρ_q is the quartz mass density, ρ_s is the surface mass density (mass/area), and ρ and η are the liquid density and viscosity, respectively. Thus the frequency change is due to two terms: the first results from changes in surface mass density (the quantity we wish to measure), the second is due to changes in liquid properties (density and viscosity). If the liquid properties are constant, then changes in frequency can be used to determine surface mass accumulation. The liquid properties, density and viscosity, should remain relatively constant under conditions where temperature is held constant and the chemistry of the fuel is restricted to small extents of reaction. Under these conditions the surface deposition can be related to the frequency as

$$\rho_s = -\left(2.21 \times 10^5 \text{ g}/(\text{cm}^2 s)\right)\frac{\Delta f}{f_0^2} \qquad 2)$$

for the fundamental resonance. The surface deposition measurements reported here occur for fuel oxidation at constant temperature (±0.4 C) and under limited oxygen conditions, where only a small fraction of the fuel molecules undergo chemical change.[2] Thus, the fuel density and viscosity remain constant during our measurements, and the above equation can be used to measure surface deposition.

Under conditions where the liquid properties are changing, the amplitude output of the oscillator circuit can be used to determine the motional resistance of the crystal.[3] The motional resistance can then be related to these changes in liquid properties and thus the changes in liquid properties can be resolved from the surface mass accumulation. We have observed changes in crystal damping for some of the additives studied in this work, despite observing no changes in liquid fuel properties. No changes in crystal damping were observed for any of the neat (unadditized) fuels during a run. The implications of these changes in crystal damping will be discussed below.

In general, the reproducibility of the mass deposition measurements on fuels is limited to ±20% for the QCM technique. This estimate of the precision of the technique was derived from multiple runs of the same fuel, performed for various fuels.

Results and Discussion

In Table II are listed the fuels studied here and their properties. We have chosen to perform additive testing using a wide variety of different fuels to insure that the additive evaluation is not biased by the study of a single fuel type. Thus this work involves the study of both hydrotreated and unhydrotreated fuels. In this paper we report on a representative sample of fuel types. The first fuel is a non-hydrotreated Jet A fuel that is a moderate to heavy depositor, called fuel F-2827. This fuel exhibits a relatively low JFTOT (Jet fuel thermal oxidation test) breakpoint and contains a measurable amount of sulfur. In Figure 1 are shown the deposition results from the QCM for fuel F-2827 at 140°C for 15 hours with varying concentrations of Betz SPEC-AID 8Q405. This additive is classified as a dispersant by the manufacturer (see Table I). The additive concentration was varied from 0 to 100 mg/l. The figure demonstrates that at all concentrations tested the additive significantly improves the thermal stability of this fuel at short times. At 10 mg/l SPEC-AID 8Q405 shows a large improvement in thermal stability until ≈7 hours, at which time the deposition rate increases. At long times the deposition begins to approach that of the unadditized fuel. Similar behavior is exhibited for the 25 mg/l run, except here the low deposition region is extended out to ≈9 hours. Also shown in the figure are runs with 50 and 100 mg/l of SPEC-AID 8Q405. These two runs exhibit low deposition during the entire 15 hour experiment. Within the experimental uncertainty the deposition at 50 and 100 mg/l are the same. We will show below that though SPEC-AID 8Q405 has limited antioxidant characteristics it works primarily as a dispersant. The concentration dependence demonstrated in Figure 1 implies that at low concentrations the dispersant capability of this additive is overwhelmed by the relatively high concentration of polar species and/or aggregate particles generated in this fuel. At 50 mg/l and above there exists a high enough concentration of the additive to disperse the polar species created by the autoxidation process over the entire 15 hour run time of the experiment. These results show how an additive concentration can be optimized for a given fuel and stressing conditions using the QCM. It is important to understand that this concentration dependence is only valid for the temperature, time, and oxygen availability conditions of this experiment. At higher temperatures, it is expected that the oxidation rate will increase, thus deposit rate increases will occur, shortening the time to the sudden deposition rate change in this fuel/additive combination. The final amount of deposition after oxygen consumption is completed is mainly controlled by the oxygen availability in the system and thus should not be greatly effected by relatively small changes in temperature. With relatively large changes in temperature, mechanistic changes will occur in the autoxidation process, resulting in changes in both oxidation and deposition.[1]

In Figure 2 are shown the deposition data for DuPont JFA-5 in fuel F-2827 over the concentration range 0 to 24 mg/l. The figure demonstrates that JFA-5 improves the thermal stability of F-2827 early in the run, but at all concentrations the deposition increases above that of the neat fuel later in the run. The 6 mg/l run shows improved deposition until 5 hours into the run, after which the deposition is ≈0.5 $\mu g/cm^2$ above the neat fuel. The 12 mg/l run shows low deposition until ≈7 hours, after which the deposition is 1-2 $\mu g/cm^2$ above the neat fuel. In the 24 mg/l run, the deposition remains low for ≈8 hours, after which deposition is 2-3 $\mu g/cm^2$ above the neat fuel. It appears that JFA-5 actually decreases the fuel thermal stability for extended stressing times. An added complication in interpreting this data is the observation that for these runs with JFA-5 the crystal damping voltage did not remain constant during the course of the run. The damping voltage was observed to increase along with the apparent increase in deposition observed at long times. Changes in damping voltage are normally caused by changes in the fuel density and viscosity. These properties were measured after the completion of thermal stressing; under the conditions employed in this study no significant changes in viscosity and density were observed. As the liquid properties are not changing during the run, the change in damping voltage must be due to some other process that causes crystal damping. One possibility is the formation of a thin viscous film on the crystal electrode surface. The formation of such a film would result in a damping voltage change and an apparent increase in deposition due to the decrease in crystal frequency caused by the film formation. We have no other evidence to support this supposition, but at this time viscous film formation appears to be a reasonable hypothesis to explain the observations.

If the formation of viscous films result in anomalous increases in deposition for JFA-5, how do we evaluate this additive properly? As we have no data on the properties of this film, it is safer to assume that its formation is a negative characteristic of the additive. It is reasonable to expect that the formation of a viscous film would add to the fouling of fuel systems and therefore be a characteristic to be avoided in a potential additive. The formation of gums in fuels is detrimental to fuel systems, and a viscous film is likely to effect fuel negatively by a similar mechanism.

The effects of the addition of SPEC-AID 8Q405 and BHT in fuel F-2922 are shown in Figure 3. This fuel is hydrotreated and oxidizes quite rapidly as shown by the relatively rapid pressure decay observed for the unadditized fuel. BHT, which is an antioxidant, is added at 25 mg/l and causes a significant slowing of the oxidation. The unadditized fuel consumes oxygen over the first seven hours, at which time the pressure decay levels as the oxygen present is completely consumed. The additized fuel continues to consume oxygen even up to the end of the 15 hour run. The additized fuel also appears to have a higher initial vapor pressure, perhaps due to the carrier oil in which the additive is dissolved. The effect of the additive on the fuel thermal stability is also shown in the figure. The additized fuel produces deposition to a smaller extent until nine hours, at which time the deposition increases above that of the unadditized fuel. The smaller deposition at short times appears to be due to the slower rate of oxidation that results from the presence of the antioxidant. But when the oxygen is consumed, the additive actually results in increased deposition. This effect has been observed for a wide variety of antioxidants in fuel F-2922. Apparently, the polar nature of the antioxidant molecules result in their causing increased deposition upon their being oxidized. It is well known that the presence of polar, easily oxidizable molecules has a detrimental effect on the thermal stability of fuels.[5] We have found, as shown below, that the addition of a detergent/dispersant additive can prevent the antioxidant from causing a reduction in the thermal stability of the fuel. Thus one gets the positive effect of the antioxidant inhibition of the oxidation process without increased deposition.

Also shown in Figure 3 are results for the addition of 100 mg/l of SPEC-AID 8Q405 to F-2922. SPEC-AID 8Q405 is classified by the manufacturer as a dispersant. The figure shows that oxidation is slowed by the addition of this additive; this pressure decay is very similar to that observed for BHT. This additive also decreases the deposition significantly up to ten hours, when the deposition suddenly increases, leveling off at a mass accumulation similar to the unadditized fuel at 14 hours. Thus, although this additive displays antioxidant properties, it also shows a significant effect on the deposition, as also observed for fuel F-2827 in Figure 1. Apparently, the sudden increase in deposition observed at ten hours is also due to this dispersant additive being overwhelmed by the large production of polar species in this fuel. Note that Figure 1 shows that the sudden increases in deposition in fuel F-2827 containing SPEC-AID 8Q405 occurs at much lower concentrations than for F-2922. We have observed previously that F-2827 consumes oxygen much more slowly than F-2922;[2] thus the optimum concentration of a dispersant will be higher for the faster oxidizing fuel (F-2922), as seen here.

The effect due to the addition of both SPEC-AID 8Q405 and BHT to fuel F-2922 is also shown in Figure 3. The oxygen decay is very slow when the two additives are present; oxygen consumption is only partially complete at 15 hours. At these concentrations the antioxidant properties of these two additives appears to be enhanced by the presence of the other. The deposition measured is extremely low during the entire run, reaching only 0.2 $\mu g/cm^2$ at the end of the run. In this hydrotreated fuel, a combination of antioxidant and detergent/dispersant appears to work quite well; the antioxidant slows the oxidation, while the dispersant keeps the polar compounds formed during oxidation in solution so that they cannot aggregate to form larger depositing species. Note that the slowly oxidizing, non-hydrotreated fuel F-2827 does not require the presence of the antioxidant additive to achieve low deposition with the addition of SPEC-AID 8Q405 (Figure 1).

We have found two requirements for a fuel to be useful in evaluating antioxidants at 140 C for use in a thermal stability additive package. The fuel must oxidize relatively rapidly so that the oxidation is easily monitored, and the fuel must produce an easily measurable amount of deposits. Fuels that are slow oxidizers, such as F-2827, are not useful for evaluating antioxidants; such fuels tend to be heavy depositors. Fuels that oxidize rapidly, such as F-2747,[2] have a tendency to be very light depositors, making it difficult to evaluate their effect on thermal stability. A fuel such as F-2922 which oxidizes rapidly and produces an easily measured amount of deposits, as shown in Figure 3, is ideal for evaluation of antioxidants.

JPTS is a special purpose jet fuel developed for the U-2 aircraft. This fuel has excellent thermal stability characteristics and contains 12 mg/l of JFA-5 by specification. We have examined the oxidation and thermal stability of a JPTS fuel (F-2799) with and without JFA-5; the data are shown in Figure 4. JFA-5 is an additive package which consists of an antioxidant, a dispersant, and a metal deactivator. Figure 4 shows that the presence of the additive greatly delays the oxidation process. The unadditized fuel oxidizes very rapidly, reaching a minimum pressure in less than two hours. The additized fuel oxidizes very slowly over the first seven hours; oxidation then occurs rapidly, reaching a minimum pressure at 12 hours. The additized fuel produces deposits slowly during the first ten hours, at which time there is a sudden increase in the deposition rate. This sudden increase corresponds to the time of pressure decrease that results from the oxidation of this fuel. The unadditized fuel produces deposits during the early, rapid oxidation, and then deposits more slowly after two hours. It is possible that some of the deposition is missed in the unadditized fuel, as the oxidation process occurs rapidly and can occur during the 45 minute heat-up time, when the deposition process cannot be monitored. It is apparent from the large delay in the oxidation and deposition of the additized fuel that JFA-5 acts as an antioxidant under these conditions. Presumably, the species responsible for this delay is the antioxidant present in the JFA-5 package.

The effect of additives on fuel F-2963 is shown in Figure 6. This is a JP-5 fuel which has been doped with ≈50 ppb copper. The presence of copper in fuel is known to result in decreased thermal stability; the U.S. Navy uses copper fuel lines in its aircraft carriers, and therefore has problems with copper contamination of its fuels.[6] Figure 6 shows that the neat fuel produces deposits quite heavily, leveling off at near 6 $\mu g/cm^2$ at 12 hours. The pressure plot also shows that the neat fuel consumes oxygen over the first nine hours of the run. The addition of 100 mg/l of SPEC-AID 8Q405 results in much decreased deposition, although the deposition rate shows a rapid increase at 11 hours before leveling off at 13 hours. The addition of SPEC-AID 8Q405 also slows the oxidation of the fuel. Also shown in the figure is the combination of SPEC-AID 8Q405 and BHT. This combination further decreases the oxidation rate and also decreases the final amount of deposits measured. No sudden change in deposition rate is observed with this additive combination. Also shown in the figure is the effect of adding SPEC-AID 8Q405, BHT, and 10 mg/l of MDA. MDA is a metal deactivator which is thought to improve the thermal stability characteristics of fuels which contain an excess of dissolved metal species. This three additive combination further decreases the deposition observed in this fuel (no pressure measurements are available for this additive combination).

We have tested the effectiveness of variety of additives and additive packages in a variety of different fuels. A comparison of four additive combinations in eight different fuels is shown in Figure 5. The mass accumulation plotted is the QCM measured final accumulation at the end of the 15 hour run at 140 C. The time chosen can affect the comparative results as some additized fuels show sudden increases in deposition following a period of relatively light deposition (e.g., see Figure 2). We have chosen the mass accumulation at 15 hours for comparison purposes as it represents a worst case for fuels which display sudden deposition increases. Thus this comparison will be biased against such additives. The horizontal line near 1 $\mu g/cm^2$ represents the deposition of JPTS; a fuel with very good thermal stability characteristics and whose mass accumulation is a goal of the additive program. The neat fuels shown in the figure display deposition over the range 2.9 to 10 $\mu g/cm^2$. The addition of SPEC-AID 8Q405 alone improves some fuels substantially (F-2980 and F-2827), some slightly (F-2985 and F-2963), and some not at all (F-2926 and F-2922). Fuels F-2926 and F-2922 are both fuels that oxidize readily (F-2922 is hydrotreated); it has been demonstrated in static tests with bubbling oxygen that these fuels produce copious deposits when given unlimited oxygen.[7] Thus, an antioxidant, BHT, was added to these fuels in order to limit the rate of oxidation. The figure shows that the addition of BHT greatly improves the behavior of F-2922 and F-2926 but shows only small improvements for the other fuels, all of which are slower oxidizers. The addition of BHT does not significantly worsen the thermal stability of fuels F-2827 and F-2980 which were strongly improved by SPEC-AID 8Q405. Thus the combination of SPEC-AID 8Q405 and BHT, a dispersant and antioxidant, significantly improves four of the eight fuels (this additive combination also improves a variety of other similar fuels). The other four fuels (F-2936, F-2934, F-2985, and F-2963) show only partial improvements with this additive package. These four relatively heavily depositing fuels have proven to be very difficult to improve with additives. It was found that the addition of a second detergent, Mobil MCP-477, to the package produced significant improvements, as shown in the figure. The addition of MCP-477 brings both F-2936 and F-2963 below the 1 $\mu g/cm^2$ goal, while F-2985 and F-2934 remain slightly above the goal. Unfortunately, it was found in flowing tests at higher temperatures that this three additive package generally increased deposition above the neat fuel. This discrepancy between higher temperature flowing tests and the 140 C QCM measurements only occurred for packages involving MCP-477. Apparently MCP-477 enhances deposition at higher temperatures; further work on the QCM at higher temperatures is being studied in order to determine the cause of this discrepancy. The fourth additive combination shown in the figure is for MDA, a metal deactivator, added to SPEC-AID 8Q405 and BHT. This gives surprisingly poor results for fuels F-2934 and F-2985, markedly increasing their deposition. The only fuel in which this package shows improvement over the SPEC-AID 8Q405 and BHT package is fuel F-2963. This result is not surprising considering that fuel F-2963 has been doped with 50 ppb of copper; a metal deactivator additive is designed to improve such a fuel. Other tests at higher temperatures have shown significant improvements for MDA;[7] future QCM work at higher temperatures will attempt to study this behavior.

In the past, jet fuel additives have been evaluated in a wide variety of experimental devices. Various workers have used modified and unmodified versions of the JFTOT at various temperatures, see for example Morris et al..[6] Flask oxidation tests have been performed to evaluate antioxidants, see for example Kendall and Mills.[8] Also, relatively large scale single tube heat exchangers have been used to measure the effects of additives, see for example Clark.[9] These various tests differ in the essential parameters for examining fuel thermal stability: temperature, stress duration, oxygen availability, and surface materials, among others. Most tests are conducted under accelerated conditions, where the temperature or oxygen availability are increased above real fuel systems conditions. The study of additives in this work was performed at 140 °C, a relatively low temperature compared with other thermal stability tests. The presence of an air headspace in our reactor yields a higher oxygen availability than a flowing test by a factor of ≈4.[2] Also, the fact that our test is conducted in static mode at low temperatures dictates that the test time be relatively long (15 hours). Aircraft fuel systems consist of extremely complex pathways for fuel flow with various residence times at various temperatures; these temperatures and residence times vary with flight conditions, e.g. higher fuel system temperatures may occur at flight idle descent. In the laboratory, it is impossible to test additives under the exact conditions of an aircraft. These QCM tests address one set of conditions that the fuel may encounter– low temperature and moderate oxygen availability– as might occur in the fuel tank or fuel recirculation line. Higher temperature flowing tests may do a better job of simulating high temperature parts of the fuel system, such as the engine fuel nozzle. High oxygen availability tests, such as flask tests with bubbling oxygen, address a different regime. The Air Force JP-8 + 100 additive program is using a wide variety of tests in an attempt to simulate most conditions to which a fuel is subjected. A successful additive package must have the ability to prevent deposition over this wide range of conditions. Despite this wide range of conditions, the QCM has been used successfully to screen dozens of additives for study in high temperature flowing tests such as the Phoenix Rig.[10] On occasion additives have been found that perform quite differently in these two regimes. Thus, the limitations of a single device at a single temperature and oxygen availability must always been kept in mind.

Conclusions

We have demonstrated the usefulness of the QCM and pressure monitoring for the evaluation of jet fuel additives. The simultaneous measurement of time dependent deposition and oxidation also permits one to determine the mechanisms by which these additives operate. Additives that behave as antioxidants should delay or slow the onset of oxidation and thus oxygen removal. Detergent/dispersants will delay or prevent the formation of deposits. We have observed additives that exhibit both antioxidant and detergent/dispersant characteristics. These time dependent measurements allow us to readily determine the optimum concentration of additives. The antioxidants studied to date all appear to actually increase the deposit formation tendency of a fuel. We have found that an antioxidant in combination with a detergent/dispersant can yield the best characteristics of the two additive types for fuels which oxidize rapidly; the antioxidant delays the oxidation, while the detergent/dispersant prevents the formation of additional deposition due to the presence of the antioxidant. Slowly oxidizing fuels, which do not require the presence of an antioxidant, also show good improvement with this additive combination. Fuels with high metal concentrations also require the presence of a metal deactivator in addition to the antioxidant and detergent/dispersant, although the metal deactivator has a deleterious effect on some fuels.

Acknowledgments

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Table I. Properties of Additives Studied

Additive Name and Supplier	Additive Classification	Type of Compound	Concentration (mg/l)	Percent Active Ingredient
Betz SPEC-AID 8Q405	Dispersant	proprietary	100	proprietary
DuPont JFA-5	High Temperature Thermal Stability Package	Mixture of antioxidant, dispersant, and metal deactivator	12	proprietary
BHT	Antioxidant	2, 6 di-t-butyl-4-methylphenol	25	100 %
MDA	Metal Deactivator	N,N'-disalicylidene-1,2 propanediamine	10	73 to 75 %
Mobil MCP-477	Detergent	proprietary	300	100 %

Table II. Properties of Fuels Studied

Fuel Number and Designation	**Hydrotreated?**	**JFTOT Breakpoint (°C)**	**Sulfur Mass %**	**Other Notes**
F-2747 (Jet A-1)	Yes	332	<0.05	Light depositor
F-2827 (Jet A)	No	282	0.10	Heavy depositor
F-2922 (Jet A)	Yes	277	0.02	Fast oxidizer
F-2963 (JP-5)	Not known	232	0.04	High copper fuel
F-2799 (JPTS)	Yes	398	<0.05	High thermal stability
F-2926 (Jet A)	Not known	288	0.10	
F-2980 (Jet A)	No	288	0.10	Merox treated
F-2936 (JP-5)	Not known	277	0.10	
F-2934 (Jet A-1)	Not known	266	0.10	High acid number
F-2985 (JP-5)	Not known	266	not measured	High in nitrogen cmpds.

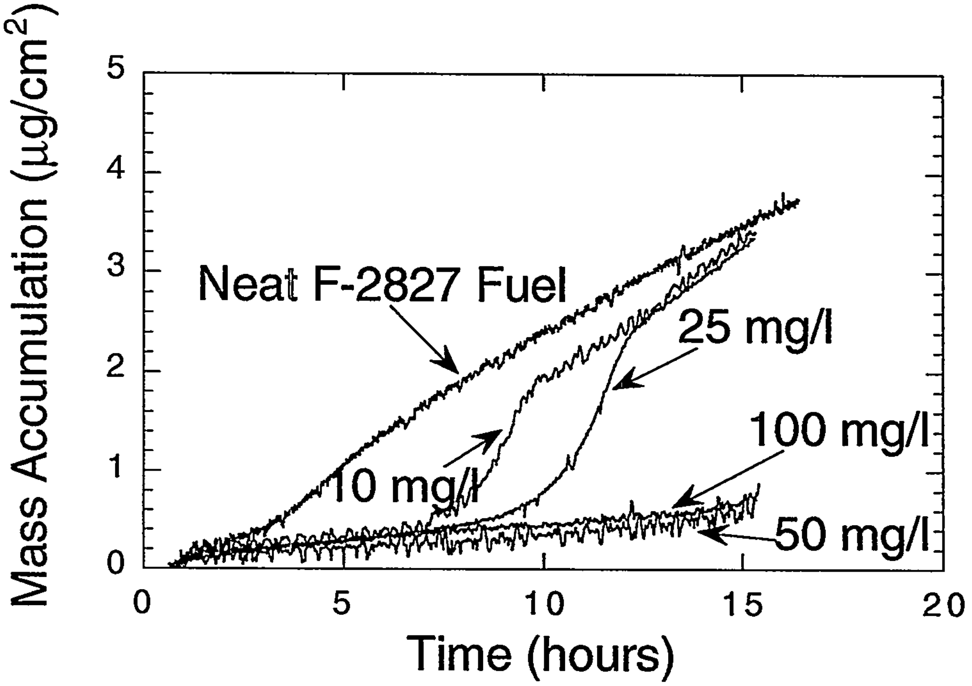

Figure 1. Plots of mass accumulation vs time for fuel F-2827 with varying concentrations of SPEC-AID 8Q405.

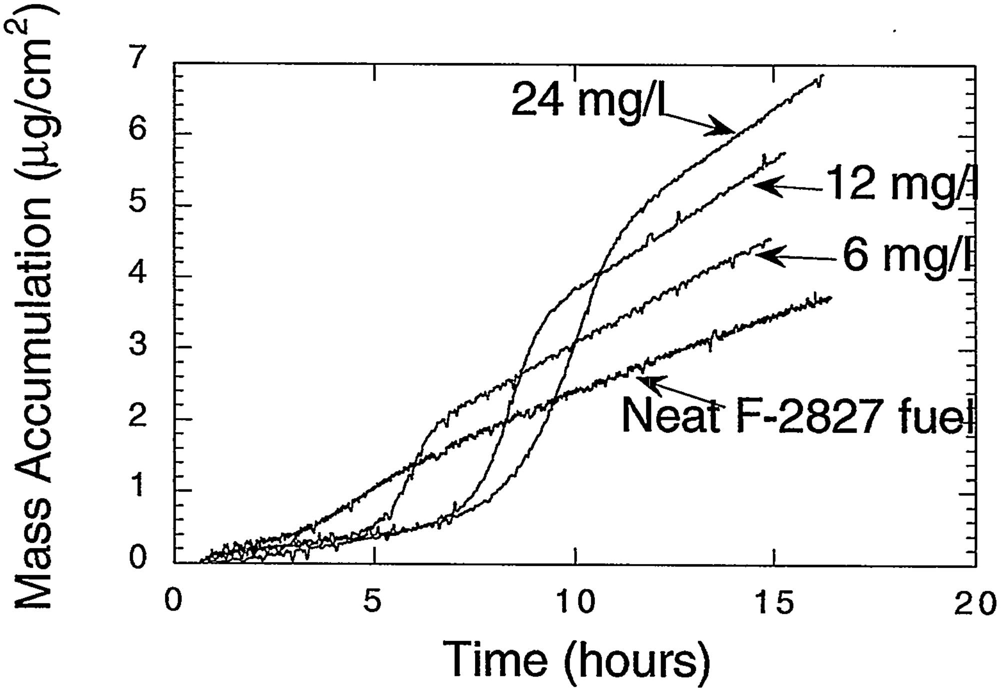

Figure 2. Plots of mass accumulation vs time for fuel F-2827 with varying concentrations of JFA-5.

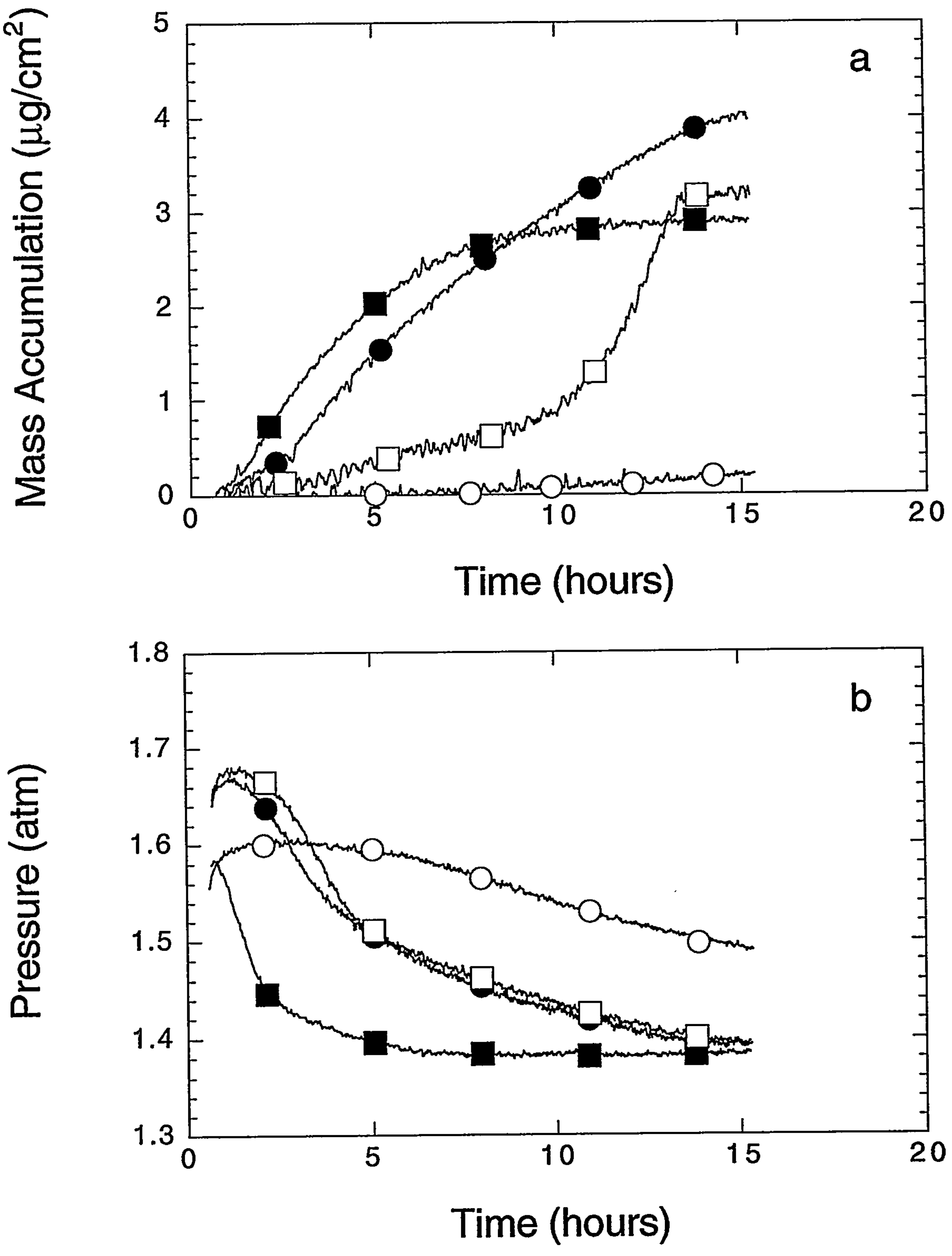

Figure 3. Plots of mass accumulation and pressure vs time for fuel F-2922: ■ neat fuel, ● with 25 mg/l BHT, ☐ with 100 mg/l SPEC-AID 8Q405, ○ with both SPEC-AID 8Q405 and BHT.

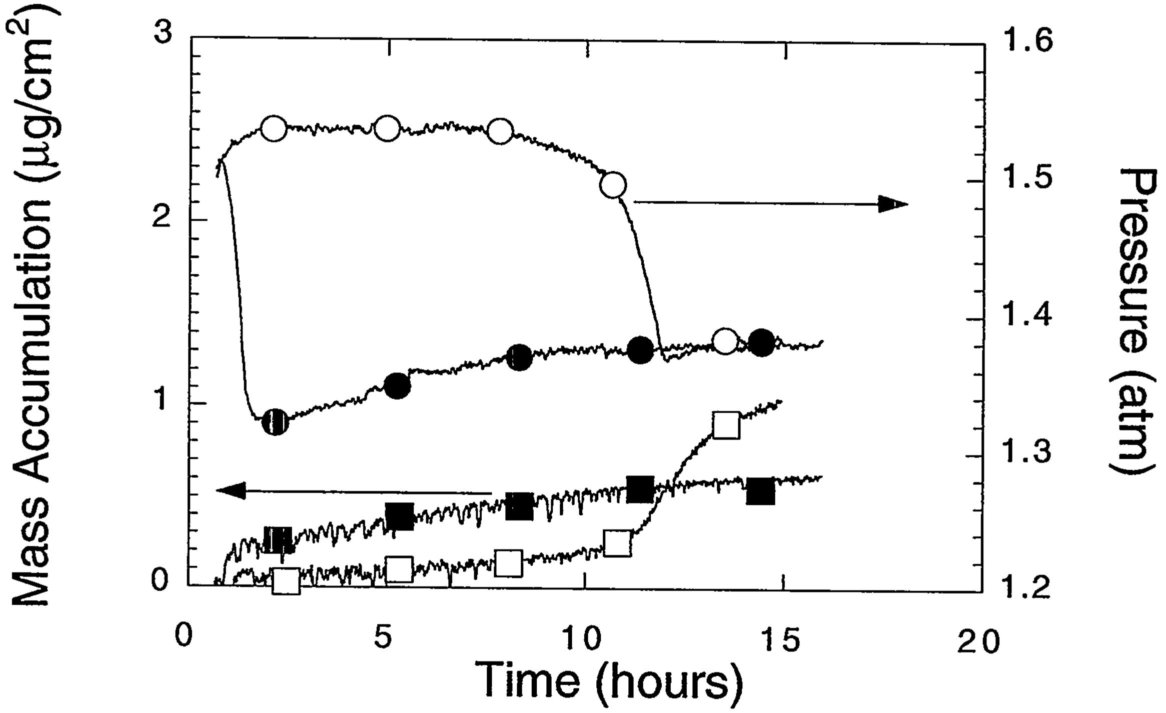

Figure 4. Plots of mass accumulation and pressure vs time for fuel F-2799 (JPTS): ❑ mass accumulation of fuel, ■ mass accumulation of fuel without JFA-5, ○ pressure of fuel, ● pressure of fuel without JFA-5.

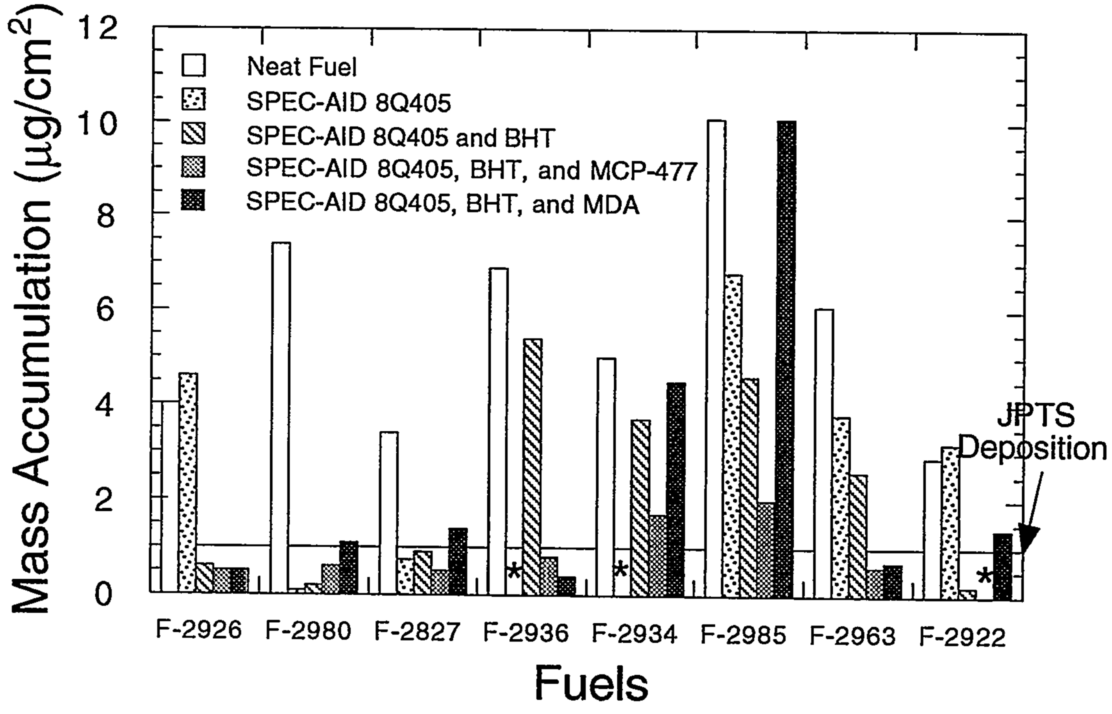

Figure 5. Comparison of mass accumulation for eight fuels with four additive packages.

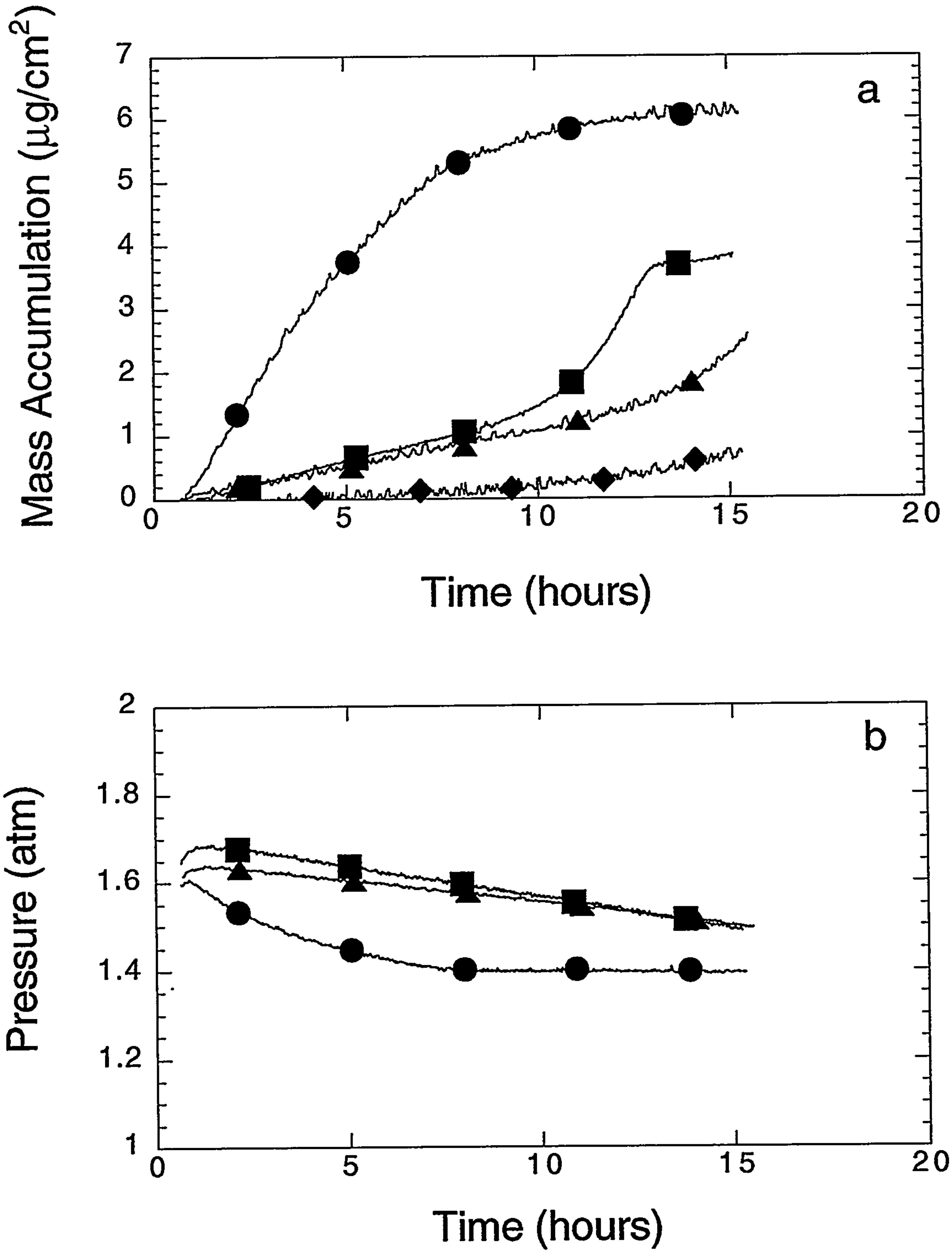

Figure 6. Plots of mass accumulation and pressure vs time for fuel F-2963: ● neat fuel, ■ with 100 mg/l SPEC-AID 8Q405, ▲ with 100 mg/l SPEC-AID 8Q405 and 25 mg/l BHT, ◆ with SPEC-AID 8Q405 and BHT and 10 mg/l MDA.

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EFFECT OF ADDITIVES ON THE FORMATION OF INSOLUBLES IN A JET FUEL

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ABSTRACT

Dynamic near-isothermal techniques have proven to be valuable in assessing the tendency of aviation fuels to form surface and bulk insolubles under thermal stress. These methods are applied in this study to the investigation of the neat Jet-A fuel POSF-2827 and changes introduced by a series of four candidate additives. In each case fuel is stressed while flowing through a heat exchanger under near-isothermal conditions at 185°C. The average surface deposition rate as a function of stress duration and the quantity of both surface and bulk insolubles have been determined after complete consumption of the dissolved oxygen. The additives, introduced individually, include a common antioxidant, a metal deactivator, a dispersant, and a combination detergent/dispersant. Of the four additives, only the dispersant-types are found to improve fuel thermal stability.

INTRODUCTION

Aviation fuels, when subjected to heat in the presence of oxygen, undergo degradation from autoxidation reactions.[1] Insoluble products formed in these reactions tend to foul heated surfaces, causing reduced efficiency and possible blockage in heat exchangers, hysteresis in servocontrols, and changes in nozzle geometry. Being the primary heat sink in modern aircraft, fuel will experience increased thermal stress as aircraft performance is enhanced.[2] Minor fuel constituents containing sulfur and nitrogen have been implicated as the primary cause of insoluble formation.

Methods of improving the stability of poorer quality fuels that are based on hetero-atom removal, such as clay- or hydro-treatment, do not always represent practical solutions because of the cost involved. The introduction of low-cost additives which may improve the thermal-oxidative stability is appealing. Additives such as antioxidants for slowing oxygen consumption, metal deactivators for chelating dissolved metals or passivating tubing walls, and dispersants for increasing solubility would appear to be the most promising from a thermal-stability standpoint.

Martel[3] has summarized jet-fuel additives including, in addition to the above, corrosion inhibitors, lubricity improvers, icing inhibitors, static dissipators, and pipeline drag reducers.

Since each fuel has a different chemical composition, the behavior of an additive for reducing insolubles will be dependent upon the reaction kinetics within the fuel. No additive is expected to be universally effective. For example, the DuPont additive JFA-5 is specified for use in JPTS (thermally stable jet fuel) because it contains a mixture of a high-temperature antioxidant, a dispersant, and a metal deactivator.[3] Similarly, to promote storage stability, hydrotreated fuels require the addition of low-temperature antioxidants to replace the natural antioxidants removed during processing.[4]

The approach in the current study was to 1) select a typical Jet-A fuel exceeding US Air Force requirements, 2) investigate its tendency to form insolubles at 185°C, and 3) individually add several candidate additives and investigate changes in the formation and quantity of insolubles. Deposition experiments were conducted over long test times to emphasize deposition on previously fouled surfaces.[5] Several criteria were applied in assessing beneficial or possibly deleterious effects introduced by the additives. The additive producing the most improvement was then subjected to further testing at several other temperatures. The goal was to address some fundamentals of additive behavior in altering the thermal-oxidation stability. In future studies beneficial synergism among these additives will be investigated by studying combinations. The advantage of the isothermal approach employed in this study is the ability to focus on chemical effects without the additional complexities associated with fluid dynamics at higher flows and without the surface-temperature changes that can occur as deposits accumulate.

EXPERIMENTAL

The baseline fuel, POSF-2827, has a JFTOT breakpoint of 266°C and a sulfur level of 0.079% (w/w). The presence of sulfur probably accounts for interest in this fuel and makes it a good candidate for the study of insoluble formation. In seeking improvement in thermal stability through the introduction of additives, it is important to select a representative, average fuel that produces measurable insolubles rather than an excellent fuel in which improvements would be difficult to detect. POSF-2827 is a typical Jet-A fuel. Kendall and Mills[6] addressed fuels of this type in which oxidation is inhibited by the presence of sulfur--but at the expense of increased insoluble formation.

The experiments were conducted using the Near-Isothermal Flowing Test Rig (NIFTR) which has been described previously.[7] Figure 1 shows the heat exchanger which was operated in the double-pass mode to extend reaction time. Fuel, which is saturated initially with respect to air and which contains 64 ppm (w/w) of oxygen, is pumped at a pressure of 350 psi through 0.125-

in.-o.d., 0.085-in.-i.d. commercial stainless-steel (304) tubing clamped tightly in a 36-in. heated copper block. Two in-line Ag-membrane filters (0.45 and 0.2 µm) collect the non-adhering bulk insolubles.

Deposition rates were measured in 72-hr experiments that were run continuously at a fixed fuel-flow rate; reaction time or stress duration was determined from the flow rate, tube dimensions, and location along the tube axis. At the end of each test, the heated tube was cut into 2-in. sections, and the quantity of carbon in the deposits was determined from surface-carbon burnoff (LECO RC-412). Deposition rates were determined from the amount of carbon in each 2-in. segment and the stress time calculated to its midpoint. Each section provides one data point representing the rate averaged over the entire test time (i.e., ~ 72 hr). Rate is expressed in units of micrograms of carbon per unit stress time per unit volume of fuel passed through the system.[7] Dissolved oxygen was measured in separate experiments using a 32-in. tube as a reaction cell and GC detection;[8] stress duration was changed by varying the flow rate. In long-term (72-hr) tests, most deposition occurs on previously fouled surfaces; for this reason a passivated tube (Silcosteel[9]) was used to minimize catalytic wall effects during oxygen measurements. In dynamic isothermal experiments, stress duration differs from experimental test time. Stress duration is the reaction time at temperature, and the experimental test time (along with the fuel-flow rate) determines the total quantity of fuel passed through the system.

Photon-correlation spectroscopy was selected for sizing of sub-micron particles, based on the techniques outlined by O'Hern et al.[10] Fuel was stressed within the NIFTR for selected times at 185°C, and particles in the effluent were sized after cooling to room temperature. The size measurements are viewed as an upper limit to the *in-situ* sizes.

The four selected additives are listed in Table 1. These include an antioxidant, a metal deactivator, a dispersant, and a combination detergent/dispersant. Concentrations of dispersants were based on manufacturers' suggestions, cost constraints, and previous tests in this laboratory.[11] Since the neat fuel does not contain measurable dissolved metals, MDA concentration was set at 2 mg/L for possible wall passivation.

RESULTS AND DISCUSSION

Oxygen Loss. The behavior of the dissolved oxygen as a function of stress duration at 185°C is shown in Fig. 2. Oxygen in the neat fuel is totally converted in about 20 min. The rate is constant down to 30% residual oxygen, indicating oxygen non-limited kinetics. Below 30% the rate becomes oxygen limited, as evidenced by tailing. Walling[12] has summarized the rate expressions for the disappearance of oxygen at high and low oxygen concentrations. Neither BHT nor MDA alters the oxygen consumption. The presence of certain types of sulfur compounds causes hydroperoxide concentration to remain low and the kinetic chain length to approach unity. Chain-breaking antioxidants such as BHT (hindered phenol) are ineffective since a molecule of antioxidant is destroyed for every molecule of oxygen consumed.[13] In the absence of dissolved metals and with inactive wall surfaces, a metal deactivator is similarly not expected to have a pronounced effect. Only one of the additives, MCP-147B, seems to perturb the oxygen consumption by increasing the reaction rate. At a concentration of 300 mg/L, this additive is directly participating in the reaction as a pro-oxidant or as an initiator.

Ideally, an additive should retard or certainly not increase the rate of autoxidation. In aircraft fuel lines, the fuel spends very little time at elevated temperature; therefore, oxygen conversion, in practice, is minimal. However, the very large fuel throughput offsets the conversion and leads to the observed fouling. In isothermal simulations only small amounts of fuel are used (~ 1.1 L); however, with 100% oxygen conversion, the extent of fouling per unit volume of fuel used is significant. In either case an additive such as MCP-147B that increases the autoxidation rate is of concern and its use should be decided based on further testing.

Dependence of Deposition Rate on Stress Duration. Figure 3 shows the deposition profiles at 185°C obtained at a flow rate of 0.25 mL/min. The 72-hr-average rate profiles for the additives BHT and MDA as well as the neat fuel appear to be the same within experimental reproducibility, displaying maxima around 9 min and completed deposition around 20 min which is consistent with the observed consumption of oxygen. The additives MCP-147B and 8Q405 cause significant changes in the deposition profiles. For stress times of less than 3 min, the former exhibits a reduced deposition rate but at longer times leads to a higher rate, maximizing around 6 min with no tailing. This additive appears to be promoting the deposition rate, as might be expected from the oxygen-loss data. The latter additive reduces the deposition rate for over 15 min of stressing and delays the maximum to around 12 min. The 8Q405 appears to behave as might be expected for an effective additive based upon a deposition-rate criterion, namely, reduced rate and delayed deposition. The MCP-147B displays undesirable behavior, based on a deposition-rate criterion.

Quantification of Insolubles. Other criteria for evaluating the additives on the basis of data from the same experiments are quantity of surface insolubles (integral under the rate profiles), bulk insolubles (carbon burnoff of the in-line filters), and finally the total insolubles (sum). In each case these quantities are expressed in terms of micrograms of insolubles per milliliter of fuel that is initially saturated with respect to air at room temperature. Insolubles are plotted in Fig. 4 for the neat fuel and each additive. Clearly, neither BHT nor MDA has a beneficial effect for POSF-2827 fuel under the test conditions; however, these additives do not reduce thermal stability. In contrast, both dispersants cause significant reduction in surface and bulk insolubles. Using quantity of insolubles produced from POSF-2827 as a criterion, both MCP-147B and 8Q405 result in a 50% reduction and would be rated as effective additives.

Bulk insolubles are quantified only at the end of 24-min of stressing or complete oxygen conversion. Surface insolubles, on the other hand, can be evaluated after any selected stress time, t, at 185°C by integrating under the curves in Fig. 3 up to time t. Thus, the performance of each additive in reducing surface deposits can also be evaluated as a function of stress duration.

Selection of Most Effective Additive. Based on the above evaluation criteria, neither BHT nor MDA improves the thermal behavior of the fuel as tested. The detergent/dispersant MCP-147B, while reducing insolubles, showed less than desirable signs both in the oxygen experiments and in the deposition rate by initiating or promoting thermal degradation. The dispersant 8Q405 does not alter the oxygen reaction rate but reduces both the deposition rate and total quantity of insolubles. For these reasons 8Q405 was selected for further testing.

It should be noted that the current study is limited to a single fuel and four additives. Development of any additive package requires the consideration of a broad family of fuels and additive combinations. Both MCP-147B and 8Q405 have quite different proprietary structures and chemistry. We expect their behavior to be different in every fuel.

Other Tests with 8Q405 Additive. Figure 5 shows a comparison between the deposition using neat and additized fuel at 165, 185, 205, and 225°C. Significant reduction in deposition rates is observed at each temperature. Similar improvements in the quantity of insolubles would be expected (see Fig. 6). Note that the inverse temperature dependence of the total insolubles that has been reported in 6-hr tests[14] is also reflected in the 72-hr experiments for both the neat and the additized fuel.

The fact that a dispersant-type additive shows the most promise in POSF-2827 fuel suggests that its role is to keep potential insolubles in solution, possibly by delaying agglomerization processes. The 8Q405 does not slow the autoxidation rate, but the subsequent chemical and physical steps leading to insolubles are delayed and the quantities are reduced. Insolubles that do come out of solution may be dispersed and kept small. Particles formed during the stressing of POSF-2827 fuel have been sized using photon-correlation spectroscopy. The measured diameter for the neat and 8Q405-doped fuel is shown in Fig. 7 as a function of stress duration at 185°C. The dispersant causes significant reduction in both particle size and number density (not shown), consistent with the earlier discussion.

CONCLUSIONS

The effect of four additives in improving the thermal stability of a particular Jet-A fuel has been evaluated in long-term (~ 70-hr) tests in which most of the deposition occurs on previously fouled surfaces. Neither the antioxidant (BHT) nor the metal deactivator exhibit beneficial effects. Some limited improvement was observed for a detergent/dispersant; however, indications of increased rates of oxygen consumption and deposition raise concerns as to its overall benefit. A dispersant additive 8Q405 exhibited significant reduction in deposition rates and quantity of insolubles over the temperature range 165 - 225°C. Improvement is explained in terms of particle-size reduction and decreased total insolubles caused by efficient dispersant activity.

Dynamic near-isothermal studies have provided details of oxidation and deposition kinetics for the Jet-A fuel, POSF-2827. These methods are currently being applied to evaluate the use of additives in other Jet-A and JP-8 aviation fuels.

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TABLE 1

ADDITIVES TESTED WITH POSF-2827 FUEL

CLASS	NAME	CHEMICAL NAME	MANUFACTUROR	CONCENTRATION (mg/L)
Antioxidant	BHT	2,6-di-tert-butyl-p-cresol	DuPont	25
Metal Deactivator	MDA	N,N'- disalicylidene-1,2,-propanediamine	DuPont	2
Dispersant	8Q405	Proprietary	Betz	100
Detergent/Dispersant	MCP-147B	Proprietary	Mobil	300

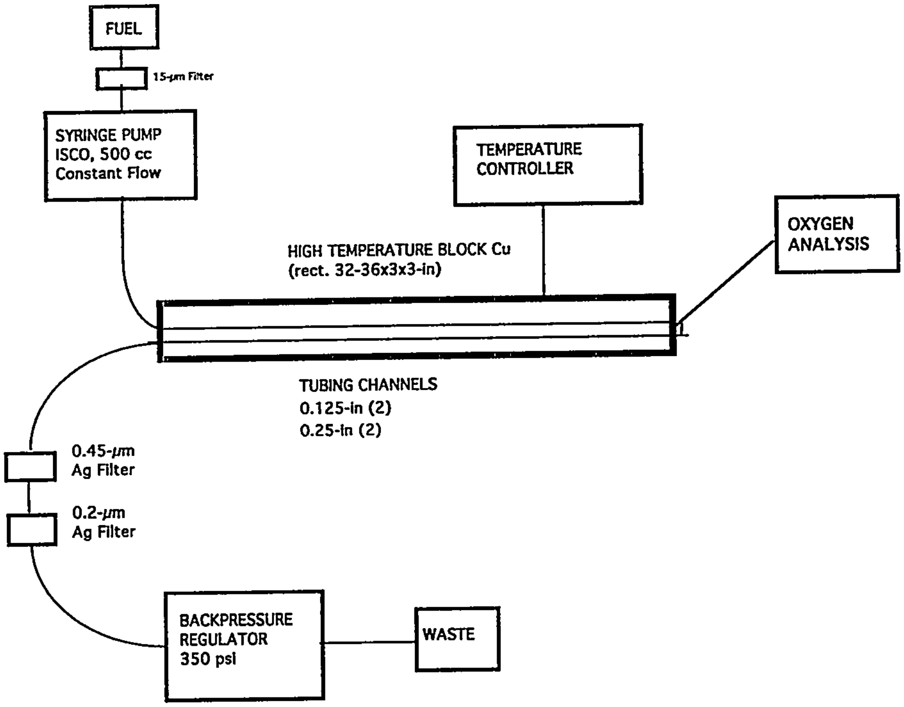

Figure 1. Schematic Diagram of Apparatus (NIFTR)

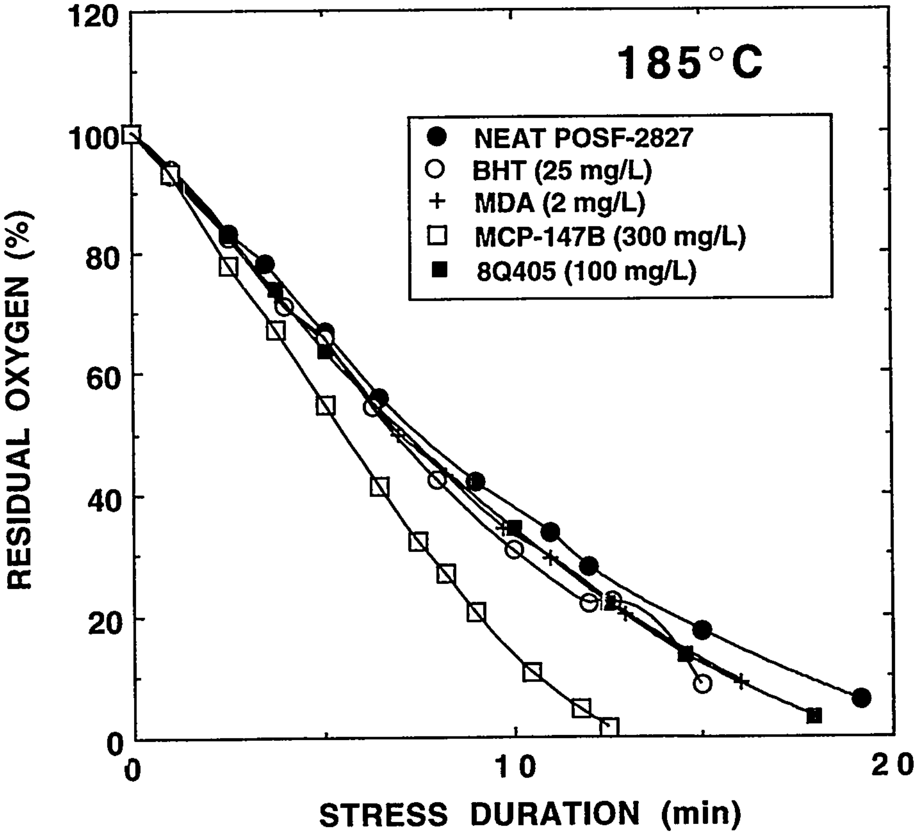

Figure 2. Consumption of Dissolved Oxygen at 185°C in Neat and Additized Fuel.

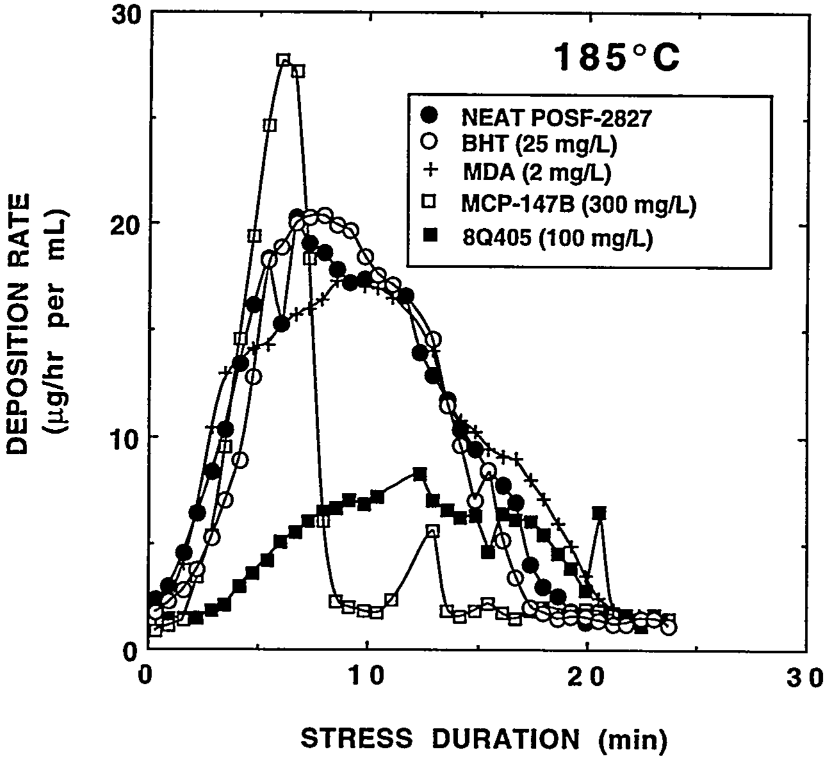

Figure 3. Surface Deposition Rates for Neat and Additized Fuel as a Function of Stress Duration at 185°C.

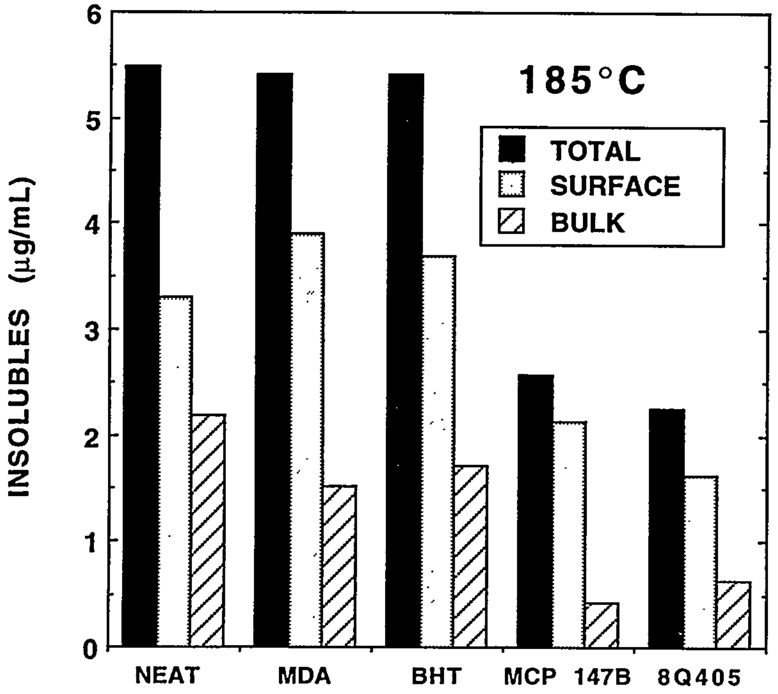

Figure 4. Bulk, Surface, and Total Insolubles Formed at 185°C.

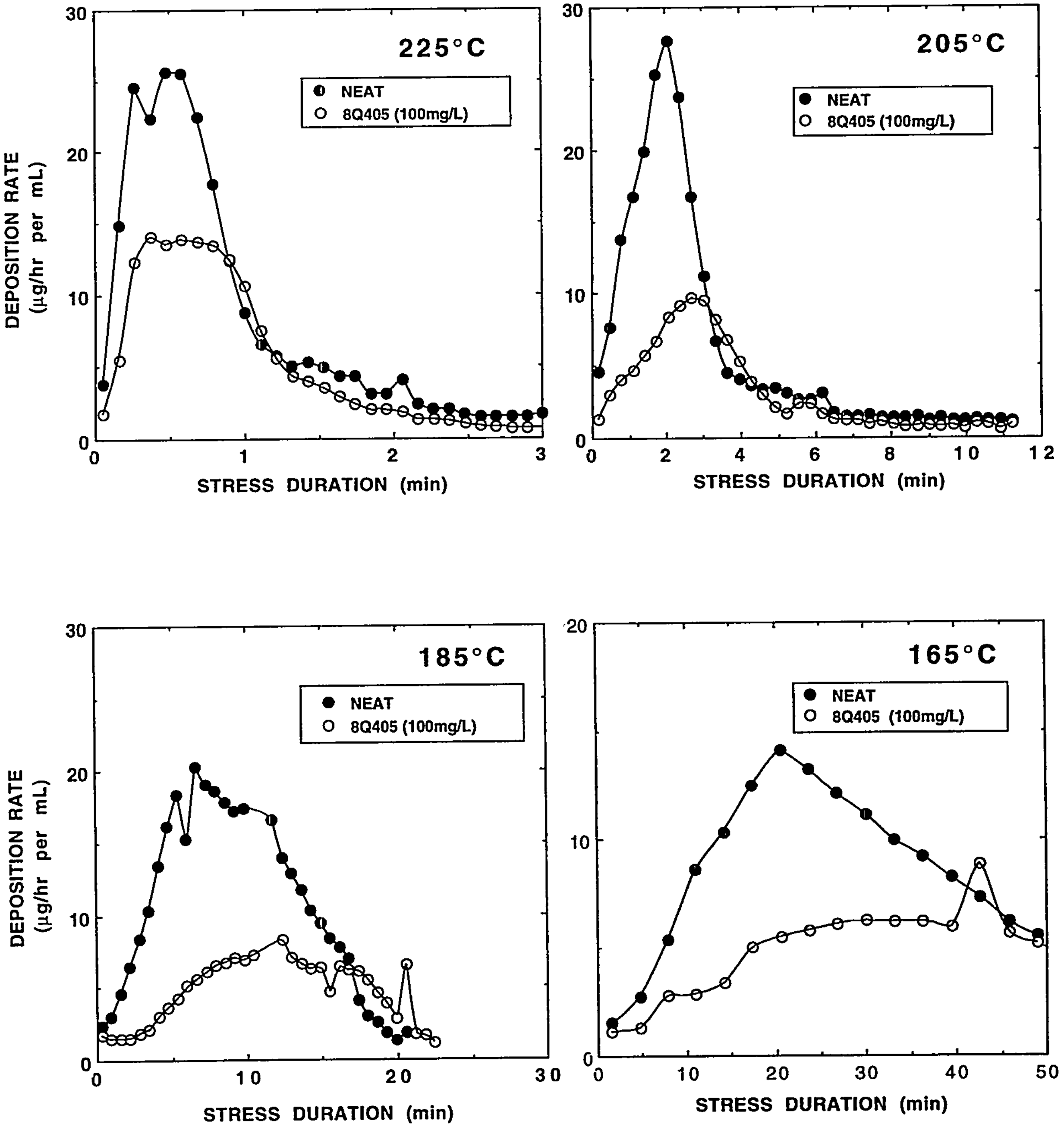

Figure 5. Deposition Rate. Stress Time Dependence at Series of Temperatures

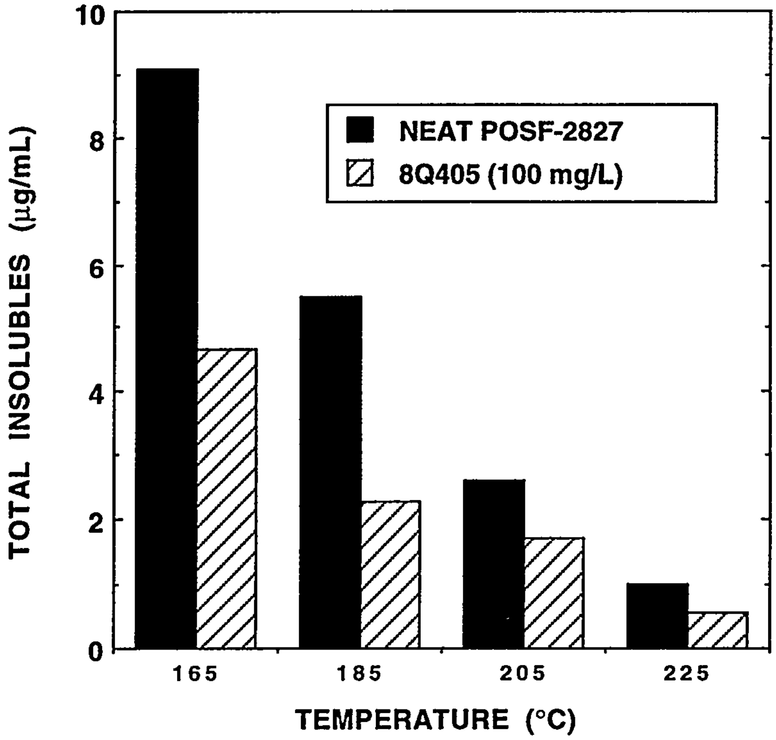

Figure 6. Total Insolubles as a Function of Temperature.

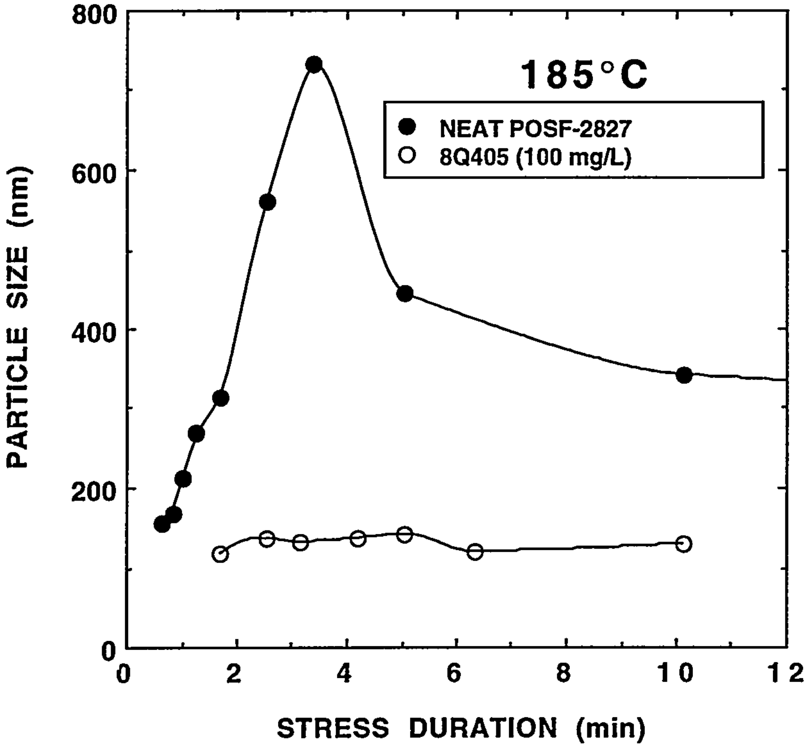

Figure 7. Particle Size of Insolubles as a Function of Stress Duration at 185°C.

5th International Conference
on Stability and Handling
of Liquid Fuels

Rotterdam, the Netherlands October 3-7, 1994

Long Term Storage of Finished Gasolines in large Salt Caverns

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Chairman, Ladies and Gentlemen

Strategic oil stocking requires large low cost storage facilities. Crude oil has been held in very large salt mines and/or artificially made salt caverns for many years, notably in Europe and the USA. Following crude oil, gasoils and refinery light feed stocks have been tried also. Military organisations tried jet fuel and early cases of underground aviation gasoline storage in steel tanks have been reported.

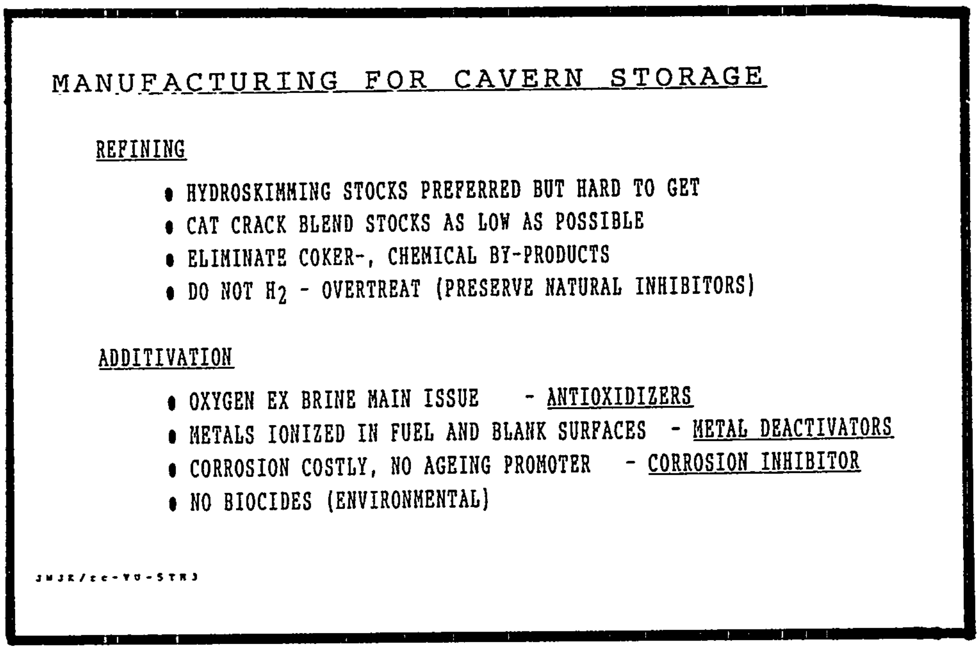
HISTORY

- CRUDE AND DISTILLATE AND FEEDSTOCK PLENTIFUL
- ATTEMPTS STRATEGIC STOCKS (GASOLINE) VERY RARE IN CAVERNS
  - UNITED KINGDOM 1940 + DURING WW II IN BURIED TANKS
    → ABANDONED
  - SWEDEN UNTIL 1994 IN ROCK CAVERNS ON WATER TABLE
    → NOW BEING TERMINATED
  - GERMANY EBV "OFF SPEC" GASOLINE AT 3 SITES IN SALT EARLY 90'IES
    → NOW "RUNNING MATE" FOR SYNCRUDE
- GERMAN STRATEGIC PETROLEUM RESERVE : FINISHED GASOLINE IN SALT
  HEIDE PROGRAMME 1985, RENEWAL 1993/94
  BLEXEN PROGRAMME 1991/92

JWJK/CC-VU-STX2

Motor gasolines have been stored in Swedish rock caverns on water table for twenty years or more, some is still there today but the programme is being phased out. In Germany naphtha/ off-specification gasolines were stored in salt caverns as syncrude blend stocks since the early eighties and large volumes are still being held today.

The real challenge started when in the "mid eighties" it was attempted to store finished premium 95 RON motor gasoline in salt caverns in Heide (North Germany) with the objective to recover the gasoline after 5 years or later and deliver it into the retail system without further processing. Now after almost 9 years, we still pump gasolines out of those caverns.



MANUFACTURING FOR CAVERN STORAGE

REFINING

- HYDROSKIMMING STOCKS PREFERRED BUT HARD TO GET
- CAT CRACK BLEND STOCKS AS LOW AS POSSIBLE
- ELIMINATE COKER-, CHEMICAL BY-PRODUCTS
- DO NOT H_2 - OVERTREAT (PRESERVE NATURAL INHIBITORS)

ADDITIVATION

- OXYGEN EX BRINE MAIN ISSUE - ANTIOXIDIZERS
- METALS IONIZED IN FUEL AND BLANK SURFACES - METAL DEACTIVATORS
- CORROSION COSTLY, NO AGEING PROMOTER - CORROSION INHIBITOR
- NO BIOCIDES (ENVIRONMENTAL)

JMJK/cc-YU-STR3

How could this be achived? Normally modern gasolines - in spite of containing oxidation inhibitors - age in 18 to 24 months in Europe, in the USA due to the higher crack stock ratios sometimes in less than a year, even though "reformulated US gasolines" may be a little bit more stable in future.

The secret is of course hydroskimming and reforming naphthas only, if possible no cracked naphthas. For economic reasons this is impractical, thus reduce it to an absolute minimum. Coker and/or chemical by-products are not allowed and overtreating of gasolines by e.g. hydrofining should be avoided, as this destroys natural ageing inhibitors like sulfur traces.

As special conditions exist in caverns careful additivation is necessary. Brine contains a fair amount of air when entering the cavern as seawater, thus antioxidants should be plentiful to catch the oxygen before it reacts with gasoline molecules. Salt contains metals like zinc and copper and iron - generally in minute quantities but enough to act catalytically, so does stainless steel which is used for sampling devices, thus metal deactivatiors should be added.

As corrosion reactions are suspected to promote ageing, also corrosion inhibitors are advisable. So far no microbial activity has been found in German caverns, thus biocides would not be needed, they would also contaminate the brine and may pose at discharge of brine an environmental hazard. This is the set of precautions, as we understand them today.

WHAT PRESERVED THE HEIDE GASOLINE ?

- LOW ON CRACKED STOCKS IN BLEND (< 17%)
- REFINERY: FED DIRECTLY INTO CAVERN
  - CRACKER: SEVERITY MODEST, UNUSUAL TYPE: "THERMOFOR" CATALYTIC CRACKER
    - OLEFIN CONTENT LOW: < 20 WT% IN BLEND
  - NATURAL PROTECTIVE COMPONENTS IN VIRGIN NAPHTHA - DISULFIDES FROM MEROX
  - ADDITIVES - BUT LOW RATE - AS ANTIOXIDIZERS (HYTEC 4733)
- SMALL TEMPERATURE GRADIENT PREVENTS CONVECTION/MIX FLOW
- SALT DOES NOT CONTAIN CATALYTIC METALS
- BRINE LOW ON OXYGEN, A GUESS ONLY

BUT: HEIDE STILL CONSIDERED RISKY IN EARLY '90IES
RESULT SOME SURPRISE AND A BIT OF LUCK

JWJK/EC-VU-STHS

But what preserved the Heide gasoline for so long as some of its stock is now 9 years old. Some of the protective measures were planned, others may have been windfalls.

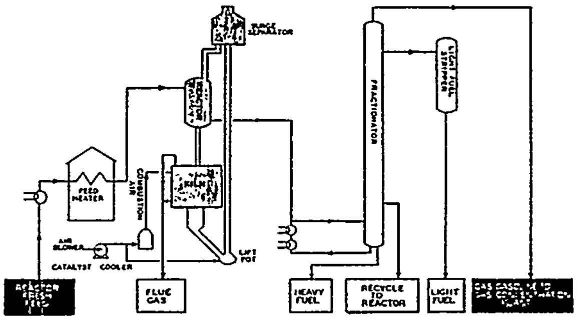
Indeed the crack stock content was kept low at 17% and the gasoline was fed directly into the caverns as the Heide refinery more or less stands on top of it.

The cracker run at modest severity is of a type known for manufacturing stable products. It is an old Thermofor process. There were disulfides from a MEROX unit sweetening the virgin naphtha portion and acting as natural inhibitors to ageing. The Heide refinery has no disulfide extraction unit normally used to increase lead susceptability in the pre-lead-free aera.

The additive addition was low, only the crack naphtha was slightly inhibited.

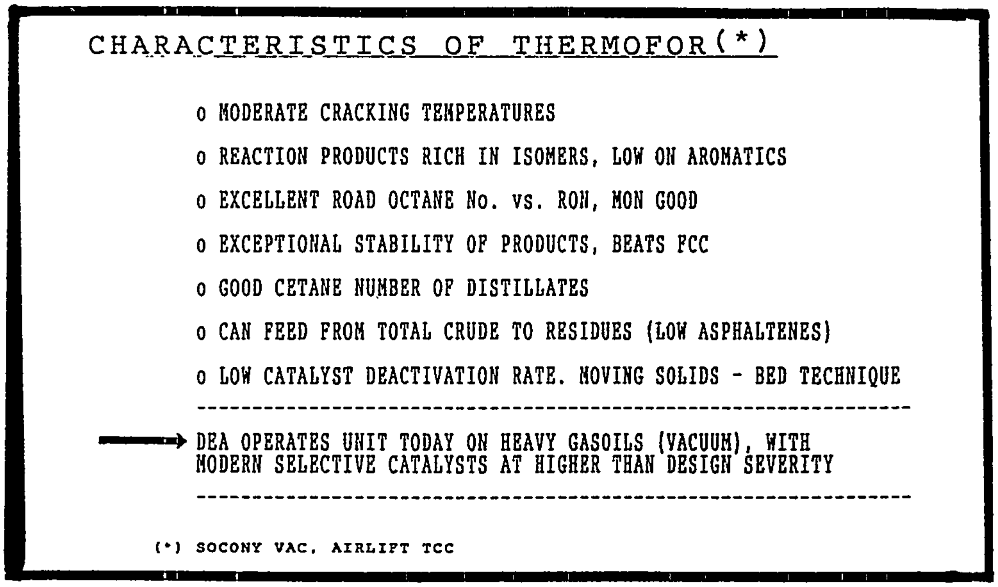
The cavern conditions were also optimal. As they are relatively shallow (not very deep into the ground) overall temperature is around 40 °C and there is hardly a temperature gradient, thus convection does not occur. The salt is rather pure with hardly any catalytic metals and we suspect that the brine was low on oxygen to start with. Still we were worried about those caverns, thus at least one may have been emptied prematurely and possibly would have been good for 3-5 more years.

Thermofor Catalytic Cracking



THE OIL AND GAS JOURNAL '57

Allow me to spend a few more words on the "friendly" cracker unit. It is a discontinued unit of mobil (socony vacuum) airlift type, of which less than a handful have survived in Europe. Its characteristics were: very high feed flexibility from total crude over low-asphaltene-residues to gas oils, and due to the moving-solid-bed-technique low catlyst deactivation;



CHARACTERISTICS OF THERMOFOR(*)

- o MODERATE CRACKING TEMPERATURES
- o REACTION PRODUCTS RICH IN ISOMERS, LOW ON AROMATICS
- o EXCELLENT ROAD OCTANE No. vs. RON, MON GOOD
- o EXCEPTIONAL STABILITY OF PRODUCTS, BEATS FCC
- o GOOD CETANE NUMBER OF DISTILLATES
- o CAN FEED FROM TOTAL CRUDE TO RESIDUES (LOW ASPHALTENES)
- o LOW CATALYST DEACTIVATION RATE. MOVING SOLIDS - BED TECHNIQUE

→ DEA OPERATES UNIT TODAY ON HEAVY GASOILS (VACUUM), WITH MODERN SELECTIVE CATALYSTS AT HIGHER THAN DESIGN SEVERITY

(*) SOCONY VAC. AIRLIFT TCC

product qualities in "its days" were exceptional as the naphthas are rich in isomers and low in aromatics and thus Road Octane Number and Motor Octane are quite good. It is said that its middle distillates show less of the low cetane number problems compared to normal FCC's and stability of all products is superior.

COMPARISON TYPICAL TCC vs. FCC NAPHTHAS (DEA)

	FCC KARLSRUHE 08.1990	TCC HEIDE 13.08.1990
ANTIOXIDANTS	POSITIV	POSITIV
ROZ	92.0	92.1
MOZ	82.4	82.1
FBP (°C)	204	210
AROMATES (VOL %)	31.5	20.6
OLEFINES (VOL %)	21.2	24.7
BROMINE No. (g BR_2/100g)	37.9	45.3
EXISTENT GUM (mg/100ml)	4/2	3/1
POTENTIAL GUM (mg/100ml) (4h, 100°C, 7 Bar O_2)	4.9/4.1	3.6/3.0
INDUCTION PERIOD (MINUTES) (100°C, 7 BAR O_2)	660	975
NITROGEN ppm	50	60
PHENOL ppm	29.2	36.5
SULFUR ppm	365	265

TCC MARGINALLY MORE STABLE

Today the owner DEA-Mineraloel AG operates the unit on vacuum gasoil similar to normal FCC feedstock. A comparison of the TCC and FCC cat naphthas (the latter from an industry refinery at Karlsruhe, where DEA is a partner) show a strong similarity but a 25-30% better stability of TCC naphtha (induction period, potential gum, low aromatics) in spite of marginally higher olefin, nitrogen and phenol contents.

TYPICAL CAVERN GASOLINE BLENDS

HEIDE CAVERN H 104A

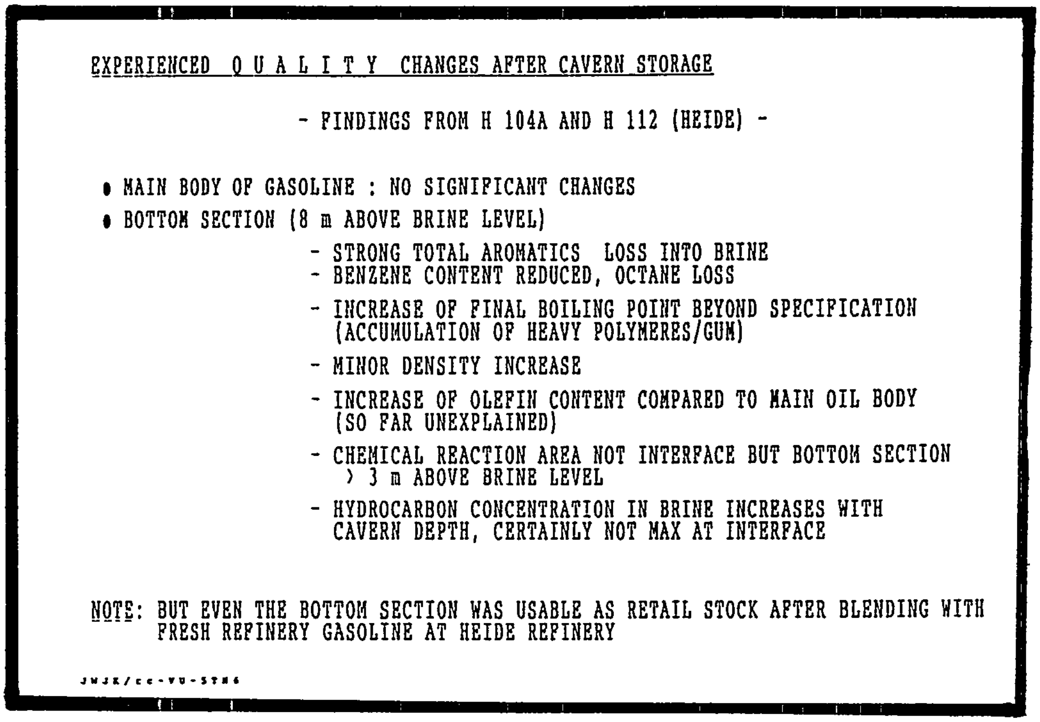
	BLEND RANGES OF BATCHES VOL %
C4	2 - 5
STRAIGHT RUN NAPHTHA	13 - 15
LIGHT REFORMATE (*)	10 - 13
HEAVY REFORMATE (*)	6 - 10
TOTAL (UNSPLIT) REFORMATE	44 - 54
CAT CRACKER (LCN)	10 - 17

CAVERN GASOLINE RETAILED ON SPEC 1992
AFTER 7 YEARS OF STORAGE

BATCHES MANUFACTURED AT HEIDE REFINERY 1985

(*) PLATFORMER (UOP)

The blend of the cavern gasoline batches produced by DEA consisted of Butane 10-17% TCC cracker naphthas and UOP reformates (with higher yield of light reformate than normally obtained from a UOP reformer); important is the 13-15% MEROX-treated straight run naphtha, whose disulfides shielded the fuel. The latter unfortunately today is not possible any more as the octane balance of the refinery requires total-reforming of all virgin naphthas.



EXPERIENCED QUALITY CHANGES AFTER CAVERN STORAGE

- FINDINGS FROM H 104A AND H 112 (HEIDE) -

- MAIN BODY OF GASOLINE : NO SIGNIFICANT CHANGES
- BOTTOM SECTION (8 m ABOVE BRINE LEVEL)
  - STRONG TOTAL AROMATICS LOSS INTO BRINE
  - BENZENE CONTENT REDUCED, OCTANE LOSS
  - INCREASE OF FINAL BOILING POINT BEYOND SPECIFICATION (ACCUMULATION OF HEAVY POLYMERES/GUM)
  - MINOR DENSITY INCREASE
  - INCREASE OF OLEFIN CONTENT COMPARED TO MAIN OIL BODY (SO FAR UNEXPLAINED)
  - CHEMICAL REACTION AREA NOT INTERFACE BUT BOTTOM SECTION > 3 m ABOVE BRINE LEVEL
  - HYDROCARBON CONCENTRATION IN BRINE INCREASES WITH CAVERN DEPTH, CERTAINLY NOT MAX AT INTERFACE

NOTE: BUT EVEN THE BOTTOM SECTION WAS USABLE AS RETAIL STOCK AFTER BLENDING WITH FRESH REFINERY GASOLINE AT HEIDE REFINERY

JWJK/CC-VU-STH6

In spite of most of the cavern volumes being useable directly without blending or reprocessing, we experienced some changes in the quality of the product near the oil/brine interface, which are worth discussing. These changes were more pronounced in the cavern emptied after 7 years than the one which was turned over after 9 years.

We saw a strong loss of aromatics into the brine, of which part was benzene. Consequently the octane level fell significantly by about 2 points.

Obviously some gum/polymers must have been formed and sank to the bottom so that the final boiling point increased well above the specification limit - and a minor gravity increase occured.

It remains unexplained, why an increase of olefines content over the average of the main oil body occured in a zone 5-8 m above brine level, while obviously near the interface those olefines had reacted to gum to a level well below average. Another unexplained finding was that the hydrocarbon content at the oil/brine interface is lower than at 2-3 meters below the interface. Theories are invited.

In spite of all those findings (see attachment A for detailed data) in the last few meters of the oil, all bottom cavern product in the end was blended down with fresh product from the refinery to marketable premium gasoline.

CAN WE REDUCE THE RISKS IN NEW STOCKS ?

- TAYLORMADE SPECIFICATIONS TO MODERN GASOLINES
- INCREASE PROTECTIVE SHIELD OF ADDITIVES
- USE OF "FRESH" CAVERNS IF POSSIBLE

BECAUSE: - GASOLINE TAKEN FROM VARIOUS MARKET SOURCES RATHER THAN ONE REFINERY ONLY
- SEVERITY OF CRACKERS INCREASE AND FEEDSTOCKS HEAVIER
- NATURAL INHIBITORS REMOVED BY OCTANE DEMAND IN LEAD FREE ENVIRONMENT

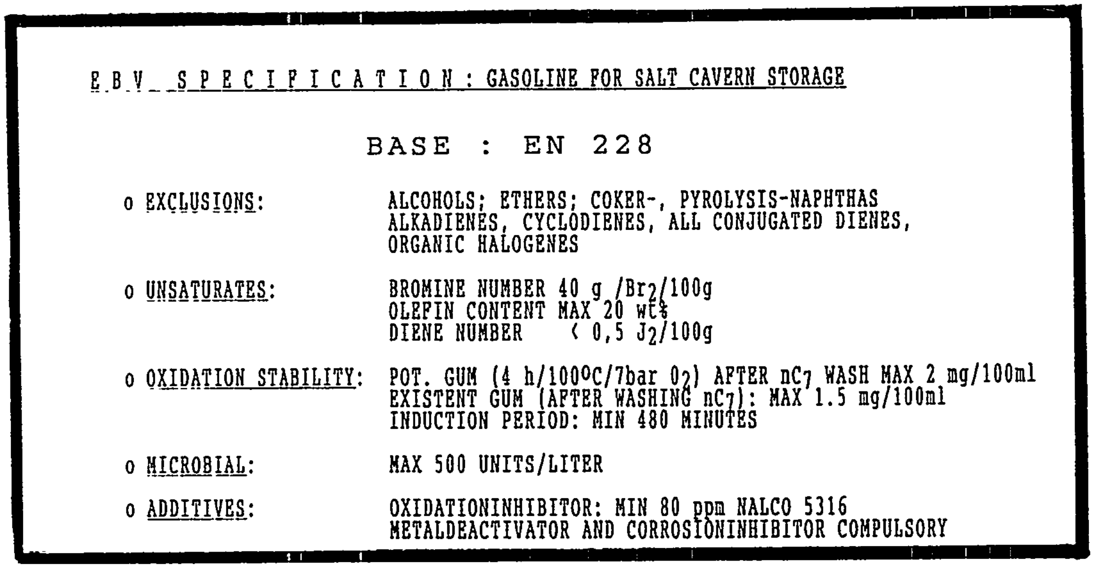
As we go from 1985/86 to 1994, or with the first refill to 1992, what will we do/have we done differently? As we can not expect to get gasoline from one "sympathetic" refinery only for our cavern storage in future, we had to issue a special cavern specification based on the EN 228, the new European Union spec. As a matter of fact we have used this spec for the 1 million m^3 fill of Blexen caverns near Bremerhaven. These caverns cover Germany's additional IEA/EU obligations for the new Eastern territories. The caverns were filled 1992.

We substantially increased the protective shield of additives, e.g. the gasoline contains now among others 80 ppm antioxidizers.

Learning from some bad experience in the past we will use new (fresh) caverns in future or only those, which contained acceptable gasoline without major signs of deterioration, since spoilage by aged product is taken as a serious problem at EBV.

These measures are significantly tougher than those in force at Heide, but when we take from various market sources, we must expect high severity cracker naphthas in the blend and the super hydrogen treating processes will almost certainly have removed all natural ageing inhibitors from the fuel.

How much tougher did we then make EN 228?



E B V S P E C I F I C A T I O N : GASOLINE FOR SALT CAVERN STORAGE

BASE : EN 228

o EXCLUSIONS:	ALCOHOLS; ETHERS; COKER-, PYROLYSIS-NAPHTHAS ALKADIENES, CYCLODIENES, ALL CONJUGATED DIENES, ORGANIC HALOGENES
o UNSATURATES:	BROMINE NUMBER 40 g /Br_2/100g OLEFIN CONTENT MAX 20 wt% DIENE NUMBER < 0,5 J_2/100g
o OXIDATION STABILITY:	POT. GUM (4 h/100°C/7bar O_2) AFTER nC_7 WASH MAX 2 mg/100ml EXISTENT GUM (AFTER WASHING nC_7): MAX 1.5 mg/100ml INDUCTION PERIOD: MIN 480 MINUTES
o MICROBIAL:	MAX 500 UNITS/LITER
o ADDITIVES:	OXIDATIONINHIBITOR: MIN 80 ppm NALCO 5316 METALDEACTIVATOR AND CORROSIONINHIBITOR COMPULSORY

JWJK/cc-VU-ST89

Due to solubility-in-brine problems we have to exclude all alcohols and ethers (including MTBE); chemical naphthas - mainly pyrolysis naphthas from "ethylene crackers" - had to be banned and anything containing any form of double unsaturated hydrocarbons (DIENES). Organic halogenes are excluded on legal/health grounds, even as additives.

A rather high olefin content of 20 wt% (40 Bromine No) is tolerated on the basis of strong additivation but Diene No should be very low eliminating practically all hyperreactive chemicals.

In line with this, gum values and induction period times are tightened over EN 228, a second prediction oxidation test (potential gum) has been added.

Antioxidizer additives have been specified at a substantial level and metal deactivator and corrosion inhibitor additives are required.

For the first time in Europe a microbial specification of 500 units per liter has been introduced, which is liberal for gasoline because we are confident (but not entirely sure) that microbes - if present - will not multiply in our high salinity environment.

We are convinced that these precautions will allow us to store gasoline 8 to 10 years. We have installed special devices to inspect the product and brine at various cavern horizons. Routine inspection is every 6 months to avoid surprises.

Reformulated gasolines and environmental specification changes (like max benzene content 1%) are to be expected over the next 10 years. Arrangements have to be made to prevent that the gasoline has to be exchanged prematurely before its designed storage life is over.

Thank you for your attention.

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E) DEA Mineralöl AG, Erdölwerke Holstein
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Interne DEA Laborberichte

F) PETROLAB (Speyer)
Laborbefunde: Cavern horizons, lab. analysis

- H 112 Nov 1992
- H 104A 19.8.1992

Analysenzertifikate.
Paid for analysis work requested by EBV

ATTACHMENT A

HEIDE 104 A SALT CAVERN GASOLINE

AVERAGE CAVERN CONTENT vs. BOTTOM 10% AND 1% AND vs. FRESH PRODUCT

	AVERAGE(+)	BOTTOM 10%(+)	BOTTOM 1%(+)	1985 FRESH PRODUCT
DENSITY (kg/m)	768.9	772.1	775.6	766.2
EXISTENT GUM (mg/100ml)	LT. BROWN	OILY, D.BROWN	DARK BROWN	LIGHT YELLOW
BEFORE nc_7 wash	60	310	2966	-
AFTER nc_7 wash	3.0	1.0	0.6	< 3
IBP ^{O}C	26	35	29	15
90 VOL% ^{O}C	172	179	190	172
FBP (^{O}C)	218	255	295	215
IND. PERIOD(MINS)	> 1000(*)	> 1000	-	> 1000
POTENTIAL GUM (mg/100ml) (4h, 100^{o}C, 7 Bar O_2)				
BEFORE nc_7 wash	120	1240	-	-
AFTER nc_7 wash	18	1.0	210	< 10
DIENE NUMBER (g J_2/100g)	0.26	0.62	0.39	-
BROMINE No. (g BR_2/100g)	3.1	7.55	-	-
TOTAL AROMATICS (WT%)	54.4	52.9	44.9	-
BENZENE CONTENT (WT%)	3.7	3.6	3.2	-
OLEFINES (WT%)	1.7	5.1	0.1	-
RON	95.2	92.4	88.1	95.3
MON	85.1	83.8	82.7	85.2

(*) NO BREAK OBSERVED FOR 2880 MINUTES (48 hl) | (+) 1990 ANALYSIS, CAVERN EMPTIED 1992

JWJK/rc-VU-5TH12

5th International Conference on
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

A STRATEGIC STORAGE PROGRAMME FOR DEVELOPING COUNTRIES - TO BE OR NOT TO BE?

Bernhard W. Morse

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0. ABSTRACT

In the industrialised world agreements between countries or legislation will dictate that there shall be strategic fuel storage of "X" amount of days. What about the developing countries, the third world? For the most part they have no storage regulations. Should they consider a strategic fuel storage programme? If so, how can they go about it? What are the obstacles? Many have neither the technical expertise nor the monies. This paper will explore how developing countries can have a strategic oil storage programme - How they can plan, justify, finance, execute and operate such a storage without having a major impact on their countries.

1. INTRODUCTION

I am honoured to have been given the opportunity to address the delegates attending the 5th International Conference on stability and handling of Liquid Fuels. The stability of the International oil business today appears to be very different from what it was when we met in Orlando, Florida three years ago. Because of this, many in the developing countries question the need for building or maintaining strategic oil stockpiling programme.

Given the past history of political instability in the main oil producing areas of the world, it is very difficult to expect the political conditions in those areas 5 or 10 years from now to look anything like they do today. It is shortsighted for developing countries not to plan ahead for potential fuel crisis.

Many will say that housing, education and schooling should take precedence over stockpiling strategic materials. After working in developing countries in Africa for the past 6 years, and 25 years in the Middle East, I cannot dispute that, but developing countries can take care of all these needs if they plan ahead.

2. BACKGROUND

Since the Gulf War, countries, especially landlocked ones, have recognized that not only are they vulnerable to the political instability in neighbouring countries as well as to natural disasters, but also to the volatility of the main producing areas of the world. Escalation of the Gulf War would have caused very serious fuel shortages. Accurate missiles launchings could have led to wide - spread destruction of oil gathering centres, export terminals, and refineries. This would have resulted in a major world-wide supply shortage and would have created economic havoc.

Studies have been undertaken by many African countries on this subject and several have or are considering implementing strategic fuel stockpiling programmes - Lesotho Swaziland, Malawi, Zimbabwe and Botswana to name a few. I had been involved in a United Nations Development Programme in Botswana from 1988 until July of this year to develop the Petroleum Management capability of that country, which included assistance to their strategic fuel programme. This also provided me with a unique opportunity to study and advise other Africa countries on this special subject.

3. PLANNING

Can you picture the chaos in your country if you had only a few days of oil storage, if suddenly your oil supplies were cut off? This happened to Lesotho, a small Southern African country, during the mid - eighties. The result was that the Government was toppled.

Several questions need to be asked by Governments interested in having strategic fuel storage programmes -
What do we gain by having a secure strategic oil storage facility?
What do we lose if we don't have a secure strategic oil storage facility?
Where can we obtain help, both financial and technical?
How do we justify the expenditure for such a programme?

Firstly, it must be clearly understood that projects of a strategic nature cannot be evaluated within the framework of a classical cost - benefit analysis. These projects are in the nature of risk insurance in order to safeguard against the effects from various possible interruptions of oil supplies, which can have temporary retarding to disastrous effects on a countries economy and the living standard of the people.

One can say that the results of the money outlays are difficult to measure, or have intangible benefits. However often these benefits can be indirectly evaluated, for example -

What is a days production of gold or diamonds worth if you must shutdown operations because of lack of fuel?

With a Government strategic oil project, prior commitment by legislative action is often the underlying justification.

A strategic oil supply can gain a country political stability. It can ensure that industrial and food production continues in a reasonable manner during a fuel crisis. It can provide a buffer for erratic and rapid international fuel price fluctuations. It can pay its operating costs if you procure fuel supplies when prices are low and sell off when prices rise.

International assistance is available for funding and providing the technical know - how for strategic projects.

While we are addressing the developing countries of the world, we should not forget those countries classified as "least developed countries" or LDCs and listed in ANNEXURE I.

As well as considered as being the poorest nations in the world, many are landlocked and totally dependent on others for their oil supplies. Poor or not poor the LDCs must also plan for fuel shortages.

4. LEGISLATION

Government regulations and the enforcement thereof is one way to have cooperation between Oil Industry and Government in establishing and maintaining strategic petroleum reserves. Strategic storage regulations differ substantially from country to country especially in the method of financing and the level of obligations. Governments differ in the extent to which the cost of strategic reserves are borne by the tax payer through a general revenue fund, or are passed on to the Oil Industry and the petroleum end users. The cost of a strategic oil storage programme should in the end, be payed for by those who benefit the most.

This may work well in the industrialised or developed nations of the world but will the oil companies in, for example, Botswana (a country of 1.2 million people) be willing to provide 60 days of storage to complement 30 days by Government even if the costs pass on to the consumer. They might, but some of these strategic petroleum stocks might be with their industrial consumers, at the oil companies depot, or even in the underground tanks at service stations. Since these petroleum stocks varying daily and some of the stocks are in a remote service station tank located in the Kalahari desert, can they really be considered part of the strategic petroleum stocks? How accessable are they in an emergency? This is the type of stockpiling I found when I first came to Southern Africa and examined storage agreements between Governments and Oil Industry (Refer Annexure II).

To want a strategic oil programme is not enough. The regulations must be realistic and enforceable. Governments should never assume that oil companies will cooperate just for good-will. They are in business to earn money for their shareholders and not to provide secured supplies for Government emergencies.

5. FINANCING A STRATEGIC PETROLEUM PROGRAMME

With proper planning and legislation, a strategic petroleum programme can come to pass without undo hardship to the consumers and to the Government's development budget. The answer, inpart, is the creation of a National Petroleum Fund, whose purpose is to meet the engineering and construction costs of the strategic storage facilities. A small levy or tax in the pump price is paid by fuel consumers to the oil companies, who monthly pay this levy into the Government's Petroleum Fund. (Refer ANNEXURE III). This fund should be managed by a private financial institution, such as a bank or other professional fund managers who have the knownhow to prudently invest the fund to retain the real value of the assets.

EXAMPLE

1. A country with a population of 2 million
2. Number of vehicles: 150,000
3. Annual fuel consumption: 450,000,000 litres
4. Assume an average pump price of 26 US cents/litre (100 US cents/gallon).
5. Petroleum fund levy at 2 US cents/litre
6. Annual Petroleum fund: 9 million US dollars

This accumulated Petroleum Fund will form the basis for building the storage facilities. Prudent investment of the fund can annually earn an additional 1.2 million US dollars.

There are three main alternatives for the actual financing of a strategic petroleum project.

- concessionary or soft loans
- export credit financing
- commercial financing

Concerning soft and export credit financing, I have limited myself to considering financing from the Nordic countries and the multilateral World Bank institution, i.e. The African development Bank and The African Development Fund. This limitation has been made because I am very familiar with the conditions of the Nordic institutions. However each country has its own soft and export credit financing system and offers conditions that are normally comparable with those from the Nordic countries, which are in accordance with the organisation for Economic Co-operation and Development (OECD) rules.

As you will see in Annexure IV, these loans have long repayment periods with low interest, making it possible for repayment using the National Petroleum Fund.

Of course financing the project through loans will result on a drain on Government finances and in the case of foreign loans increase overseas debt burdens. However, this disadvantage will be outbalanced by the fact that this financing will be cheaper than commercial financing.

6. LEVELS OF STRATEGIC STORAGE RESERVES

The rationale for establishing the level of fuel reserves within a country has in it a large element of judgement, based on experience. One of the prime factors is the elapsed time during an emergency that it will take trying to find a new supplier, and the delivery time from the source of supply to the consumer. For a coastal country, many believe 60 days should suffice. For a landlocked country, it might take 90 days or more for supplies to reach consumers.

It should be noted that during any serious disruption in supply the rationalisation of the usage of petroleum supplies will extend the number of days available. This is, ofcourse an intregal part of strategic fuel planning.

The fuel consumption rate based on the level of industrialisation, and the size of the transport network within a country are also key factors in judging the levels to be stored. Southern African countries mainly receive their petroleum products from South African refiners/marketers. My experience in that part of the world has shown that to develop an alternative source of supply, including contract agreements ordering and delivery will take between 60 and 90 days.

7. TECHNICAL ASPECTS

Once Government decides that there shall be a strategic petroleum storage programme, the next step is to engage an internationally recognized consultant to study locations and the suitability and cost of the various types of possible fuel storage facilities - aboveground steel tanks, underground rock caverns, solution mined salt caverns or underground concrete caverns. The consultants should be familiar with these various types of storage facilities and when and where they are most applicable and what is the most cost-effective for your application.

Conventional welded steel tank farms, came into existence in the early 1920 in the United States and have been used around the world.

The storage of petroleum underground had its beginnings during World War II in rock caverns in sweden. By 1969, the first large scale storage of crude oil in salt caverns started in Europe and today is extensively by used in the United States Gulf Coast region since it is the cheapest form of storage and very secure.

Converted mines and underground or semi-buried concrete caverns were used by the South Africans for strategic petroleum supplies when sanctions were applied in the mid - seventies.

Since salt caverns are limited to the United States, some parts of Europe and possibly some parts of the former Soviet Union, there has been a trend to study and build facilities in rock caverns. Cost trends for storage aboveground have entailed that it is now economic to construct caverns even in "poor - quality" rock. ANNEXURE V refers.

ANNEXURE VI tabulates fuel storage plant costs in Southern Africa in 1992 in US dollars.

The advantages of underground storage facilities are:

- fire and explosion hazards are more or less non - existent.
- very high safety factors also in terms of potential sabotage considerations.
- environmental problems limited.
- valuable surface areas are not occupied.
- operation temperature constant thereby eliminating breathing and evaporation losses.

It has been traditional in the oil and gas industry, especially in developing countries, for the design and construction of facilities to be let on a "turnkey" basis. This method of contracting has been used successfully for petroleum storage projects.

Government officers should be assigned to the project as an active part of the Project Management Team to gain invaluable experience that can only be provided by a competent engineering company. It is most important for developing countries to be able to receive, retain and absorb relevant technological knowledge and action should be taken to ensure that acquired skills would not be lost by transferring trained personnel to other jobs.

Wherever possible indigenous engineering capabilities and construction skills should be developed within the framework of the project through sub - contracting some of the work.

I trust this has given you some insight into the problems and solutions for strategic petroleum projects in the developing world.

ANNEXURE I

LIST OF COUNTRIES

BY CATEGORY AND REGION

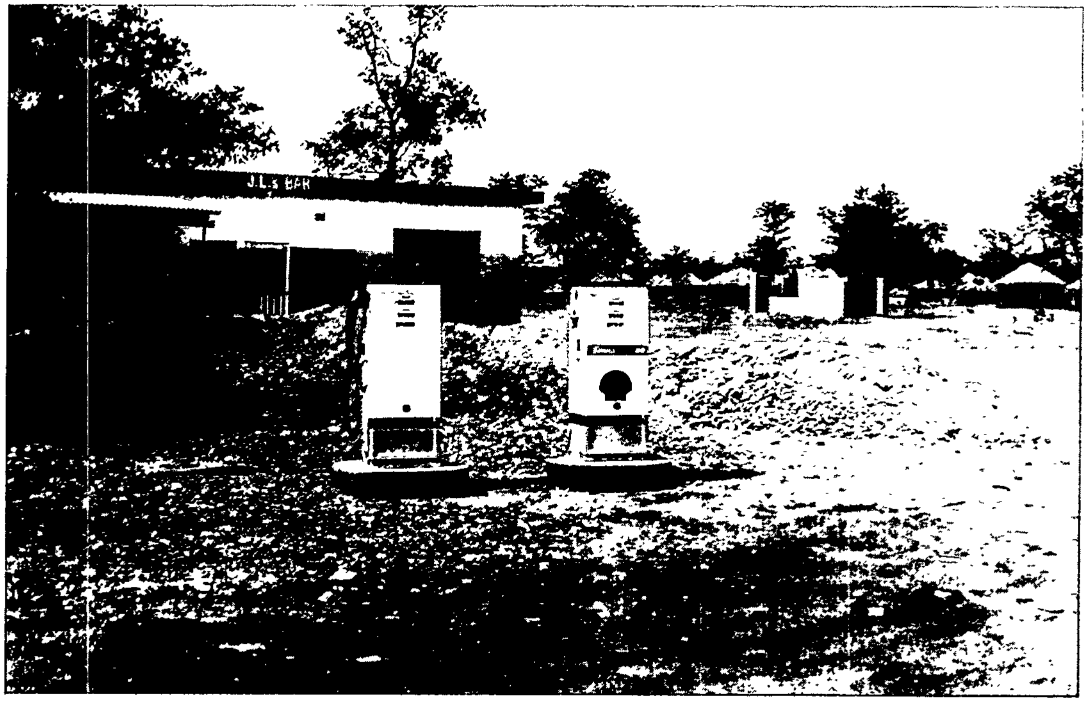
LDCs (Least Dev. Countries)	Africa	Asia and the Pacific	Latin America	Arab States
	Benin	Afghanistan	Haiti	Djibouti
	Botswana	Bangladesh		Somalia
	Burkina Faso	Bhutan		Sudan
	Burundi	Kiribati		Yemen
	Cape Verde	Lao People's Democratic Republic		
	Central Af. Republic			
	Chad	Maldives		
	Comoros	Myanmar		
	Equatorial	Nepal		
	Guinea	Samoa		
	Guinea Bussau			
	Liberia			
	Madagascar			
	Lesotho			
	Malawi			
	Mali			
	Mauritania			
	Mozambique			
	Niger			
	Rwanda			
	Sao Tome			
	Sierra Leone			
	Togo			
	Uganda			
	United Republic of Tanzania			
	Zaire			
	Zambia			

"As if" LDC	Africa	Latin America
	Angola	Nicaragua
	Senegal	

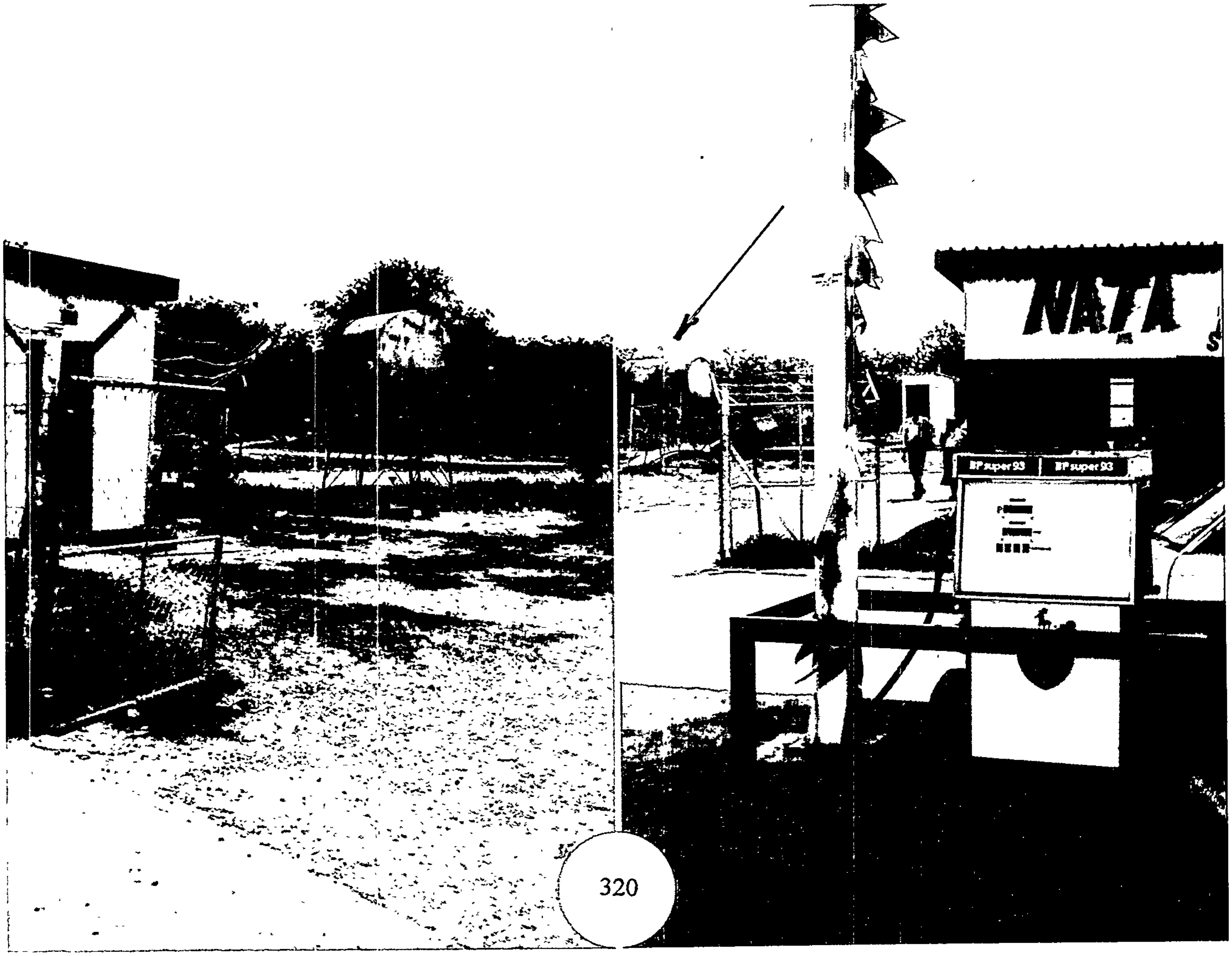
Other	Asia and the Pacific	Latin America
	Tonga	Bolivia
	Viet-Nam	

ANNEXURE II

THESE 4,500 AND 9,000 LITRE SERVICE TANKS ARE CONSIDERED PART OF STRATEGIC OIL STORAGE UNDER THE TERMS OF MANAGEMENT AGREEMENT.




CALTEX


NATA
BP super 93
BP super 93

ANNEXURE III

NATIONAL PETROLEUM FUND ORDER, 1992

(Published on 29th May, 1992)

ARRANGEMENT OF PARAGRAPHS

IN EXERCISE of the powers conferred on the Minister of Finance and Development Planning by section 25 of the Finance and Audit Act the following Order is hereby made—

Citation

1\. This Order may be cited as the National Petroleum Fund Order, 1992, and shall be deemed to have come into operation on the 1st February, 1986.

Establishment of Fund

2\. A special fund to be known as the National Petroleum Fund, hereinafter referred to as "the Fund", is hereby established.

Purposes of the Fund

3\. The purposes of the Fund are to—

(*a*) meet the engineering, construction and operational costs of the strategic storage facilities for Government fuel;

(*b*) purchase petroleum products for the Government's strategic oil stocks;

(*c*) stabilize prices charged by the oil industry;

(*d*) meet insurance premiums in respect of the insurance of Government's strategic oil installations and oil stocks.

Administration of the Fund

4\. (*a*) The Permanent Secretary, Ministry of Commerce and Industry, hereinafter referred to as "the accounting officer", shall be the public officer responsible for the administration of the Fund.

(*b*) The Minister shall appoint a management committee charged with determining the investment strategy and disbursement procedures of the Fund.

(*c*) The Minister may appoint an independent auditor to undertake audits of the Fund on such conditions as he shall in writing require.

(*d*) The management committee, shall, with the written approval of the Minister, cause the assets of the Fund to be prudently invested so as to retain the real value of the assets.

(*e*) The accounting officer may, with the written approval of the Minister, appoint a financial institution licensed in terms of the Financial Institutions Act, or a wholly owned subsidiary of such a financial institution, to undertake the day to day activities of the Fund. Cap 46:04

Payments into the Fund

5\. There shall be paid into the Fund—

(*a*) all monies received in respect of levies charged under the Control of Goods (Petroleum Products) (Levy) Regulations; Cap 43:07 Sub. Leg (*b*) such other money as shall be received from Government or which Government instructs to be paid into the Fund;

(*c*) income from the investment of moneys of the Fund.

Disbursements from the Fund

6. There shall be paid from the Fund —

(*a*) costs for the engineering, construction, and operation of the strategic storage, and distribution facilities for Government fuel;

(*b*) sums of money to the oil industry for the stabilization of prices in respect of petroleum products;

(*c*) such sums of money to the oil industry or Consolidated Fund as the Minister may from time to time determine;

(*d*) costs of the purchase of petroleum products for Government's strategic oil stocks;

(*e*) insurance premiums in respect of Government's strategic oil installations and oil stocks;

(*f*) management and audit expenses of the Fund;

(*g*) such other sums as the Minister may in writing approve.

Accounts of the Fund

7. (1) The accounting officer shall —

(*a*) keep and maintain proper accounts and records of the Fund;

(*b*) prepare in respect of the Fund for each financial year a balance sheet and statement of income and expenditure in such form and manner as the Accountant-General may approve;·

(*c*) at the time of submission of the balance sheet and statement of income and expenditure, submit to the Minister proposals for dealing with any surplus in the Fund;

(*d*) maintain an account in which shall be recorded all receipts into the Fund; and all disbursements from the Fund accounts shall be reconciled monthly.

(2) The balance sheet and statement of income and expenditure shall be included in the annual statement of the Fund of the Accountant-General to the Auditor-General in accordance with section 34(2) of the Finance and Audit Act.

Repeal of S.I. 45 of 1988

8. The National Petroleum Fund Order, 1988, is hereby repealed.

MADE this 15th day of May, 1992.

ANNEXURE IV

SOFT AND EXPORT CREDIT FINANCING

A. The Swedish Agency for International Technical and Economic Cooperation (BITS).
BITS co-operation is aimed at developing countries classified by the World Bank as low or middle income countries.
Financial Description
- Tenor: construction time + up to 10 years
- Interest: essentially none
- Fees: normal bank fees
- Security: Government guarantee.

B. The Nordic Investment Bank (NIB).
NIB provides financing on normal banking terms for investment projects of Nordic interest within and outside the Nordic countries. These loans are granted to credit worthy developing countries and countries in Central and Eastern europe.
Financial Description
- Tenor: Max. 5 + 15 years (normally 15 years)
- Interest: Market rate in respective currency
- Fees: Commitment fee 0.25 - 0.50% p.a. Management fee (sometimes)
- Comments: 15 - 20% of contract value originating from at least two Nordic countries. Possibility of co-financing with ADB.

C. Nordic Development Fund (NDF).
NDF is part of the Nordic cooperation in the area of development aid to poorer developing countries. Particular importance is attached to projects with a positive impact on the environment.
Financial Description
- Tenor: Max 10 + 30 years
- Interest: 0.75% p.a.
- Fees: Commitment fee 0.50% p.a.
- Comments: Max amount 5 million US dollar co-financing offered with World Bank Group, Regional Development Banks and NIB.

D. Swedish Export Credit Corporation (SEK) lending pertains mainly to the export financing of capital goods contracting assignments and consulting or service work.
Financial Description
- Tenor : Construction time + up to 10 years
- Interest: CIRR or market rate
- Fees: Normal bank fees
- Comments: Financing of Swedish exports
- Security: Government guarantee.

E. African Development Fund (ADF)
Mainly projects and technical assistance financing as well as studies. Loans and grants are directed towards African member countries.
Financial Description
- Terror: Construction time + 10 - 15 years
- Interest: market rate
- Fees: Normal bank fees
- Comments: Priority on project loans. Possibility of co-financing

F. African Development Fund (ADF)
Loans and grants are directed towards the poorer members of ADB.
- Terror: Construction time + max 50 years
- Interest: 0.75% p.a.
- Fees: Normal bank fees
- Comments: Priority on project loans with the possibility of co-financing.

ANNEXURE V

Here caverns can be built.

The geological prerequisites for constructing caverns exist all over the world. Today storage facilities are constructed in granite, gneiss, schist, limestone, sandstone and chalk. Cost trends for storage above ground have entailed that it is now economic to construct caverns even in "poor-quality" rock. In these cases special reinforcement work is required.

Naturally the local possibilities must be specially appraised in each particular case.

Different areas on the world map can be divided into four groups—depending on the ground conditions for cavern storage.

Red area group

Plentiful supply of suitable areas for cavern storage.

Yellow area group ≡

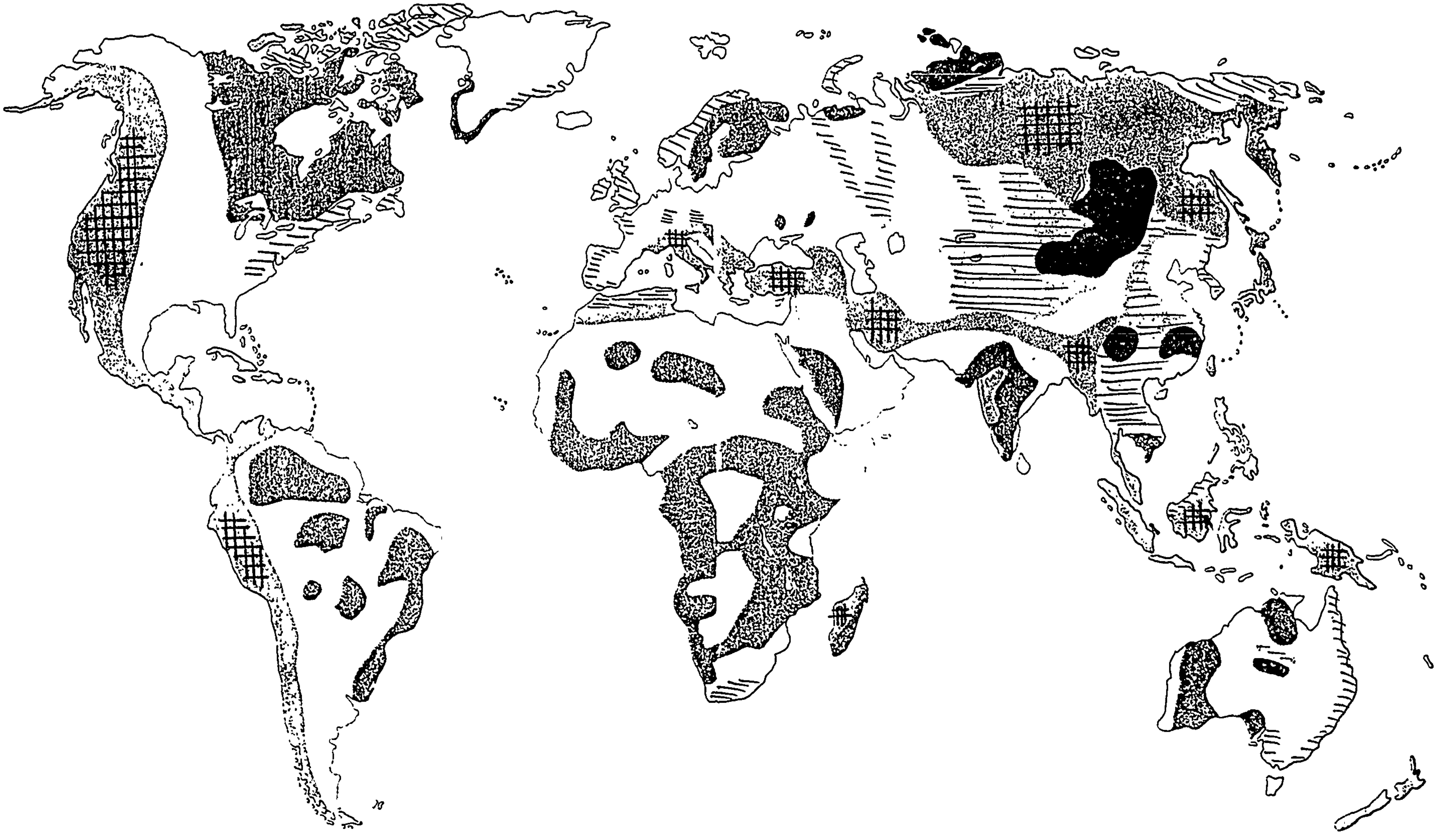
Good supply of suitable areas for cavern storage.

Green area group ▦

Fair supply of suitable areas for cavern storage.

Non-coloured group

Sparse but usable supply of suitable areas for cavern storage.



ANNEXURE VI

FUEL STORAGE PLANTS COSTS

* 1.	BOTSWANA	additional tanks only 3 x 2600 cubic metres.	221 USD/cm (35 USD/Bbl)
** 2.	LESOTHO	Grassroots Steel tank farm	315 USD/cm (50 USD/Bbl)
* 3.	BOTSWANA	New Oil Industry tank farm, Horizontal tanks, Armoured Rock Covered	870 USD/cm (138 USD/Bbl)
* 4.	BOTSWANA	Additional 1250 cm tank for existing Oil Industry tank farm	225 USD/cm (35 USD/Bbl)
** 5.	BOTSWANA	Grassroots Steel tank farm for 220,000 cm products	200 USD/cm (32 USD/Bbl)
** 6.	ZIMBABWE	Rock Cavern Storage for 360,000 cm products	143 USD/cm (23 USD/Bbl)
** 7.	BOTSWANA	Rock Cavern Storage for 220,000 cm products	109 USD/cm (17 USD/Bbl)
** 8.	SOUTHERN AFRICA	Grassroots - inground Concrete tanks	(136 USD/cm) (21 USD/Bbl)
** 9.	UNITED STATES	Salt Dome Storage Caverns	50 USD/cm (8 USD/Bbl)

* **Actual Cost**

** **Estimate**

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
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USE OF ASTM D5304 IN ASSESSING UNSTABLE DIESEL FUEL

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The storage stability, or the length of time a fuel can be stored, is of great concern to diesel fuel users. This paper reports on the use of the new ASTM accelerated test for storage stability by oxygen overpressure (D5304) to predict future storage life span of 63,000,000 gallons of a diesel fuel for U.S. Naval vessel use. This paper demonstrates the use of ASTM D 5304 at storage times of 16, 40 and 96 hours to accurately determine the length of time that this large quantity of diesel fuel could be stored at ambient temperatures before the maximum allowable amount of particulate contamination was reached.

INTRODUCTION

The Defense Fuel Supply Center (DFSC), Cameron Station, Alexandria, Virginia retained ownership of 1.5 million barrels of off-specification F-76 during the 1992-1993 time period. This fuel had originally been procured by DFSC using the military specification MIL-F-16884.[1] Although this fuel had passed specification requirements at the time of purchase, it rapidly showed signs of degradation when in storage.

Since the military conducts operations worldwide, it is necessary to store fuel at strategic locations for extended periods of time. The period of storage between production and usage varies greatly, depending upon tactical operations, therefore, there must be assurance that when the fuels are used they have not deteriorated during that time.

Storage quality is measured by the fuel's tendency to react with dissolved molecular oxygen to form undesirable products. These undesirable products can range from solid particulates and gums to highly reactive soluble fuel molecules of peroxides and acids. It is extremely important to the military that we include a test method within our procurement specification to address the predictive stability characteristics of the products at the time of production. Unfortunately, at the time DFSC had procured this particular F-76 product, the ASTM D 5304 (ASSESSING DISTILLATE FUEL STORAGE STABILITY BY OXYGEN OVERPRESSURE) had not yet been included in MIL-F-16884.

BACKGROUND

Beginning in 1992, the U.S. Navy and Coast Guard reported numerous problems during shipboard propulsion use of the suspect F-76. The complaints all indicated a degraded fuel product and were reported from various sources. This fuel was reported to be a dark product which had very fine black particulates. This increased particulate was clogging filters, causing high filter change-outs. Also, there were some instances of a drop in fuel supply pressure to main engines at full power.

These problems were not isolated cases, but confined to vessels which had refueled on the U.S. West Coast area supplied by one refiner. Test results for this fuel in October 1992 revealed a color rating of ASTM 3 by ASTM D150 and had variable levels of particulate content. The storage stability test by ASTM D 2274 (OXIDATION STABILITY OF DISTILLATE FUEL OIL) indicated that about half of the fuel tested failed. Therefore, if this fuel were stored for more than six months it would not achieve acceptable standards of stability.

Over the next six months, this fuel was closely monitored and the user problems increased. Since ASTM D 2274 indicated that much of this fuel would continue to degrade with time, with the combination of high existent particulates along with predicted additional particulates, it became evident that a "clean up" procedure would be necessary.

In November 1992, DFSC funded the Naval Research Laboratory (NRL) to assess the extent of the problem and the magnitude of the particulate levels at the fuel storage sites. In addition to evaluating the current existent solid contamination, the potential solid production was measured using the ASTM D 5304 test. Finally, the "clean-up" procedure was assessed in the laboratory by simulating the field operation of filtration of existing particulates and the stabilizer additive injection to prevent further degradation.

Because of results obtained during this vigorous field simulated laboratory test, DFSC and the U.S. Navy were able to successfully "clean-up" and issue acceptable product to shipboard vessels without jeopardizing the rate of filter changes and plugging of shipboard coalescers.

RESULTS

ASSESSMENT OF THE EXTENT OF THE PROBLEM AND THE MAGNITUDE OF THE PARTICULATE LEVELS AT THE STORAGE SITES:

Samples were assessed by a modified ASTM D2276 for particulate contamination. This modified method consisted of immediately removing a 250 mL aliquot from the well shaken original container and filtering through a pre-weighted nylon membrane filter (0.8 micron porosity and 47 mm diameter). The resulting filter weight gain was multiplied by four to place the weight on a per liter basis and corrected by subtracting a blank filter weight change (usually 0.1 mg/L). The pass/fail use limit for this test for NATO F-76 type fuel is 15 mg/L for U.S. Navy use.

The results in Table 1 represent the currently existent particulate amount in the tanks from storage site #1. This is only true if a representative sample has been taken. The difficulty in obtaining small representative samples from very large tanks is demonstrated by examining some of the results in Table 2 which gives the results from a second set of samples obtained from storage site #1 in February 1993. The values for tanks 7 and 13 in Table 2 are about 25% lower, while the value for tank 8 is about 100% higher. Although this demonstrates the problems of obtaining a representative sample, it does not change the overall interpretation of the results from both Tables 1 and 2 that almost all of the tanks sampled at storage site #1 have very high particulate contamination levels which are above the use limit established by the U.S. Navy. These levels can be compared with values obtained by a recent worldwide survey of 22 OCONUS F-76 fuel storage depots. The average particulate contamination level from all level samples was less than 2 mg/L.[2] To put the very low concentration of solid particulate in this fuel in the context of filtering very large volumes to remove the particulate, one can take the permitted solids value to 10 mg/L (ppm) and calculate that this is about 1.6 grams per barrel. Most Military fuel filters are qualified to be able to remove about 70 grams of solids per filter element at a cost of about $20 per element. Most of this data represents about 10-60 mg/L of solids. Thus, in order to filter 10 mg/L from 1,000 barrels would require about 20 filters at a cost of about $400. In order to filter 100,000 barrels of 10 mg/L solid would require 2,000 filters and a filter cost of about $40,000, while filtering 1,000,000 barrels would require 20,000 filters at a filter cost of $400,000. This represents about one cent per gallon additional cost. For 30 mg/L solid, this extra cost for filters would be three cents per gallon.

ASSESSMENT OF THE RATE OF FUTURE DEGRADATION IN INSOLUBLES AND COLOR AND THE USE OF STABILIZER ADDITIVES TO RETARD THIS DEGRADATION:

In addition to evaluating the current existent solids contamination levels above, the potential for future solids production was evaluated using the new ASTM D5304 test method. Using this test, a fuel is first filtered to remove all existent solids. Then, a filtered sample is heated at 90° C under a 100 psi oxygen atmosphere for 16 hours, cooled and then filtered to determine the amount of solids which formed during the accelerated oxidation test. The test conditions are roughly equivalent to the fuel being aged at room temperature for about 1 to 1.5 years in glass vessels under atmospheric air pressure.

Based upon results generated during the eight-year development of this new predictive storage stability test, it has been found that if a fuel does not exceed 1.5 mg/100 which is equal to 15 mg/L (i.e., 15 ppm) of filterable solids at the end of the test, then it can be considered a typical stable fuel suitable for bulk storage up to several years. Using this as a criterion for future additional particulate contamination, it can be seen in Tables 3 and 4 that most of the fuel at storage site #1 exceeds this upper limit.

The use of these predictive data may be further clarified by examining Figure 1. Using the criteria of future solids levels at 1.5 mg/100mL and 3.0 mg/100mL 15 and 30 mg/L (or ppm), one can effectively rank each of the tanks shown in both figures. Storage site #1 tanks 14, 34, and 10 were judged to have an effective future life of about three years, tank 7 had a future life of less than one year, tanks 8 and 36 should be consumed before six months and tanks 13 and 12 should be consumed immediately.

An additional test for even further future storage of these same samples was run by extending the test time of ASTM D5304 from 16 hours to 40 hours (on separate samples). The data for the fuels thus tested indicate no slowing of the increase of particulate production after very long storage times at ambient temperature (see Table #5). Similar data was also obtained from the other three storage sites.

Based on all of the above data, DFSC decided to attempt a filtration clean up of most of the fuel at storage site #1, followed by the addition of an after-market stabilizer additive. The predictive storage stability test data allowed DFSC to designate batches of fuel for immediate consumption all the way up to storage for three years, if necessary.

The new predictive test ASTM D 5304 was used to determine any future degradation of the fuel. As seen in figures 2-4, this fuel continues to degrade in a linear fashion. This behavior is quite unusual in that most fuels either never degrade or tend to degrade mainly in the first one to two years, followed by significant reduction in degradation.

Most of the F-76 samples/fuels were greater than six months old and thus the effects of adding a stabilizer at typical concentrations of about 24 ppm (w/v) would be expected to be much lower than adding the additive during the production at the refinery. There is a beneficial effect by adding a typical additive and the shelf life of the treated fuel would be expected to increase about 50 percent.

ASSESSMENT OF THE FIELD OPERATION OF FILTRATION/ADDITIVE INJECTION TO CLEAN UP THE PROBLEM F-76 FUEL

It was decided in order to "clean up" the fuel, it must be passed through a FAUDI precoat filtration system. This system consisted of diatomaceous earth pre-coated filters coupled with a micronic filter system. Downline of the filtration system, a stabilizer additive injection system was installed to inject 24 ppm of the additive.

The laboratory samples collected to establish the effectiveness of this procedure were:

> A representative all-level sample of fuel from the feed tank;
>
> A line sample just before the FAUDI pre-coat filter system;
>
> A line sample just after the FAUDI filter;
>
> A line sample just after the downstream micronic paper filter and stabilizer injection; and
>
> An all-level sample from the full holding tank at the end of the process.

Microscopic examination of the particulate contamination from the post FAUDI filter line sample indicated that a significant part of the weight was due to diatomaceous earth from the filter. It was estimated that the FAUDI filter probably was removing about half of the 15 mg/L of original solid contamination but adding about an equal weight of diatomaceous earth. From the viewpoint of settling out of fuel, the diatomaceous earth (density about 2.2 g/mL) would settle much more rapidly than the organic sludge contamination (density about 0.9 g/mL). However, from the viewpoint of potential abrasive harm to pumps, injectors and engines, the diatomaceous earth would be much worse than an equal weight of non-abrasive organic sludge contamination.

The final sample after additive injection after micronics paper filtration gave a particulate contamination level of about 12 mg/L. This 12 mg/L sample also showed significant diatomaceous earth contamination. This means that either break-through of the micronics paper filter has occurred or that fines from the diatomaceous earth are capable of passing through the intact filter.

In all cases, the addition of 24 ppm of the additive was quite beneficial regarding the future storage stability as gauged by long and very long term ASTM D5304 accelerated tests. The effect of the additive was essentially to double the future storage life of this fuel. Unfortunately, this would mean that instead of problems in the 6 to 12 month future time frame, the fuel would begin to exhibit problems in the 12 to 24 month time frame. That is, the additive slowed the solids formation rate by half but did not stop it.

CONCLUSIONS

Using the new ASTM D5304 accelerated storage stability test, it was possible to accurately assess the storage life of most of the bulk tanks containing then up to 1.5 million barrels of product. This allowed DFSC to initiate an orderly issue schedule for most of the product which minimized problems for the U.S. Navy.

The ASTM D 5304 test also allowed DFSC to make a decision to add the storage stabilizer additive as part of the clean up operation. Finally and most importantly, the ASTM D5304 test was instrumental in convincing the refinery to change its processing so that F-76 fuel produced subsequent to January 1993 would be stable for long term storage. Since this storage instability was the major cause of high levels of sludge/solid buildup in the bulk fuel tanks, this means that future bulk stored samples should not exhibit this problem (which is manifested by the particulate contamination ASTM test D2276/D5452).

Regarding the use of diatomaceous earth coated (pre-coat) filtration to clean up high concentrations of existent solids (greater that 10 ppm or mg/L), it was found from laboratory tests that this method should not be used for F-76 diesel type fuels. It is important to note that this clean up technique has been quite successful at several field sites when used by DFSC in the recent past. However, all of these uses to date have involved jet fuel. These previous clean up processes use a particular diatomaceous earth specifically for jet fuels, which is not specified for diesel fuels. This is the probable reason for the current problems in clean up using this method. In addition, this diesel fuel had very high levels of contamination and thus presented a much more serious challenge to any type of filtration clean up method.

It was found that during the movement of fuel through the Pacific supply line, the high levels of particulate were essentially diluted by other cleaner fuels in the system. This dilution factor, coupled with the filtration/injection procedure,successfully cleaned up the fuel to an acceptable particulate level. Most of the fuel was issued and consumed by November 1993.

(The views expressed in this article are those of the author and do not reflect the official policy or position of the Department of Defense or the U.S. Government.)

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FIGURE 1

STORAGE STABILITY BY ASTM D5304

Samples From Storage Site #1 (Nov. 92)

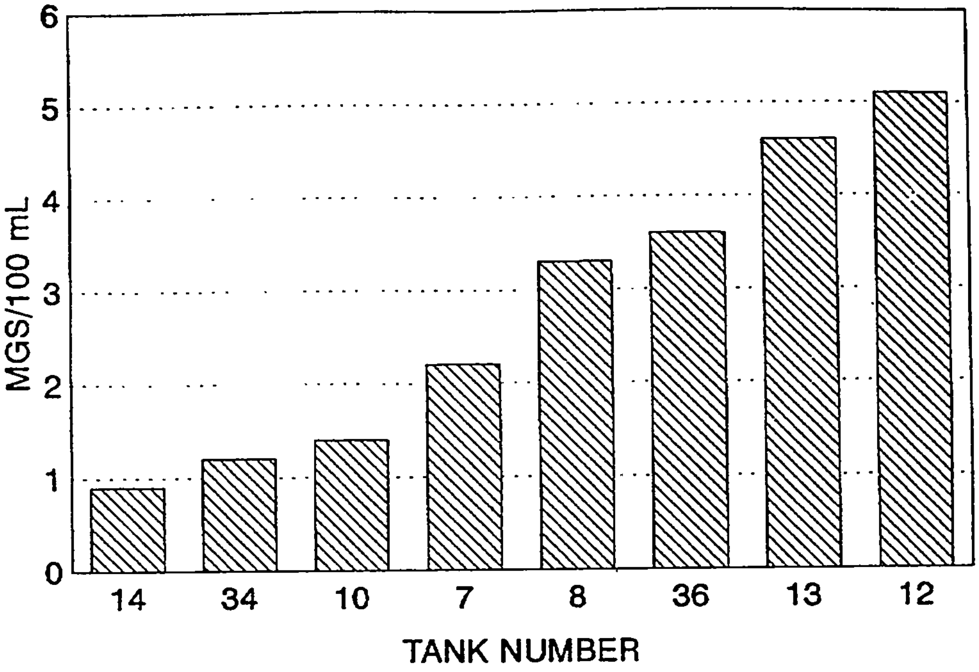
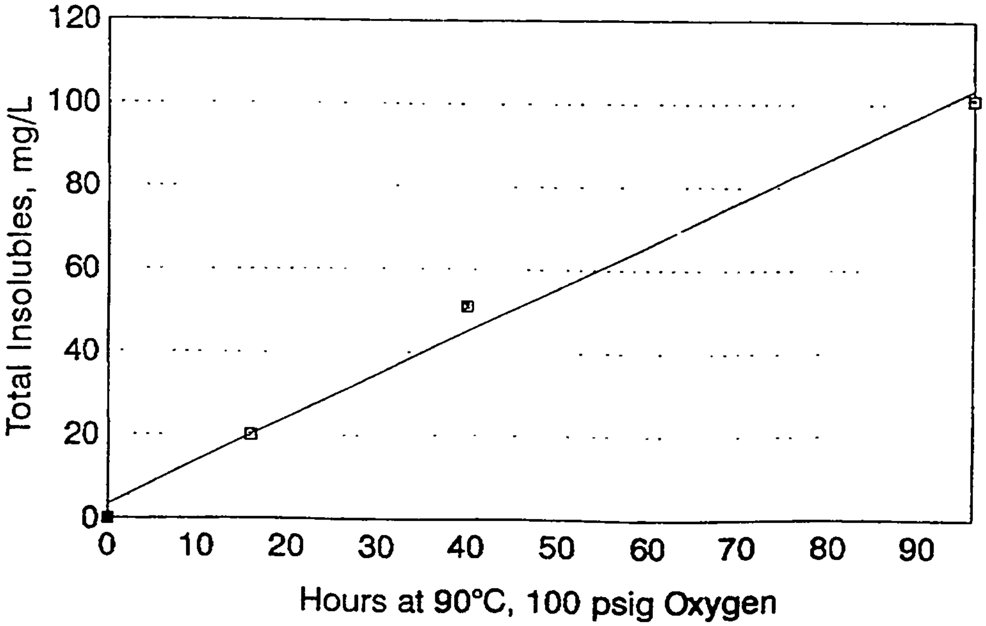


FIGURE 2

D5304 RESULTS

Storage Site #1, Tank #7

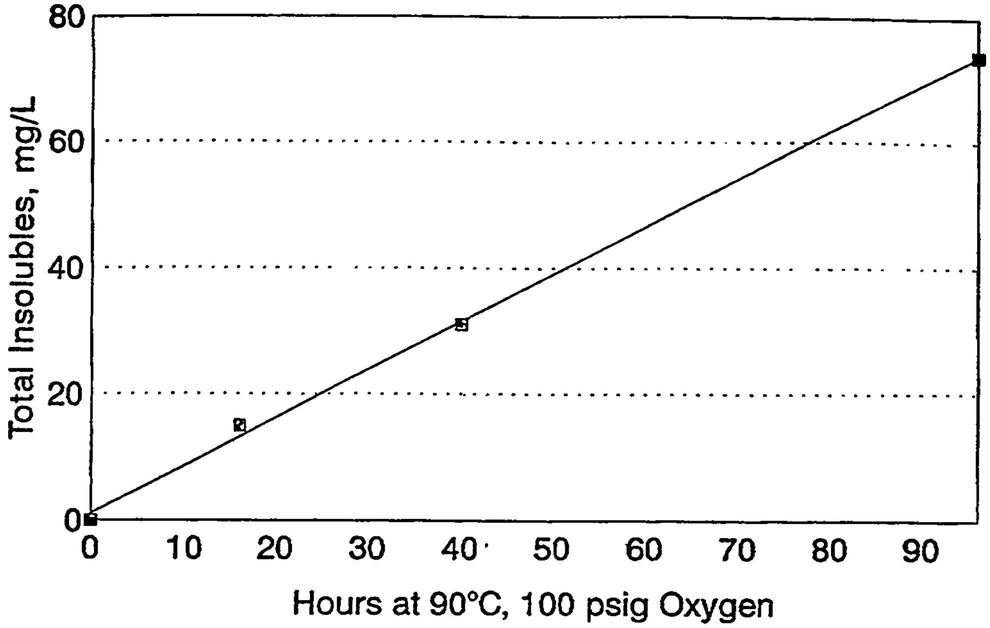


R squared = 0.991

FIGURE 3

D5304 RESULTS

Storage Site #1, Tank #16

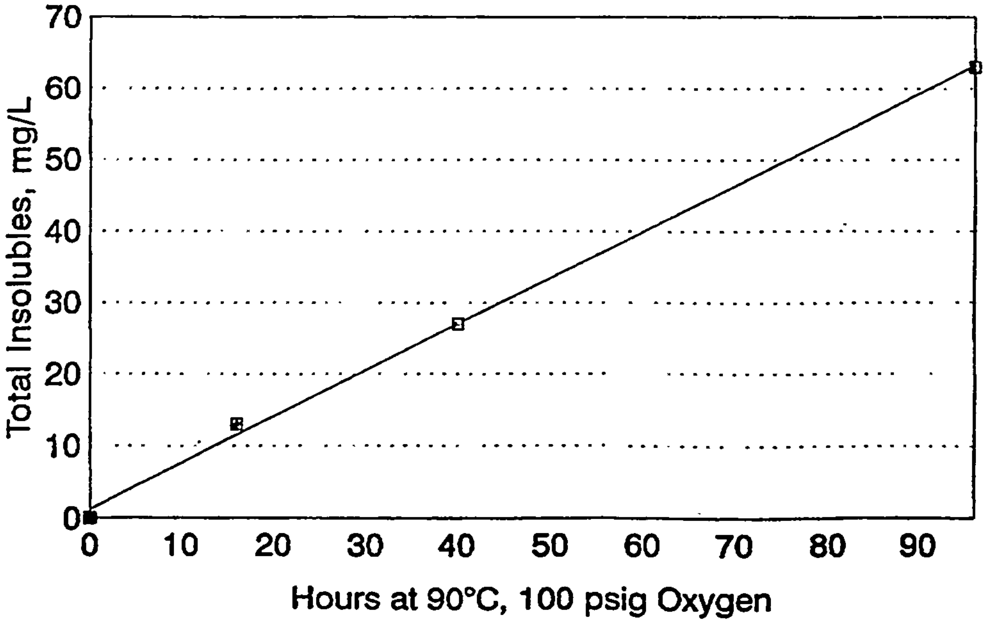


R squared = 0.999

FIGURE 4

D5304 RESULTS

Storage Site #1, Tank #9



R squared = 0.098

Table 1

PARTICULATE CONTAMINATION BY ASTM D5452 (MODIFIED)

250 mLs of sample filtered

Samples From Storage Site #1
November 1992

Tank Number	Sample Level (from bottom)	Contamination mgs/L
7	10'	32.0
8	10'	16.4
10	10'	11.6
12	8' Tap (Lowest)	38.8
13	10' Tap (Lowest)	32.8
14	75'	38.8
34	All Level	16.8
36	All Level	20.0

Table 2

PARTICULATE CONTAMINATION BY ASTM D5452 (MODIFIED)

250 mLs of sample filtered

Samples From Storage Site #1
February 1993

Tank Number	Sample Level (From bottom)	Contamination mgs/L
7	10'	26.0
8	10'	30.4
9	10'	22.0
10	10'	15.2
13	10'	23.6
16	10'	11.6
36	All Level	14.8
37	All Level	19.2

Table 3 (also see Fig. 1)

STORAGE STABILITY BY ASTM D5304
16 hour stress time

Samples From Storage Site #1
November 1992

Tank Number	Contamination mgs/100 mL
7	2.2
8	3.3
10	1.4
12	5.1
13	4.6
14	0.9
34	1.2
36	3.6

Table 4

STORAGE STABILITY BY ASTM D5304
16 hour stress time

Samples From Storage Site #1
February 1993

Tank Number	Contamination mgs/100 mL
7	2.0
8	3.9
9	1.3
10	1.7
13	3.7
16	1.5
36	2.9
37	0.9

Table 5

STORAGE STABILITY BY ASTM D5304
40 hour stress time

Samples From Storage Site #1
November 1992

Tank Number	Contamination mgs/100 mL
7	4.0
8	7.3
12	9.0
13	9.7
14	1.1

5th International Conference
on Stability and Handling of Liquid Fuels
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METAL-DEACTIVATING ADDITIVES FOR LIQUID FUELS

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ABSTRACT

The metal-deactivating and the antioxidant properties of 1-phenyl-3-methyl-pyrazolone-5 derivatives have been investigated both in the model reaction of low temperature oxidation of ethylbenzene and in gasoline oxidation. The study of the ability of these derivatives to reduce the catalytic effect of copper naphthenate demonstrates that they are promising as metal deactivating additives for light fuels. Some of the pyrazolone compounds appear to be of special interest for the long-term storage of liquid fuels due to their action as multifunctional inhibitors.

INTRODUCTION

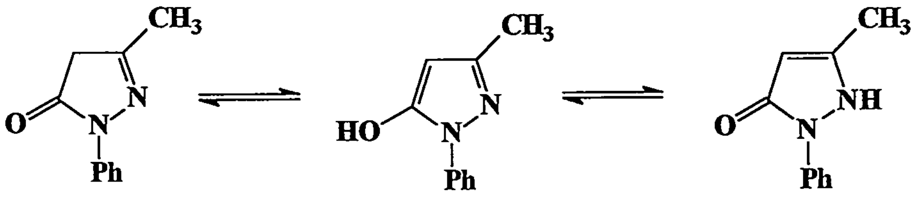
The problems concerning the fuel stability during their long-term storage and operation have been the subject of intense research in recent years[1-3]. Increased emphasis is being placed on the development of ecological nonmetal-containing multifunctional additives for various fuels. Of special interest are compounds that may function as a multidentate ligand to chelate copper and exhibit radical-scavenging properties[4]. The conventional packages for light fuels comprise besides the antioxidant additive a metal-deactivating one. The Schiff bases, i.e. the condensation products of salicylic aldehyde with polyethylenepolyamines[5,6] derivatives of 8-hydroxyquinoline, pyridinecarboxylic acids[1] are among the most popular metal- deactivating additives. A problem related to their utilisation is their low thermal stability which may be of concern for the stabilisation of fuels and lubricating oils under more severe operational conditions. Acylpyrazolone derivatives being polyfunctional compounds are widely used as chelate reagents in the analytical practice. These compounds possess high complexion ability which makes quite possible their using as metal deactivating additives for various lubricants.

The aim of this paper was to assess not only the reducing properties of some acyl pyrazolone derivatives towards the catalytic effect of copper, but also their efficiency as radical scavenging agents during gasoline oxidation and in model oxidation system.

EXPERIMENTAL

1-Phenyl-3-methyl-pyrazolone-5 derivatives were synthesized according to procedure described in Ref.7. The pyrazolone derivatives which have been the subject of the present study are presented in Figure 1.

It is known that these derivatives are used mainly for the production of medicinal compounds and they are highly soluble in water. Their ability to tautomerize is shown below. The tautomeric forms I and III are most the probable species in nonpolar medium as gasoline/ethylbenzene.



I II III

The radical-deactivating properties were assessed by the duration of the induction period (τ_{ind}) and the metal-deactivating properties by the degree of the reduction of initiation rate (W_i) during the oxidation of ethylbenzene/gasoline containing copper naphthenate as initiating additive.

The efficiency of the pyrazolone derivatives was evaluated by applying two test methods:

Test A - gasoline oxidation

The investigations were carried out in autoclave equipment as described earlier[8]. Two gasoline samples A-86 and A-86p have been studied. The base sample A-86 contains 50 % catalytically cracked fraction, 0.2 % wt. Pb as ethylate and 0.6 % wt. dyer. This gasoline sample has been additionally subjected to purification in order to eliminate the metal ions and the natural macromolecular compounds, and thus sample A-86p was obtained. For this purpose 1 l gasoline was passed through a column packed at the bottom with silica gel HS_{254} and HS_{60} (Merck) - 20 g. and at the top with silica gel HS_{254} (40 g.) previously treated by bis-(4-carbonyl-pyrazolone-5)-p-phenylene (2.5 wt % with respect to silica gel).

Test B includes a model oxidation reaction of ethylbenzene at 353 K, P = 0.1 MPa in the presence of azobis-isobutyronitrile (AIBN) as radical initiator and copper naphthenate (CuNf) as a source of soluble copper ions. Neat ethylbenze was purified according to the procedure in Ref. 9. The initiator AIBN was used after recrystallization from ethanol, acetone and benzene. Copper naphthenate was synthesised and purified as described in Ref.10. The rate of oxygen absorption was measured in manometric apparatus [11].

RESULTS AND DISCUSSION

Test A: The results from the oxidation of gasoline A-86 and A-86p in the presence of the pyrazolone additives DM-3 -DM-8 are given in Table 1. The inhibiting properties of the compounds studied are evaluated by comparing the value of the induction period with that of the typical radical acceptor of phenolic type -4-methyl-2,6-di-tert-butylphenol (further denoted as ionol).An essential difference in the behaviour of the pyrazolone derivatives towards the oxidation of the base gasoline A-86 and the purified one A-86p has been observed. All compounds tested are not effective in scavenging of the active free radicals generated in the course of the oxidation of A-86p (τ_{ind} is the same as τ_{ind} of the pure gasoline)

However, the oxidation of A-86 is found to be successfully inhibited by additive DM-4 (with terephthalic bridge between the pyrazolone cycles) and its antioxidant activity is similar to that of ionol (τ_{ind} = 238 min for DM-4 and 236 min for ionol, respectively). The additive DM-8 which has an analogous structure to that of DM-4, but without possibility for\ conjugation between the two pyrazolone cycles does not manifest any significant inhibiting properties - the induction period (168 min) is the same as without it (160 min)

On the basis of the kinetic data the rate of the thermal initiation for the both samples and the concentration of the natural inhibitor can be estimated:

$\tau_1 - \tau_2 = f\,[C_o]/W_i$ 1)

where: τ_1 is the induction period of the gasoline oxidation in the presence of additives in sec.;

τ_2 is the induction period of gasoline without inhibitor;

f is the stoichiometric coefficient of inhibition showing the number of free radicals deactivated by a molecule inhibitor;

$[C_o]$ is the initial concentration of the additives, mol/l ;

W_i is rate of initiation, mol./l. s .

For A-86p gasoline the value of W_i is found to be $6.1.10^{-8}$ mol./l .s and the concentration of the natural inhibitor = 1.4 10^{-4} mol./l.s. For A-86 these parameters have the following values: W_i = 8.8 . 10^{-8} mol./l .s and 4.2 10^{-4} mol./l . These data show that the " purified" gasoline sample A-86p practically does not contain natural inhibitor (its concentration is reduced almost three fold). From the other side, the reduction in the value of W_i points also to the removal from the stock gasoline of components possessing initiating properties. The data suggest that the mechanism of action of the tested pyrazolone derivatives during the oxidation of the both gasoline samples is more complex and requires further research. Another interesting and at the present state unexplained observation is the behaviour of the most efficient antioxidant additive DM-4 (with respect to the oxidation of the base gasoline sample A-86) during the oxidation of A-86p which does not contain Pb compounds, artificially introduced nitrogen-containing dyers, natural high molecular compounds, etc. It does not exhibit any ihibiting properties (τ_{ind} = 72 min and 187 min for ionol, respectively). It could be assumed that the pyrazolone additive either interacts with some of these components resulting in the formation of more efficient antioxidant or forms synergistic mixtures with them.

The stoichiometric coefficient of inhibition of DM-4 (f = 2.1) has been determined by applying eqn.1 and is found to be similar to that of ionol

In Table 2 are presented the results of the study on the metal-deactivating properties of the pyrazolone derivatives. As a standard metal-deactivator we have used N,N-disalicylidene diethylenetriamine (DM-2) whose mechanism of action has been studied earlier [8,12]. It can be seen that the additives DM-4 and DM-8 demonstrate high complexing ability towards copper ions thus reducing its catalytic activity in the promoted gasoline oxidation. The value of the induction period in its presence is similar to that of the standard

DM-2 additive. In addition the results of the oxidation of gasoline with DM-4 which has been kept for 24 hours followed by filtration reveal an unusual increase in τ_{ind} (215 min for reaction B against 170 min for reaction A, respectively) and the stoichiometric coefficient of inhibition estimated by eqn.1 amounts to 51.2. This suggests that the formed copper complex of this derivative appears to be effective antioxidant compound. Most probably, the increased efficiency observed in reaction B is due to the better dissolving of the polar pyrazolone additive with the time (the equilibrium is shifted to tautomers I and III) and thus its effective concentration is increased in the non polar medium.

Test B- oxidation of ethylbenze.

The data obtained from the gasoline oxidation provoke us to check whether these compounds can be used both as antioxidant and metal-deactivating additives. Another goal of the present research as to find more simple, reliable and quick test method for preliminary evaluation of their multifunctional effect. For this purpose, we have carried out a model low temperature oxidation reaction of ethylbenzene and tried to characterise thie complex inhibiting action by performing two model reactions: reaction A and reaction B.

Reaction A comprises the oxidation of ethylbenzene in the presence of AIBN and the compounds studied (Table 3).The rate of the initiation was determined in the presence of ionol whose f is equal to 2. The radical-scavenging properties of the pyrazolone derivatives were evaluated on the basis of the experimentally determined induction periods and are characterised by the value of f. Some of the compounds, i.e. DM-5, DM-9 and DM-10 appear to be efficient radical acceptors with f similar to that of ionol. Taking into consideration the various tautomeric forms of the acyl pyrazolone compounds their deactivating properties towards free radicals might be due: for tautomer I- to electron transfer; for tautomer II - to the hydrogen abstraction from the hydroxy group and for tautomer III, which in our opinion is the most probable reactive species in the system stidied, to the presence of sterically hindered NH group. The effect of the structure of these derivatives on their inhibiting properties could be also explained by the changes occurring in the equilibrium constant of this tautomerism.

Reaction B - In order to assess the metal-deactivating properties of the pyrazolone derivatives we have carried out the oxidation of ethylbenzene (353 K) both in the presence of AIBN and copper naphthenate as a source of soluble copper ions. The rate of the initiation due to the presence of copper naphthenate (W_i^{CuNf}) was determined by subtracting from the value of the total rate of the initiation (ΣW_i, calculated by the method of the inhibitor -Table 4) the value of initiation rate due to the presence AIBN (W_i^{AIBN} determined in reaction A, Table 3). Taking into consideration the value of f (from Table 3) and the experimentally obtained τ_{ind} we have estimated the rate if the initiation in their presence (W_i^B)). Subsctracting from these values the value of (W_i^{AIBN}) we obtain the rate of the initiation which is due to the remained (noncomplexed) copper ions. In order to compare the metal-deactivating properties of the various pyrazolone derivatives with that of the standard (DM-2) we have introduced a parameter MDA which is given by the following expression:,

$$\text{MDA}\ \% = 100 - [(W_i^B - W_i^{AIBN}) / W_i^{CuNf}].100$$

where: W_i^B is the initiation rate given in Table 4

W_i^{AIBN} is equal to 1,33. 10^{-6} mol/l.sec

$W_i^{CuNf} = \Sigma W_i - W_i^{AIBN}$ and is equal to 2,47. 10 -6 mol/l.sec

This parameter shows the degree of the reduction of the initiation rate with copper naphthenate in their presence and is a criterion of the copper-deactivating efficiency of the compounds studied. The data of Table 4 reveal that some of the pyrazolone derivatives possess metal-deactivating properties similar to those of DM-2. Among them, the additives DM-4, DM-14 and to a some extent DM-12 show remarkable metal-deactivating efficiency and are superior to the standard additive. Evidently, the various bridges between the pyrazolone cycles affect this parameter. However, the elucidation of this effect needs some more experimental evidences which will be the subject of future investigations.

The low values of the rate of the initiation obtained in the presence of the additives DM-4 and DM-14 (W_i^B = 0.61. 10^{-6} mol./l.s and 0.70.10^{-6} mol./l.s, respectively) suggest that the formed copper complexes of these additives are efficient radical acceptors during the ethylbenzene oxidation. These data support the results of test A with respect to the behavior of DM-4. Generally, the data of Table 4 reveal that although some of the pyrazolone derivatives are not efficient antioxidants (as their f values show) the additives DM-4 and DM-14 manifest excellent multifunctional action in the presence of soluble copper and are very promising as antioxidant additives.

CONCLUSIONS

1. The model oxidation reaction of ethylbenzene can be successfully used for preliminary evaluation of the antioxidant and metal-deactivating properties of various compounds.

2 . Some of the pyrazolone derivatives, as DM-4, DM-12 and DM-14 manifest good deactivating properties towards copper.

3. The additives DM-4, DM-12 and DM-14 show both high antioxidant potential and significant metal-deactivating properties and appear to be promising as multifunctional inhibitors for the long-term storage of liquid fuels.

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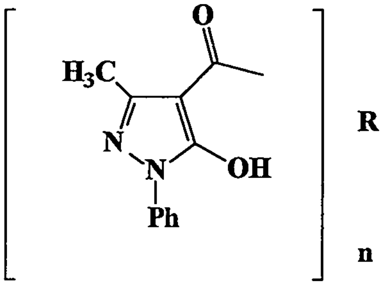


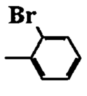
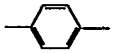
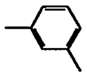
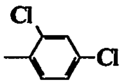
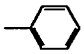
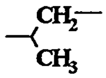
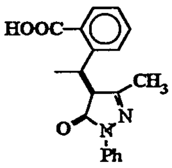
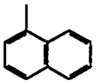
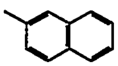
compound	n	R
DM-3	1	
DM-4	2	
DM-5	2	
DM-6	1	
DM-7	1	
DM-8	2	$-CH_2-CH_2-$
DM-9	2	
DM-10	1	
DM-11	1	
DM-12	1	
DM-13	1	$-C_{11}H_{23}$
DM-14	1	$-C_{15}H_{31}$

Figure 1. Structure of the acyl pyrazolone derivatives studied.

Table 1. Inhibiting properties of pyrazolone derivatives during the oxidation of gasoline A-86 and A-86p at 393 K, P O_2 = 1,0 MPa, $[C_o] = 2.10^{-4}$ mol/l.

No	Additive	A-86, τ_{ind}, min	A-86p, τ_{ind}, min
1.	-	160	78
2.	ionol	236	187
3.	DM-3	140	77
4.	DM-4	238	72
5.	DM-6	148	80
6.	DM-7	146	78
7.	DM-8	168	72

Table 2. Metal-deactivating properties of pyrazolone derivatives during the oxidation of gasoline A-86 at 393 K, P O_2 = 1,0 MPa, $[C_o] = 1.10^{-4}$ mol/l.

No	Additive	Reaction A, τ_{ind}, min	Reaction B, τ_{ind}, min
1.	-	40	40
2.	DM-2	170	170
3.	DM-3	44	65
4.	DM-4	162	215
5.	DM-6	44	52
6.	DM-7	42	59
7.	DM-8	152	172

Table 3. Kinetic data of ethylbenzene oxidation in the presence of pyrazolone derivatives at 355 K, P O_2 = 0,1 MPa, $W_i = 1{,}33.10^{-6}$ mol/l.sec.

Additive	Concntr. mol/l.10^3	τ_{ind}, min	f
DM-2	4,0	6	0,12
DM-4	2,0	16	0,5
DM-5	0,5	10	1,6
DM-9	1,0	21	1,7
DM-10	1,0	17	1,4
DM-11	1,0	9	0,7
DM-12	4,0	19	0,4
DM-13	4,0	10	0,12
DM-14	4,0	11	0,23

Table 4. Kinetic data of ethylbenzene oxidation in the presence of pyrazolone derivatives, AIBN and CuNf at 355 K, P O_2 = 0,1 MPa, W_i^{AIBN} = 1,33.10^{-6} mol/l., [CuNf] = 5.10^{-5} mol/l

Additive	Concntr. mol/l.10^3	τ_{ind}, min	W_i^B mol/l.sec .10^6	MDA in %
DM-2	4,0	6	1,30	100
ionol	1,0	9	3,70	-
DM-4	1,0	14	0,61	>100
DM-5	0,5	7	1,70	84,4
DM-9	1,0	8	1,77	81,3
DM-10	1,0	12	1,94	74,3
DM-11	1,0	6	1,90	76,0
DM-12	1,0	5	1,30	100
DM-13	4,0	12	1,10	84,4
DM-14	4,0	18	0,70	>100

5th International Conference
on Stability and Handling
of Liquid Fuels

Rotterdam, the Netherlands, October 3 - 7, 1994

The EBV Quality Prediction System (EQPS)

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Chairman, Ladies and Gentlemen,

An oil product is said to be ageing, if over time it changes appearance, performance characteristics or environmental properties. Ageing - and so is quality - is a summary term - embracing many influencing factors and observed behaviours. Ageing quality is a function of inherent or added immunity, environmental factors or exposure and of course age. Inherent factors are themselves a function of raw materials from which the product was made and the manufacturing processes used in the refinery.

WHAT IS OIL QUALITY DETERIORATION

$$Qt = f\ (I_i,\ E_j,\ T)$$

$$I_i = g\ (M,\ S)$$

CONDITIONS

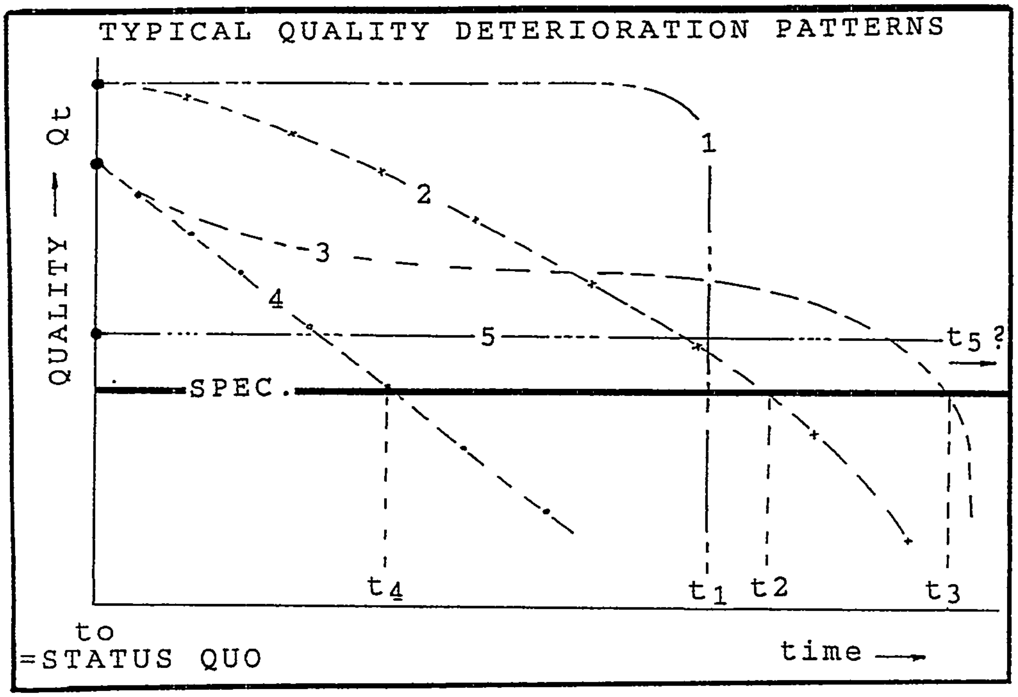
$$Qt = \left\{SPEC_k\right\}_{k=1,n} + \left\{R_{k_t}\right\}_{k=1,n}$$

$$R_{k_2} - R_{k_1} \geq 0$$

Q_t = product quality at time t
I_i = Inherent ageing susceptibility and protection factors i
E = environmental factors j
T = time since virginity
M = manufacturing process
S = source material (e.g.crude)
$SPEC_k$ = quality specification indicators k
R_{k_t} = quality reserve at time t
t_2 = target life time (date)
t_1 = current date

$\{\ \}_{i=1,n}$ = set of all indicators 1 to n

Quality is generally expressed by a set of quality indicators (measurements), which are themselves constrained by specified max or min values. If measurements do not meet specification values there is a positiv or negativ quality reserve. If quality indicators change with time, a fresh product should have a quality reserve, whose size establishes the storage life span of a product.

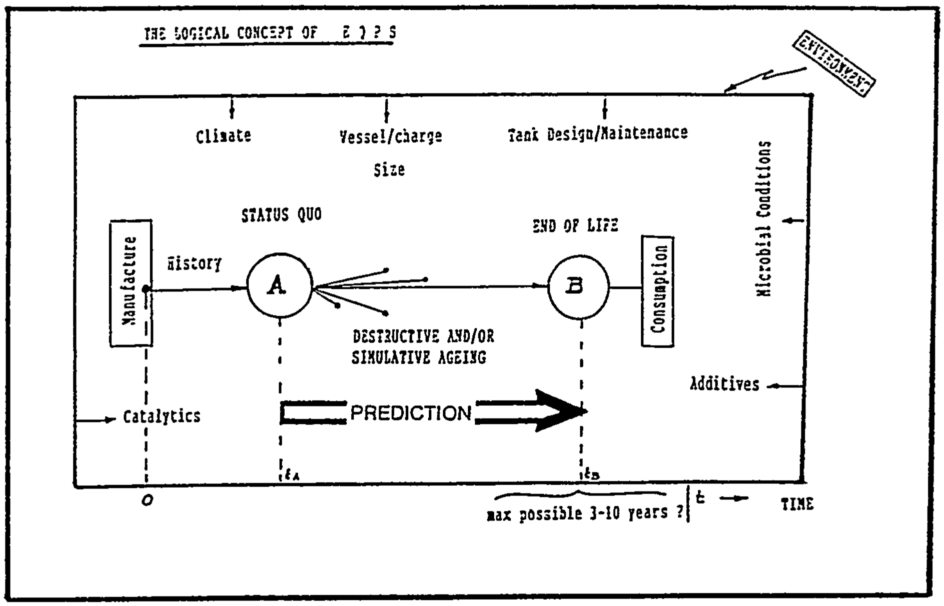

TYPICAL QUALITY DETERIORATION PATTERNS

Product quality - used here as the summary term - changes with time along many possible and remarkably different paths, some of which can be observed well in strategic stocking of the "first generation", which stored mainly hydroskimming type products (FDO (Denmark) and Berlin Senatsreserve stocks).

EQPS is an attempt to predict the quality change = ageing through analysing as many as possibly influencing factors, whose effects often can not be well explained but qualititatively or even quantitatively measured.

Let me define ageing in another way:

Product starts ageing when it is created i.e. through manufacturing where its inherent qualities are "laid down". Normally it gets into our (EBVs) hands later, when it has reached the "status quo" position. At that point we test it, sometimes by simulative tests (often "product destroying" methods like forced oxidation) which normally do not predict



future ageing behaviour well. On the path from creation to the final consumption external factors like climate, vessel size (average temperature), tank maintenance, microbes, additive and all sorts of other catalytic effects influence the ageing paths, retard it or accelerate it. The objective of EQPS is to capture as many as possible of such external factors and join them with the inherent product quality into a prediction of the most likely lifetime.

What looks so simple as a general formula shown above becomes extremely complicated if one would attempt to build a mathematical model joining all the factors in a set of reaction kinetic, chemical/physical and energy balance describing equations. Even if we could know all those equations, we could not really fill them with data. The dream of having one simple ageing equation will possibly never be fulfilled.

AGEING THEORY/MODEL BEHIND EQPS

o VARIOUS DIVERSE THEORIES, SOMETIMES CONTRADICTIVE

- TAKEN IF EXPERIENCE SHOWED, THAT IT HAPPENED -
- EXPERT WORD TAKEN FOR GRANTED, EVEN IF REASON. PARTLY CONCLUSIVE ONLY

o NOT A MATHEMATICALY DERIVED SINGLE AGEING FORMULA

- TOO MANY COMPONENTS INFLUENCING (E.G. 90 FOR DIESEL) -

o RISK ANALYSIS WITH PROBABALISTIC ELEMENTS

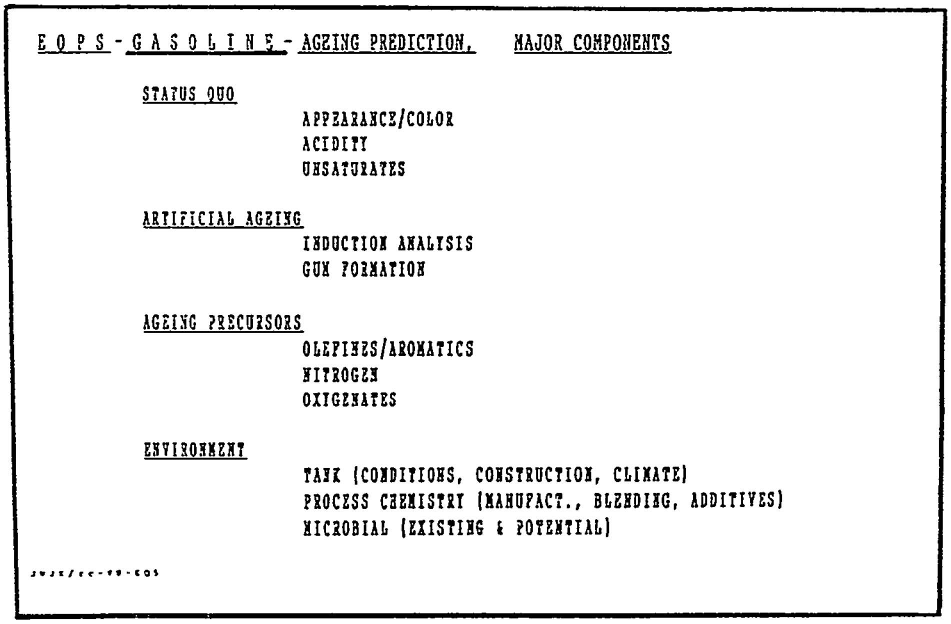
- SO CALLED 'EXPERT SYSTEM' USING LOGICAL DEDUCTIONS FROM DECISION TREES
- PROGRAMMED DECISION OPTIONS, DECIDED ON BY EXPERT PROGRESSING ALONG DECISION .TREE BRANCHES, STRICTLY LOGICALLY

o PROBLEM TOO LARGE FOR HUMAN BRAIN TO CONSIDER ALL OPTIONS

- ELIMINATES 'PET FAVOUR' DECISIONS BY EXPERTS

Should we give up at this point? NO! There are many experts out in the field who can predict an ageing process without being able to explain why it all happens, it is just experience: "it always happens that way". If such experience could be gathered and logically formulated into a "cause--->result" system and linked to some kind of probability that under the various different circumstances it really happens, then a prediction could be made. There is a mathematical technique called "expert system", which does exactly that. Dr. Hartman will describe this in detail in the following presentation.

The problem is too large for the human brain to handle all the options simultaneously and quickly; every expert has his own view, why ageing occurs, he normally follows one or two theories, because they fit to his personal experience. He tends to overlook facts, which do not fit into his theory or which he considers marginally important only. The EQPS does not discard any fact, it weighs it, but if many marginal danger signals appear, it decides often against the experts. EQPS combines theories, which have their value taken on their own, but do not fit all together; it takes an expert opinion for granted concluding that experience showed once a problem under those given circumstances, thus there is a potential risk that it may occur again.



EQPS - GASOLINE - AGEING PREDICTION, MAJOR COMPONENTS

STATUS QUO
- APPEARANCE/COLOR
- ACIDITY
- UNSATURATES

ARTIFICIAL AGEING
- INDUCTION ANALYSIS
- GUM FORMATION

AGEING PRECURSORS
- OLEFINES/AROMATICS
- NITROGEN
- OXYGENATES

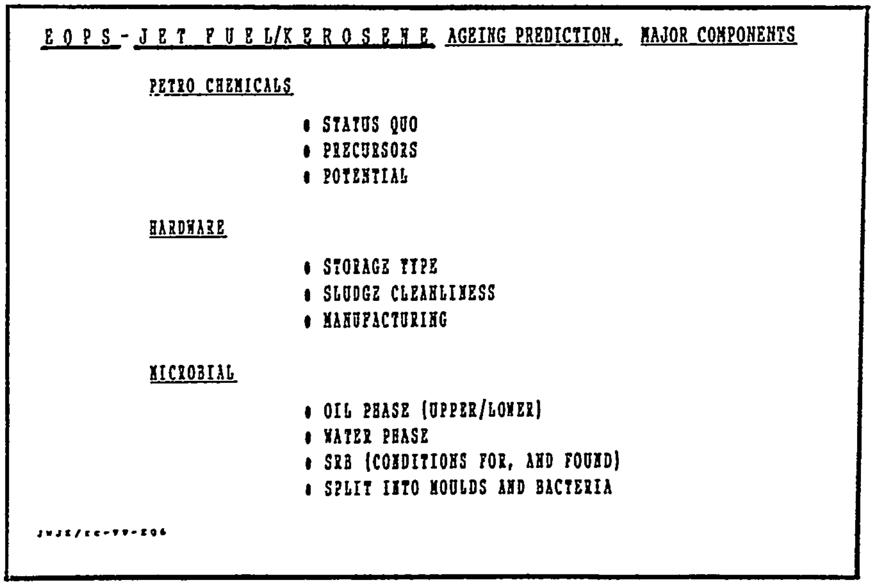
ENVIRONMENT
- TANK (CONDITIONS, CONSTRUCTION, CLIMATE)
- PROCESS CHEMISTRY (MANUFACT., BLENDING, ADDITIVES)
- MICROBIAL (EXISTING & POTENTIAL)

Gasoline ageing Prediction

Certainly those "given circumstances" are normally manifested as laboratory test results, knowledge about the manufacturing process, storage conditions etc; thus EQPS does not encapsulate the "gut feeling" or "crystal ball" rather stays on firm ground of measurable (quantifiable) facts and observations.

For gasoline the main components are a set of data about the current quality (status quo), behaviour under forced oxidation ageing (artificial ageing), a chemical analysis allowing the indentification of compounds which have not yet but may lead to ageing (precursors) and a set of environmental facts ranging from storage conditions, climate over manufacturing processes to microbial spoilage, the latter being "low rated" as it still seldom occurs in gasolines.

The full structure and complexity of the EQPS gasoline module can be illustrated by the hirarchical block diagramme, which we call "flow plan", a term taken from chemical engineering, even though here information of course is "flowing" through it only. It just shows, how the various parameters are logically linked. There will be more explanation of such structures and its use in the following paper by Dr. Hartman.



EQPS - JET FUEL/KEROSENE AGEING PREDICTION, MAJOR COMPONENTS

PETRO CHEMICALS

- STATUS QUO
- PRECURSORS
- POTENTIAL

HARDWARE

- STORAGE TYPE
- SLUDGE CLEANLINESS
- MANUFACTURING

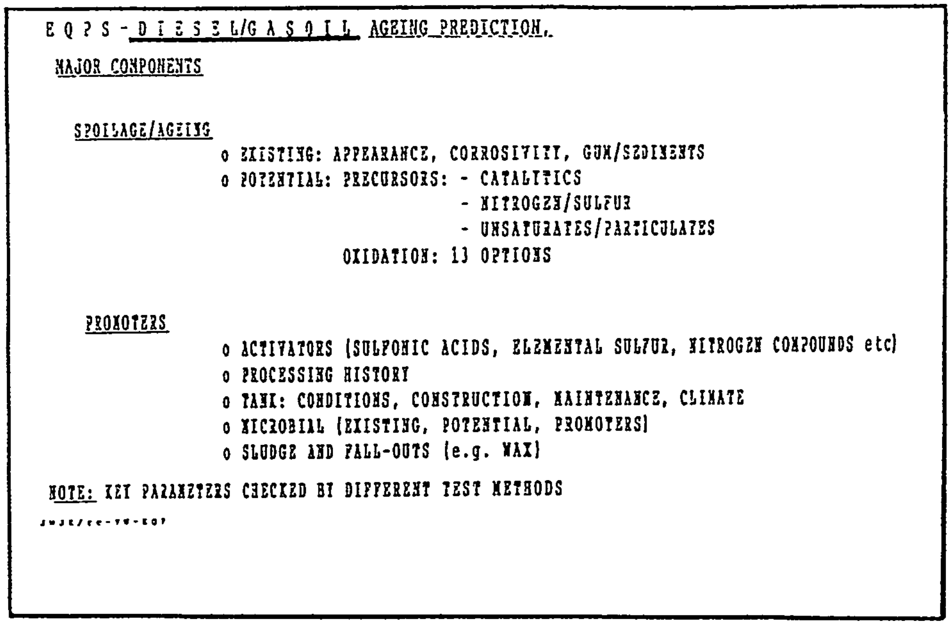
MICROBIAL

- OIL PHASE (UPPER/LOWER)
- WATER PHASE
- SRB (CONDITIONS FOR, AND FOUND)
- SPLIT INTO MOULDS AND BACTERIA

[illegible]

<u>The jet fuel/kerosene</u> module is much simpler, mainly due to the fact that international airline and military have boxed-in jet fuel qualities by such tight specifications, that at least the petrochemcial part leaves little room for variations. It also is a chemically much simpler product than gasoline or diesel/gasoils.

There is of course a petrochemical section dealing with some straight forward indicators of the status quo quality and any chemicals, which may in future cause ageing problems. The biggest part of the system however deals with outside influences on a basically stable product.
The microbiological section is rather detailed, since biological deterioration is the main danger to paraffinic hydrocarbons of a chain length $C_8 - C_{18}$.



EQPS - DIESEL/GASOIL AGEING PREDICTION.

MAJOR COMPONENTS

SPOILAGE/AGEING
- EXISTING: APPEARANCE, CORROSIVITY, GUM/SEDIMENTS
- POTENTIAL: PRECURSORS: - CATALYTICS
  - NITROGEN/SULFUR
  - UNSATURATES/PARTICULATES
  - OXIDATION: 13 OPTIONS

PROMOTERS
- ACTIVATORS (SULFONIC ACIDS, ELEMENTAL SULFUR, NITROGEN COMPOUNDS etc)
- PROCESSING HISTORY
- TANK: CONDITIONS, CONSTRUCTION, MAINTENANCE, CLIMATE
- MICROBIAL (EXISTING, POTENTIAL, PROMOTERS)
- SLUDGE AND FALL-OUTS (e.g. WAX)

NOTE: KEY PARAMETERS CHECKED BY DIFFERENT TEST METHODS

[illegible]

The EQPS module for diesel, gasoils and light heating oil is so far the most complex. Again the emphasis is on existing quality or spoilage and any potential for further deterioration. The ageing theories behind it are of course quite different from those assumed to be applicable for gasoline and jet fuel.

There is an extensive set of oxidation methods measuring essentially the same; but since the ASTM D 2274 now contained in the EN 590 spec is notoriously inaccurate and most other similar tests are not much better, the system tries to draw conclusions from tests controlling other tests. Besides this the standard environmental factors like storage facilities, climate, microbiology are of course there. In addition the system evaluates strong ageing promoters like acids, elemental sulfur, basic nitrogen compounds etc. Another speciality is a section on sludge formation, incompatibility and fall-outs.

As you can see from the "flow plan", the non straight chemical part of the system is almost the biggest. You will also note, that several measurements are used in double activity, e.g. describing the status of spoilage as well as being enhancers, promoters, catalysts for further ageing.

MAIN AGEING MECHANISMS BEHIND EQPS I

GASOLINE

- POLYMERIZATION/CONDENSATION
- HYDROPEROXIDE FORMATION/PEROXYRADICLES
- CATALYTIC PROMOTION
  - METALS FROM TANK STRUCTURE
  - METAL SALTS/OXIDES FROM SLUDGE
  - METALS IN FUEL
  - CLIMATE
  - MICROBIAL AS MINOR EFFECT
- MANUFACTURING PROCESSES

JET FUEL

- POLYMERIZATION
- SULFUR/NITROGEN EFFECTS/ACIDIFICATION
- MANUFACTURING PROCESSES AND TREATING
- CATALYTICS (MAINLY TANK, SLUDGE, CORROSION ON HARDWARE)
- MICROBIOLOGY (EXTENSIVE DETAIL)

[illegible]

Ageing mechanisms used by EQPS

As said earlier EQPS does not subscribe to one single ageing theory. Thus it "worries" about several.

With gasoline of course polymerisation/condensation into gums, peroxyradical formation and all sorts of catalytic promotion is in the forefront. This is directly or indirectly linked to the manufacturing processes.

With jet fuel polymerisation is considered a minor effect (as it contains none or hardly any conversion components in Europe) but sulfur, nitrogen and acidification reactions are being watched and a lot of emphasis is laid on microbioloogical spoilage both as acid and biomass producer as well as catalysing other ageing reactions.

MAIN AGEING MECHANISMS BEHIND EQPS II

DIESEL/LIGHT HEATING OILS/GASOILS

- OXIDATION
- NITROGEN/SULFUR COMPLEX COMPOUNDS (e.g. CYCLICS)
- ORGANIC ACIDS
- REACTIVE OLEFINES
- STRAIGHT POLYMERISATION (AS MINOR EFFECT ONLY)

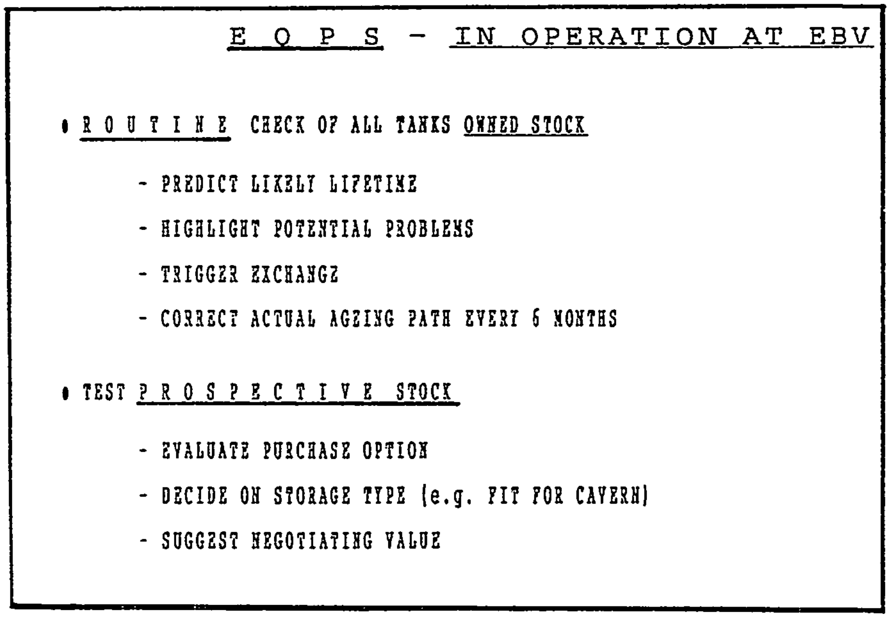
FOR DETAILS SEE "DERST PAPER" ON MECHANISMS: THIS CONFERENCE

OTHER PROMOTERS AND RETARDERS

- CATALYTICS
  - METALS
  - ACIDS
  - SULFUR, N-COMPOUNDS
  - SLUDGE/MAINTENANCE/CLEANLINESS OF TANK
- PROCESS ORIGIN (REFINERY)
- MICROBIOLOGY
- ADDITIVES (TO BE ADDED TO THE SYSTEM)

For <u>diesel/light heating oils/gasoils</u> the presence and/or formation sulfur/nitrogen compounds are being predominantly analyzed, less so any straight polymerisation reactions. Weight is also laid on all sorts of catalytic promotion possibilities and the processing origin of the product.

The system deals with stocks containing none or few additives only (antioxidizer, wax antisettling). It does not deal with the modern "additive culture" at the diesel loading rack, where today up to 12 additives are being mixed with the diesel fuel for multiple purpose. The system could be expanded into this field but the EQPS users do not see any need for it since they store "base stock" product without those additive packages. Many of those additives loose their activity over time, but experience is limited - often company secret. The extension could be very complex.

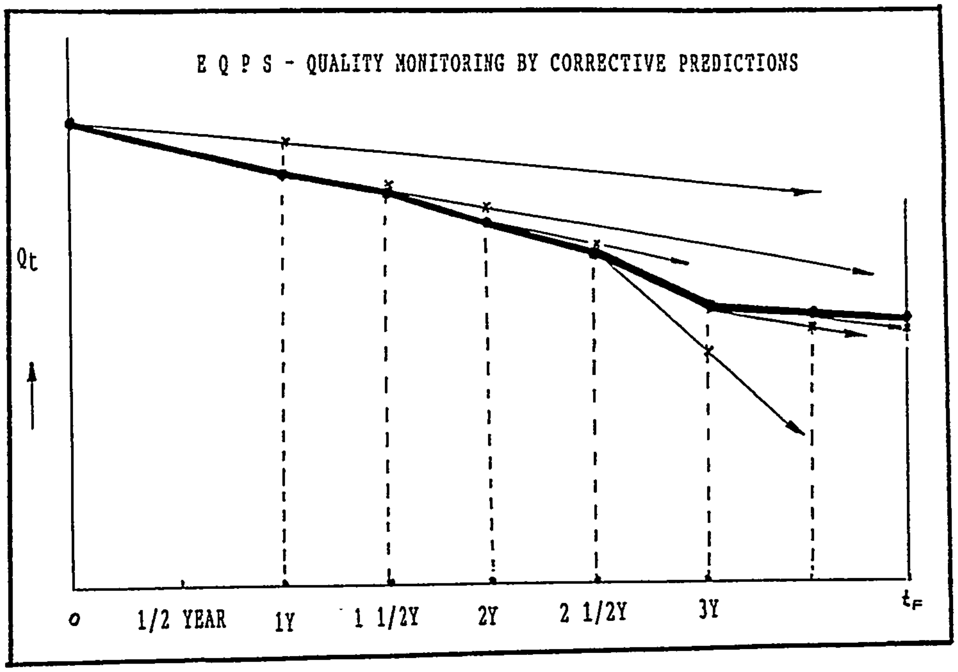


EQPS - IN OPERATION AT EBV

- ROUTINE CHECK OF ALL TANKS OWNED STOCK
  - PREDICT LIKELY LIFETIME
  - HIGHLIGHT POTENTIAL PROBLEMS
  - TRIGGER EXCHANGE
  - CORRECT ACTUAL AGEING PATH EVERY 6 MONTHS
- TEST PROSPECTIVE STOCK
  - EVALUATE PURCHASE OPTION
  - DECIDE ON STORAGE TYPE (e.g. FIT FOR CAVERN)
  - SUGGEST NEGOTIATING VALUE

WJK/EC-VG-E013

<u>How is EQPS being used?</u> The system is available since over a year and has been in test use prior to that for almost also a year. Results are pleasing. Some scaling work is still going on for the diesel/gasoil module. The programme is PC based and can be/is being used by quality inspectors with little knowledge on chemistry, oil manufacturing and oil quality. Since decisions are recommended by the system which can be extremely costly, there should always be an expert at hand to do a brief plausibility analysis - as I said - when it becomes costly. A vast number of cases can be decided solely on EQPS. In general EQPS tends to judge ageing somewhat on the pessimistic side.



EBV tests all old and marginal tanks every 6 months and adjusts the ageing predictions accordingly. Good and perfect tanks with a "life" prediction of 3-5 years are checked annually. While predictions are generally accurate for the next 18 months, with fresh products, the variations between predicted and experienced quality loss generally increases with the age of the products.

Incoming cargoes, purchases etc. can also be assessed by EQPS, which gives advice as to buy or not to buy or buy at discount, or buy just for keeping it 1-2 years, or fit for long term cavern storage etc.

The analysis highlights every potential problem in plain language and quantified, much more than you ever wanted to release to the customer or seller. The system also indicates off-spec situations on non ageing relevant parameters, but this is done in the peripheral data base system. Automatic data transfer from 7 labs into EQPS will start early 1995 for EBV.

EQPS - A TRUE JOINT INTERNATIONAL EFFORT

- MANAGED BY EBV - HAMBURG
- DEVELOPMENT-TEAM: EBV (HAMBURG), IIBR/J.H. CON.EX (ISRAEL)
- FINANCIAL CONTRIBUTERS AND CURRENT USERS:
  CARBURA (SWITZERLAND), COVA (NETHERLANDS), EBV (GERMANY)
  FDO (DENMARK), SAGESS (FRANCE)
- TWO NEW PROSPECTIVE USERS MAY JOIN SOON, AVAILABLE FOR ALL STOCK ENTITIES
- 15 INTERNATIONAL OIL QUALITY EXPERTS LENT EXPERTIZE (INCL. UK, US, EUROPE)
- SALE TO COMPANIES CONSIDERED, NOT YET DECIDED
- EXPANSION INTO CRUDE OIL INCOMPATIBILITY HAS BEEN STARTED, LOOK FOR PARTNERS

JWJK/cc-93-EQ12

EQPS is not only used by EBV. Its development was a true international effort. The origins go back to an 1989 British Institute of Petroleum meeting on microbiology, during which an expert system concerning the microbial spoilage of jet fuel was presented. Out of this grew a strong EBV interest to expand the concept to overall oil product quality deterioration. EBV joint with CARBURA of Switzerland and FDO of Denmark to finance such undertaking, later COVA of Netherlands and SAGESS of France joined. All five organizations are currently EQPS users. We are in the process to talk to potential new customers, predominantly stock holding agencies.

Over a period of 2 1/2 years the development team of EBV Germany and IIBR, later J.H. ConEx of Israel joint forces with input by 15 top international quality experts from member countries and elsewhere, which were interviewed to place their expertize into the hands of the team. The late Nahum Por was among them.

The work is by no means complete. We just finished work on lab input automation and look forward to join up with other customers to expand into the field of crude oil incompatibility and sludging, possibly under the umbrella of an International Energy Agency joint project.

Dr. Hartman, who was the key man on the Israeli side of the development team, will now go into more detail on the functioning and structure of EQPS

Thank you for you attention

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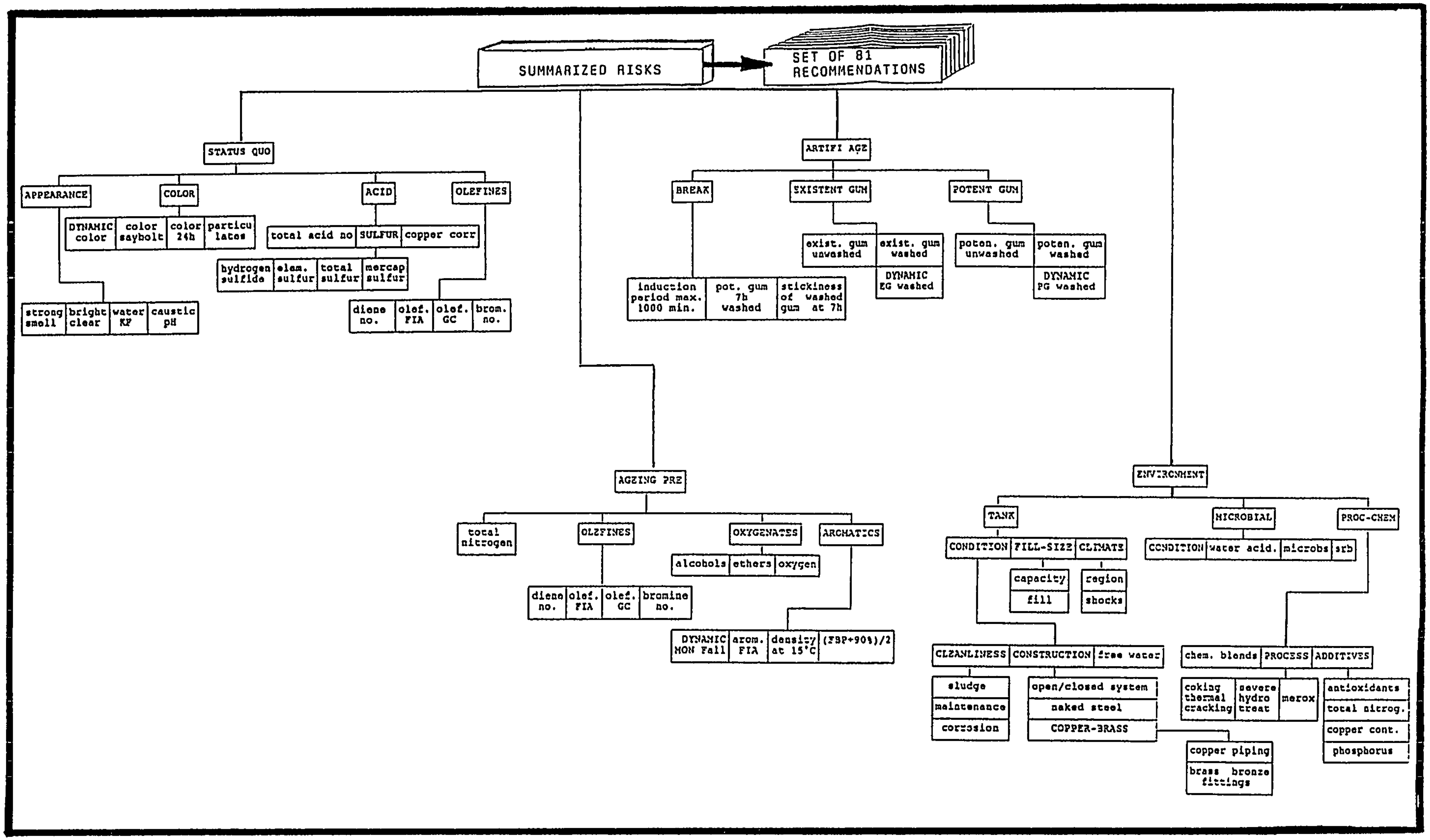
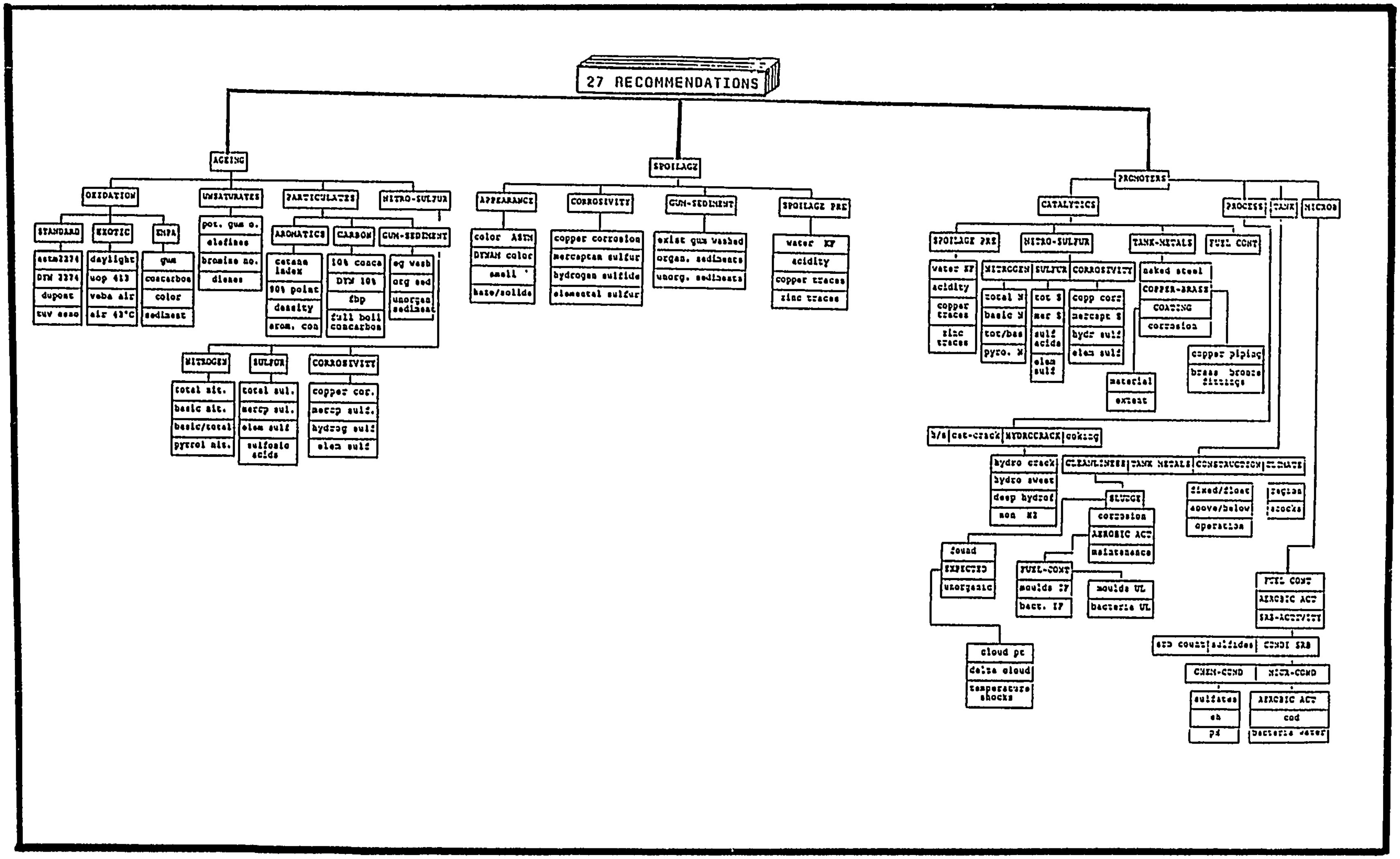


EQPS FLOW PLAN

EQPS - "FLOW PLAN"

Diesel



5th International Conference
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THE MATHEMATICAL APPROACH TO EQPS - AN EXPERT SYSTEM FOR OIL QUALITY PREDICTION

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1. INTRODUCTION:

EQPS is an expert system for prediction of ageing processes in long term storage of oil products. EQPS contains a data base with detailed information on the user's stored stocks, and a diagnostic Expert System which is used for analysis, evaluation and quality prediction of a given storage site. An extensive body of knowledge and information concerning oil products is included in the program. Petrochemical and petrobiological laboratory test results, source and product processing data, storage conditions, environmental and climatic factors, are all considered in the evaluation.

The objective of EQPS is to serve as a tool which allows a quality control of strategic oil reserves, assistance in oil purchase decisions, selection of appropriate storage site for a given product, and to provide guidance consultation and instruction in the field of product ageing.

EQPS is a rule based expert system. The rules are expressed mainly in form of decision trees. Each input item is rated according to its potential relevance to ageing of the product. Various 'functions', expressing ageing phenomena are defined and assessed. Finally, a recommendation and indicative remarks conclude the assessment.

The system applies Artificial Intelligence concepts. Implementation uses PDC - Prolog software, one of the leading Logical Programming tools. [Forsyth (7) and Bratko (8)].

In references [1], [2], [3], earlier expert systems for microbial problems in jet and diesel fuel were discussed. EQPS deals with the whole spectrum of ageing, chemical, physical and biological. The knowledge acquisition and logical structuring was done with the help of more than a dozen international experts in various facets of the problem. Special mathematical and programming tools were developed to accommodate the extensive knowledge, information, and reasoning capabilities of the system.

We emphasis in this paper, the mathematical structure, logical architecture and programming tools. The subject matter will be discussed in [Koenig (9)].

2. AGEING OF A PRODUCT:

A product is said to be 'ageing', if over time it changes its performance, appearance, or environmental properties. Ageing may be caused by chemical reactions (sometimes promoted catalytically), physical treatment, exposure, climatic situation, storage conditions, and microbial attack.

Ageing will have usually detrimental results. Formation of chemical compounds (e.g. acids), attacks and may destroys engine components. Filter plugging may result from formation of heavy molecules by polymerization or condensation. Heavy molecules, which boil at higher temperatures than the original product components, lead also to carbon black formation (smoke), mechanical corrosion, poor combustion (energy loss), and pollution. Formation of biomass, which often is related to increase in acidity, plugs filters, corrodes and blocks pipes, and sometimes destroys components necessary for performance.

Ageing could be prevented or slowed down by additivation, such as antioxidants, anti corrosion, metal deactivator, biocides, wax dispersors and others. Maintenance conditions of storage sites is an important factor in ageing. Manufacturing modifications may also be applied to this end.

Obviously, it is desirable to detect an ageing trend as early as possible, then effective prevention methods could be applied. EQPS is intended to give an early warning - prediction of an ageing trend. The system estimates the present degree of ageing by looking at color, existent gum, sediments, pour point, CFPP, microbial counts etc. In addition to the current deterioration level, forced (artificial) ageing tests (potential gum, ASTM 2274, VEBA airblow, TUV/ESSO test etc.) are considered. Outside ageing factors such as climate, tank design, tank cleanliness, oxygen exposure, water and others, coupled with inherent ageing potential caused by manufacturing (olefins, aromatics, nitrogen, sulfur, phosphorous etc.) complete the predictive picture.

EQPS contains at the present three product modules for assessment of gasoline, diesel/heating oil, and jetfuel.

The gasoline module will be used in the demonstration of the system. The structure of the other modules is similar.

3. EXPERT SYSTEMS:

An expert system is a computer program that encapsulates specialist knowledge about a particular domain of expertise. It should be capable of making intelligent decisions within its domain. Such a system is a simulation of the human expert knowledge and his way of reasoning.

In general, an expert system contains three main components:

1. The knowledge base.
2. The inference engine.
3. The user interface.

The knowledge base consists of facts or assertions and rules that summarize the field of expertise. PROLOG a special declarative-logical programming language which have been developed for this purpose allows convenient expression of the knowledge base as a set of logical rule of the type 'If A then B'. Unlike conventional data bases which are normally passive, an expert system tries actively to conclude logical consequences of the rules. In case of partial information, the system attempts to fill in the gaps. An expert system should be able to "think" creatively. Thinking is due to the inference engine, which supplies the system with reasoning capabilities. This component generates a 'line of reasoning' leading from known facts (input data) to logically consistent conclusions.

The user interface is the channel of communication between the user and the program. This component allows the user to enter data into the program in a simple manner and displays the system's conclusions and decisions in a clear and intelligible form.

An expert system should have a sort of 'growing' capability. As time passes, new information, knowledge and experience are usually acquired. These are incorporated, automatically or manually in the system. As a result, the system improves, and it's predictions become more accurate. Thus an expert system is viewed as a dynamic body of knowledge and experience, which could give up to date expert advice to the user.

4. EQPS GASOLINE MODULE STRUCTURE:

EQPS contains a specially designed database which can handle data of many oil storage sites. Each storage site (above or below ground tank) record file includes data on the site and it's environment, and laboratory test results of samples taken at various points in time.

The following is a typical tank data screen.

Product: *gasoline* Grade: *S V K* Last Fill Date: *15/11/92*
Tankfarm owner/operator: *Bominflot*
Location: *Hamburg*
Location detailed address: *Tankweg 1*
2000 Hamburg
Tel.:040-740007.20
Tank number: *81* Status of tank: *active*
Year of construction: *1956* Capacity (m^3): *9583*
Safety classification: *A1*
Diameter/height ratio: *2/1*
Tank Underground? *no*
Roof fixed/floating: *float* Double seal: *yes*
Floating roof inside of fixed roof tank: *no*
Closed System: *no*
Automatic gauging/sampling: *no* Coloring (outside paint): *gray*
Drainage facilities: *yes*
Operation (static/rare turnover/continuous turnover): *static*
General Maintenance: *weak*
Last date cleaning: *06/91*
Sludge found: *no*
Method of last cleaning: *water washed*
State of internal corrosion: *light*
Naked steel (e.g. sandblasted bottom or walls): *no*
Coating Material: ...
Coating Extent: ...
some - bottom and lower walls ...
Copper piping: *no*
Brass/bronze fittings: *no*
Climatic Region (continental/inland(moderate)/seashore): *sea*
Sudden temperature shocks: *few*

The gasoline content of this tank will be evaluated later in this paper by EQPS.

Corresponding to the tank data, the system holds a history of test results of samples taken from the tank. The test list is comprehensive, meant to include all known and conventional tests on the specific product. Obviously, the more input data points supplied to the program, prediction accuracy and reliability improves. The system, however may reason and assess the storage site, even in cases where less than a dozen input values are available. Each test is defined by known methods and standards. EQPS contains extensive 'help' texts defining the test, its methods, precision, significance, repeatability, etc. The texts could be easily retrieved on screen by the user. Specs depend on regulations in the storing country, and on the different types of product. The system allows the user to alter, add, or delete tests, and to modify the help texts accordingly. The following is an example of a few tests from the gasoline module.

Type of Test	Units	Method	Specs	Expert System Ranges		
				low	medium	high
Bright & Clear		Visual		yes	odd	no
Climatic Region				sea	mod	cont

Type of Test	Units	Method	Specs	Expert System Ranges			
				<-l->	<-m->	<-h->	
Density at 15C	g/ml	ISO 3675	.74-.79	0.60	0.74	0.78	0.88
Research Octane No.	RON	ISO 5164	>95	70	90	97	120

EQPS classifies input items into 'high', 'medium' or 'low', according to their impact on the product's ageing process. Thus the visual test of 'bright & clear' will be classified low (risk), if test result is 'yes', high if result is 'no', and 'medium' if input is 'odd'. Tank items, such as 'Climatic Region', are also classified. Numerical values in the second table, have also classification ranges. 'Density at 15C' test result will be graded low for values X if $0.60 <= X <= 0.74$, medium if $0.74 < X < 0.78$, and high if $0.78 <= X <= 0.88$. A value X, such that $X < 0.60$, or more $X > 0.88$, is considered by the system an input error, and prompts a message on screen. The permitted range, as well the classification range could easily modified by a non programmer user.

Some items are calculated by the system, expressing the difference between previous and current measurements, or averages of certain values, and not actual test values. The system will label the calculated value as high medium or low.

The next task performed by EQPS, is to divide the tests into relation groups. The groups, represented by predefined functions, exhibit an ageing relevant aspect, or situation. This serves as an intermediate decision related to the product's ageing. For instance, the olefines function in gasoline, which influences the existing ageing, is evaluated using four test values; 'diene number', 'olefines FIA', 'olefines GC', and 'bromine number'. Depending on the classifications of the four input parameters, function '**OLEFINES**' will be classified into high, medium, or low. To distinguish between input test values and evaluated functions, the latter will be designated in capital letters. Functions will be evaluated even if some input parameters are missing. Test values may enter several functions, and functions often have other function classifications, as their input parameters.

The following displays the logical flow diagram of function **STATUS QUO**, which assesses the current deterioration level. The lower case values are individual input values, whereas the capital letters represent functions. **SULFUR** for example, is evaluated by a tree with input parameters listed above it. **ACID** function will consider the level of **SULFUR**, and the levels of total acid number and copper corrosion test result. All input parameters of **STATUS QUO** are function classifications.

strong smell
bright&clear
water KF
caustic pH
↓
APPEARANCE

dyn. color
color saybolt
color 24h
particulates
↓
COLOR

hydrogen sulfide
elem. sulfur
total sulfur
mercap. sulfur
↓
SULFUR

diene no.
olefines FIA
olefines GC
bromine no
↓
OLEFINES

SULFUR
copper corrosion
↓
ACID

APPEARANCE
COLOR
ACID
OLEFINES
↓
STATUS QUO

A passage through a function box, depicted by capital letters, involves an activation of an appropriate decision tree. For any combination of available input values, the system will apply a different decision tree. In the following section, decision trees will be discussed.

Similarly, three additional (main) functions as follows, will be evaluated. Each has its own logical flow diagram.

AGEING PRECURSORS - Combines chemical measurements and some physical data which are known to be potential degradation promoters.

ARTIFICIAL AGEING - Various tests which simulate deterioration by bringing the product under severe condition for a short period of time.

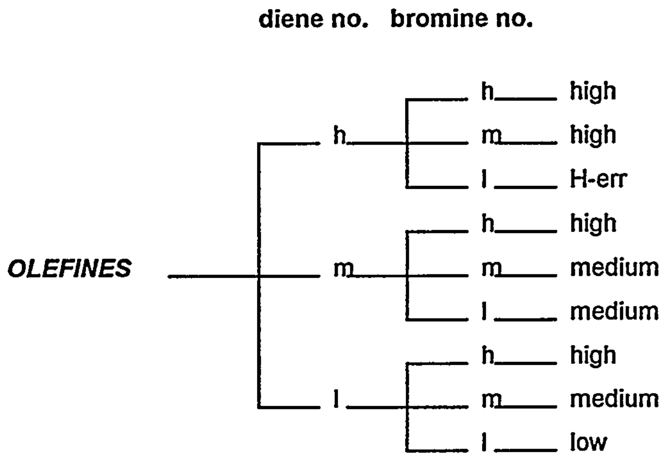
ENVIRONMENT/HISTORY - Combining risk factors based on storage

Each main function could be classified in one level out of three, therefore there will be 81 different combinations, each corresponding to a diagnosis-recommendation.

STATUS QUO
AGEING PRECURSORS
ARTIFICIAL AGEING
ENVIRONMENT/HISTORY
↓
RECOMMENDATTION

5. DECISION TREES:

Function evaluations are performed by an appropriate predefined decision tree. **OLEFINES** for example, in case of 'olefines FIA' and 'olefines GC' missing, will be evaluated by the following tree.



Thus, if diene and bromine number are classified low and high respectively, **OLEFINES** function will be classified high. The decision tree, built according to expert knowledge, places more weight on bromine number. This implicit weighing of input parameters, both test values and function classifications, exists of course in all the hundreds of trees EQPS contains. The H_err symbol attached to the high-low path, is a high classification, with an error message, which is issued by the system. The message conveys an expert opinion that a sample with a high diene and low bromine numbers is unlikely, and may be an error. Individual decision trees exist for all EQPS defined functions.

Decision trees are flexible, in the sense that any number of input parameters will trigger a decision. This is achieved by defining a tree for each combination of input parameters. For **OLEFINES** function, for example, there are 16 possible parameter combinations, as follows

1. All four input values available. (1)
2. Three out of four available. (4)
3. Two out of four. (6)
4. Only one available. (4)
5. None of the four. (1)

A special tree exists for each case. Therefore for **OLEFINES**, the system stores 15 decision trees. If no parameter exists, no decision is made, and the next tree (**STATUS QUO** in this case), will miss the **OLEFINES** input. The same is valid for many functions in each of the different product modules.

To store in the computer the large volume of trees, and to allow quick retrieval and assessment, a special tree structure was designed. Automatic logical tree consistency checks are built into the system, to avoid clashes between tree decisions.

A trees may contain contradictions between its own branches. For example, the rule for **SULFUR** function based on elemental sulfur and mercaptane sulfur is high if the first test has low result and the second has high. If the same tree will contain a rule saying that **SULFUR** function will be rated as medium when the first test yields medium and the second high, the tree is obviously inconsistent. Similarly any branch in a tree may be inconsistent with other branches. EQPS will automatically color any branch decision blue if an upper branch contradicts it. Thus the high in the first branch in the previous example will have a blue color.

Inconsistencies may occur between trees of different size belonging to the same function. Take the previous example where **SULFUR** function is high when elemental sulfur is high and mercaptane sulfur is low. Assume that **SULFUR** function in the presence of the three tests elemental sulfur, total sulfur, and mercaptane sulfur is not high when elemental sulfur is high, mercaptane sulfur is low, independent of total sulfur. This case is an inconsistency between a 2-tree and one of it's 3-trees. Branch decisions in these cases are colored red.

6. FINAL ASSESSMENT:

EQPS creates a final site assessment which lists all input data items and defined functions with their risk classification. The final report consists of several additional parts:

1. A list of comments, which point at some warning sign as a result of an important function or test result classified as risky.
2. A recommendation, an action to be taken. This could be a time span before deterioration is likely to occur, an advice whether to purchase the product if offered as cargo etc.
3. A comment related to the age of the product in storage. That is, an advice how to consider the previous recommendations given the storage time.
4. Any inconsistencies concerning the test results.
5. A list of all test values which have been classified by EQPS as high risk.

The system displays the final assessment on screen, and prints it upon request.

The following is an EQPS assessment of the previous gasoline tank example. Missing values are labeled by the symbol -?-.

GASOLINE EXPERT SYSTEM EVALUATION

of samples taken at 01/10/93 Tank No 81

Product: *gasoline* Location: *Hamburg* Owner: *Bominflot*

*** *This Assessment is Using 39 Items* ***

TEST	*VALUE*	*LEVEL*
Hydrogen Sulfide	**0.99**	**low**
Elemental Sulfur		**-?-**
Total Sulfur	**0.02**	**low**
Mercap Sulfur	**3**	**medium**
SULFUR	⇒	**medium**

TEST	*VALUE*	*LEVEL*
Strong Smell	**no**	**low**
Bright&Clear	**yes**	**low**
Water_KF	**105**	**low**
Caustic pH	**6.7**	**low**
APPEARANCE	⇒	**low**

Total Acid no.	**0.01**	**low**
SULFUR		**medium**
Copper Corrosion	**1**	**low**
ACID	⇒	**low**

Diene No	**0.6**	**low**
Olefines FIA	**8.3**	**medium**
Olefines GC		**-?-**
Bromine No	**24**	**medium**
OLEFINES	⇒	**medium**

Dy Color Saybolt	6	low
Color Saybolt	-16	low
Color 24h Daylight		-?-
Particulates View	none	low
COLOR	⇒	low

APPEARANCE		low
COLOR		low
ACID		low
OLEFINES		medium
STATUS QUO	⇒	low

Alcohol Content	0.499	low
Ether Content	0.199	low
Total Oxygen	0.499	low
OXYGENATES	⇒	low

Aromatics FIA	29.4	medium
Density at 15C	0.7425	medium
(FBP+90%)/2		-?-
DY MON Fall	0	low
AROMATICS	⇒	medium

OLEFINES		medium
Total Nitrogen		low
OXYGENATES		low
AROMATICS		medium
AGEING PRECUR	⇒	low

Ex. Gum Unwashed	3.4	low
Ex. Gum Washed	0.99	low
DY Ex. Gum W	0.09	low

Pot. Gum Un	4.0	low
Pot. Gum W	0.991	low
DY Pot. Gum W	0.991	low

EXISTENT GUM	⇒	low
Induct Pd 1000m	1000	low
Pot. Gum 7h W	2.0	low
Stickiness WG at 7h	dry	low
BREAK	⇒	low

POT GUM	⇒	low

BREAK		low
EXISTENT GUM		low
POTENTIAL GUM		low
ART AGEING	⇒	low

Coke/Therm Crack		-?-
Severe Hydrotreat		-?-
Merox/Unextracted		-?-
PROCESS	⇒	-?-

Antioxid	0	low
Total Nitrogen	15	low
Copper Content	0.99	low
Phosphor Cont	1.2	medium
ADDITIVES	⇒	low

Copper Piping	no	low
Brass/Bron Fittings	no	low
COPPER-BRASS	⇒	low

Chemical ByBlends		-?-
PROCESS		-?-
ADDITIVES		low
PROCESS/CHEM	⇒	low

Closed System	no	high
Naked Steel	no	low
COPP-BRASS		low
CONSTRUCT	⇒	medium

☐

Sludge		-?-
CLEANLINESS		medium

Maintenance	**weak**	**medium**
Internal Corrosion	**light**	**low**
CLEANLINESS	⇒	**medium**

CONSTRUCT		**medium**
Free Water		**-?-**
CONDITION	⇒	**medium**

Capacity	**9583**	**high**
Fill Rate		**-?-**
FILL-SIZE	⇒	**high**

Climatic Region	**sea**	**low**
Temp Shocks	**few**	**medium**
CLIMATE	⇒	**medium**

CONDITION		**medium**
Water Acidity		**-?-**
Microbs in Low Oil		**-?-**
SRB in Water		**-?-**
MICROBIAL	⇒	**medium**

CONDITION		**medium**
FILL-SIZE		**high**
CLIMATE		**medium**
TANK	⇒	**medium**

TANK	**medium**
MICROBIAL	**medium**
PROCESS/CHEM	**low**
ENVIR/HISTORY	**medium**

Shaded areas display input values the next column shows the input value's level given by the system. Function level are displayed in framed areas, the function evaluation depends on the levels above. For example, **ACID** function has been evaluated as low, resulting from 'Total Acid no' (0.01) and 'Copper Corrosion', both being low, and **SULFUR** function evaluated as medium. The sequential evaluation process follows similarly. The major function evaluations are double framed.

A **'Full Recommendation'** will take into consideration **STATUS QUO, AGEING PRECURSORS, ARTIFICIAL AGEING** and **ENVIRONMENTAL/HISTORY.** A **'Partial Recommendation'** will not consider the last function. The later will be used when many data items related to the environment and/or product processing are not available. The system supplies the following text.

Partial Recommendation no. 27 (does not consider ENVIRONMENTAL/HISTORY)

Please note, that your information was not complete and can be improved by more quality data.

The following highlights some major quality issues of this product:

* The color of the product does not give any cause of concern.

* There is no potential gum problem detected.

* So far, judging from the existent gum level, there has been little ageing.

* The level of unsaturates could allow relatively fast ageing.

Concluding from the above major issues and all other available data, the following can be concluded:

This is an excellent product, which does not fall under any applied ageing condition and does not exhibit worrisome ageing precursors. Under the right storage conditions it could last up to 10 years. If offered you may buy it at substantial premia, perfect material for storage in caverns.

The product in hand has been stored in this tank by your organization for about 2 years. It is reasonable to assume that the product was fresh when it was taken in. Modern products containing cracked stocks are inhibited against ageing by additives, to maintain quality for 18 to 24 months. You are beyond this time frame already, thus any deterioration sign mentioned above should be taken seriously. There is a reasonable chance, that above life span is on an optimistic side.

Please pay attention to the following values rated 'High Risk':

Closed System - no

Capacity - 9583

Explanation capability is an important feature in expert systems, as it enhances the reliability of the conclusions. EQPS has a few features which provide means to justify the system's decision. The expert system assessment screen could be used as a logical spreadsheet, where it is possible to type in values and to observe their impact on the evaluation process. This could be used for instance to select the best storage site to a given product, by entering on screen all the test and product details and tank details of a particular site. The system will give a quality prediction of the product as if it is stored in that site. The user may ask for a list of all high risk and missing values, and for a complete reasoning sequence, listing the logical path of decisions.

7. CONCLUSIONS:

This paper describes an existing expert system geared toward product aging phenomena. The flexibility of the software, especially the separation between the logical shell structure and a specific knowledge base allows to replace the knowledge base to fit other fuels, e.g. crude oils. The namely aging prediction could also be replaced by another objective function, expressing for instance operability features of fuels. Thus, the system could be viewed as a logical shell for the general subject of fuel assessment and diagnosis.

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5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

A RAPID COLORIMETRIC METHOD FOR PREDICTING THE STORAGE STABILITY OF MIDDLE DISTILLATE FUELS

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ABSTRACT

Present methods used to predict the storage stability of distillate fuels such as ASTM D2274, ASTM D4625, DEF STAN 05-50 Method 40 and in-house methods are very time consuming, taking a minimum of 16 hours. In addition, some of these methods under- or over-predict the storage stability of the test fuel.

A rapid colorimetric test for identifying cracked, straight run or hydrofined fuels was reported at the previous Conference. Further work has shown that while a visual appraisal is acceptable for refinery-fresh fuels, colour development may be masked by other coloured compounds in older fuels.

Use of a spectrometric finish to the method has extended the scope of the method to include older fuels.

The test can be correlated with total sediment from ASTM D4625 (13 weeks at 43°C) over a sediment range of 0-60mg/L. A correlation of 0.94 was obtained for 40 fuels.

INTRODUCTION

Middle distillate fuels that are unstable in long term storage have been reported for at least 30 years[1] . The fuels darken in colour and form gums and microparticulate sediments. The insoluble degradation products can cause operational problems in fuel systems and engine components. Fuels containing unhydrogenated light cycle oil components have been shown to be particularly associated with such instability problems[1-4].

At present, the storage stability of middle distillate fuels is assessed by using one or more of a number of standard tests, such as Def Stan 05-50 Method 40, ASTM D2274 and ASTM D4625. These tests accelerate the ageing process using elevated temperature, with or without additional oxygen. The high temperature tests such as Def Stan 05-50 Method 40 (short test) and ASTM D2274 do not reflect the behaviour of some fuels in ambient storage conditions, in particular those fuels containing unhydrogenated light cycle oil[5,6].

Correct prediction of the storage stability of fuels is obviously a requirement of any predictive test. ASTM D4625 has been considered to reflect the sedimentation processes which occur at ambient conditions the most accurately of any of the accelerated ageing tests. However, the test is long term, taking up to 24 weeks to complete and hence while of use as a research tool, is not acceptable as a specification test.

Several researchers have developed alternative tests to overcome the shortcomings of the present tests. Bahn et al[7] and Hardy et al[8] developed tests at elevated temperatures and measured the subsequent sediment and colour change. Por et al[9] accelerated fuel deterioration in a number of automotive diesel fuels by irradiation with laser light, measuring the sediment produced. White[10] has reported improvements in repeatability of D2274 by using a pyrrole as a reference.

DRA and DSTO Australia have developed colorimetric methods to identify unstable fuels under a joint UK/Australia research co-operation agreement. Solly[11] described a rapid colorimetric method using a solid phase to identify fuels containing unhydrogenated light cycle oil. The test may also be used to quantify the concentration of LCO in automotive diesel fuels. The test is very rapid and requires little sample.

DRA Cobham has developed a liquid phase test in parallel with the DSTO method, and results obtained from using this method were reported at the previous conference[12]. 5cm^3 of fuel were mixed with a similar volume of a reagent mixture (immiscible with fuel). The phases were allowed to separate and the reagent phase examined visually after 30 minutes. For refinery fresh blends, a blue or green colour in the reagent layer indicated the presence of unstable fuel components; a pink or red colour indicated the presence of hydrofined products. Straight run fuels produced a yellow or brown coloration. Assessment of the colour of serial dilutions of the sample allowed an estimate of the storage stability of the fuel to be made.

This paper describes the continued development of the method to give a quantitative assessment of middle distillate fuel stability, and the application of the test to fuels other than refinery fresh products.

VISUAL ASSESSMENT OF FUELS: ASSESSMENT OF COLOUR AND INTERPRETATION OF RESULTS

Some initial instances of incorrect interpretation of results from operators led to the initiation of a programme to improve the robustness of the method.

A series of fuels including marine gas oils, F-76 diesel fuels and refinery fresh research blends were examined using the same procedure by 3 operators. Some of the fuels had been dyed for customs and excise regulations. The operators were requested to carry out the colorimetric test, report the colour obtained and obtain a visible spectrum of the reagent layer for each sample. The fuel samples were also tested for the presence of chemical species known to be present in and peculiar to unstable LCO components, namely phenalenones and phenalenes using HPLC[13,14]. The fuels ranged in age from refinery fresh to 1.5 years, and their colour by ASTM D1500 ranged from <1.0 To 3.5. Samples were stored at -30°C until analysed and they were thawed in the dark to maintain the integrity of the sample.

The results are given in Table 1. Visual colour assessment, even with a reference colour card, often varied widely between operators. The best correlation was, as expected, for refinery fresh blends where fuels containing unstable LCO were readily identified. As fuels age additional reactions may occur which mask the colours observed in fresh fuels.

The spectra obtained for each fuel were identical from each operator and correctly identified those fuels containing unstable products, even when the fuels were known to be up to 1.5 years old. The presence of unstable components was correctly identified in fuels containing dyes.

This data, coupled with the information presented at the last conference, indicated that a spectrometric finish to the test procedure, giving a numerical estimate of storage stability, would be feasible.

DEVELOPMENT OF SPECTROMETRIC FINISH TO METHOD.

Serial dilution was previously used[12] to estimate the stability of the fuel sample. This indicated that the method could be further developed to give a quantitative finish and hence be used as a rapid test to define unstable fuels.

Fresh gas oil components were obtained from a number of UK and European refineries, which process crudes from sources including several North Sea crude oils and also Middle East crudes. Components included straight run light gas oil (LGO), untreated LCO, and hydrofined LCO (both from catalytically and thermal cracking plant). Raw cracked components had been stored at -30°C until blending took place.

22 fuels were blended from these components: blends of 2%, 8%, 12% and 20% LCO in LGO or stable gas oil blends, and blends of 25% and 50% hydrofiner product in LGO. 17 gas oil components from these refineries were also tested. 7 samples of diesel fuel were tested (Table 2).

The storage stability of the fuels was assessed using ASTM D4625 (13 weeks storage at 43°C). Each fuel was tested in duplicate. The total sediment in mg/L was recorded.
The fuels were also analysed in duplicate using the colorimetric test. The visible spectrum of the reagent layer was obtained for each sample and the absorbance measured.

The storage stability of the fuel as measured by ASTM D4625 was plotted against the absorbance obtained from the reagent layer for each fuel. This is shown in Figure 1. Linear regression carried out on these results gave a correlation of 0.94 for the 46 fuels.

An absorbance of greater than 0.2AU was found to equate to a total sediment by ASTM D4625 (13 weeks at 43°C) of greater than 10mg/L. The specification limit for storage stability of F-76 diesel is 10mg/L (using Def Stan 05-50 Method 40).
Fuels blended from old components (5 years) also followed the correlation shown in Figure 1. Results for fuels giving greater than 60 mg/L total sediment by ASTM D4625 have been

included for correlation purposes, although the absorbances recorded were extremely high - above 1.0AU.

The repeatability of the procedure was good, results obtained on duplicate analyses were within ±0.008 AU for absorbances up to 0.40 AU.

The results of this programme indicate that the colorimetric test may be used as a rapid test to determine the storage stability of middle distillate fuels. Further samples of fuels, including marine gas oils are being tested (colorimetric test and ASTM D4625) to extend the database and improve the reliability of the test. It is anticipated that a test kit, including a portable spectrometer will be field tested in the near future for fuels testing.

SURVEY OF MARINE GAS OILS USING THE COLORIMETRIC TEST.

201 samples of marine gas oil (MGO) were obtained during 1993 and the colorimetric test was used to determine their storage stability. This work is part of an ongoing programme to survey the properties of such fuels, which were obtained from world-wide sources.

The results are summarised in Figure 2 and Table 3.

The highest number of fuels were obtained from Europe (94), with smaller sample numbers obtained from the USA, Central and South America, Africa, the Middle East and Asia. Overall, 51 of the samples showed the presence of unstable components - 25% of the sample. Approximately half of these gave absorbances in excess of the limit of 0.2AU, indicating the presence of high concentrations of unstable components in these fuels.

All the fuel samples from the USA were obtained from the Eastern Seaboard and all the samples gave very high absorbances, indicating high concentrations of unstable components in the fuels. No fuels obtained from Asia or Africa showed high absorbances, although the majority of these samples were known to be straight run products. Hence low absorbance readings would have been expected. Fuels containing unstable components, obtained from the remaining areas, have been placed in one of three categories: those giving absorbances greater than 0.2AU; those with "borderline" absorbances (0.15 -0.2AU) and those fuels giving lower absorbances (0.1-0.15AU) which would be expected to contain low concentrations of unstable components. These latter fuels were tested for the presence of phenalenones using HPLC and all showed trace levels (1-5mg/L). The distribution of these fuels is shown in Figure 2.

CONCLUSIONS

The colorimetric test has been developed to provide a numerical estimate of storage stability of middle distillate fuels which correlates well with ASTM D4625 total sediment measurements when stored at 43°C for 13 weeks. Use of a spectrometric finish has extended the scope of the method to include older fuels. The correlation was found to be 0.94 for 46 fuels.

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Figure 1 Correlation between ASTM D4625 total sediment and Colorimetric test absorbance for 46 fuels

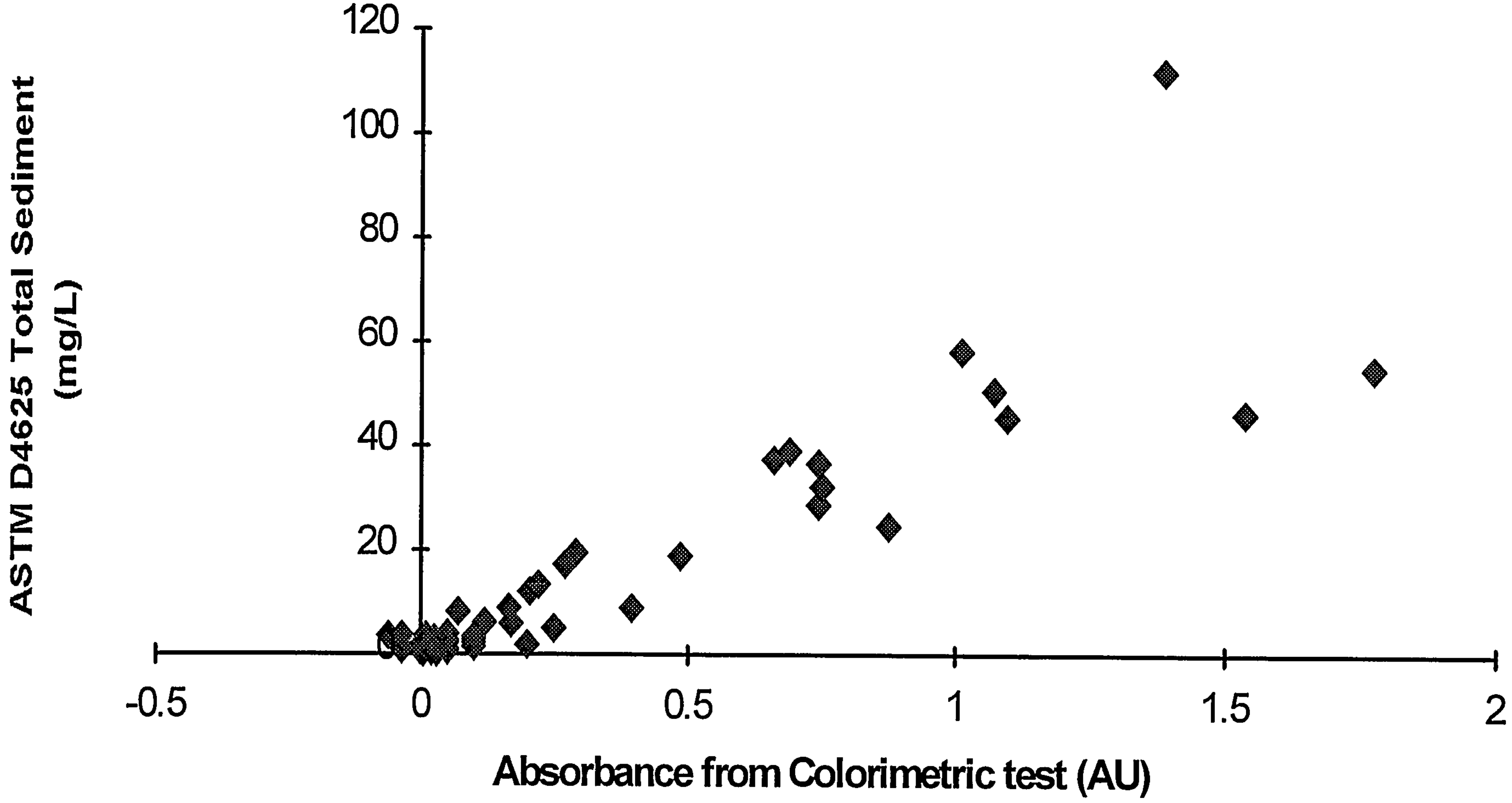

Figure 2 Distribution of marine gas oils tested by geographical area

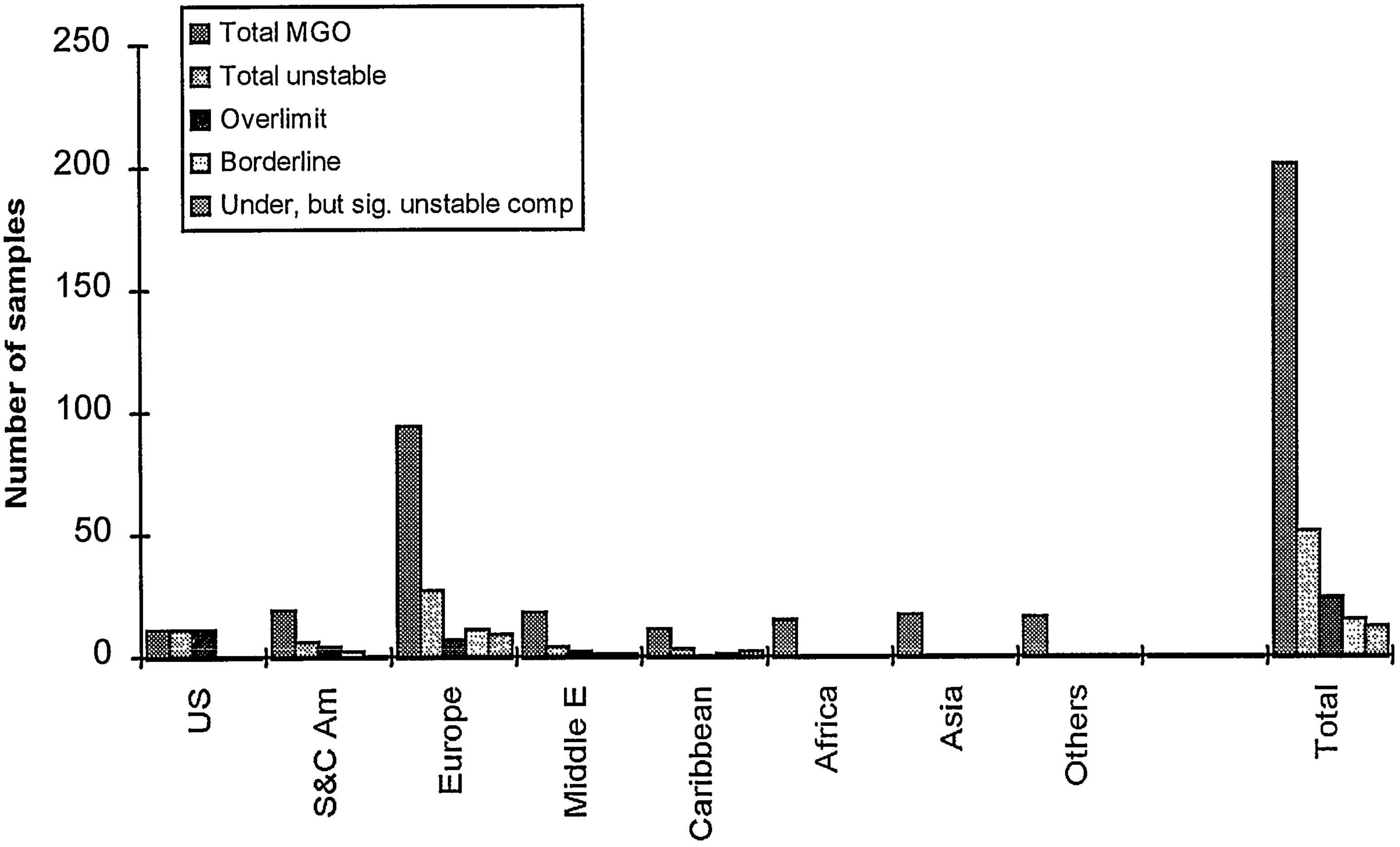

Table 1: Results of visual assessment of fuels using the colorimetric test

Fuel	Colour of reagent layer reported			Phenalene/ Phenalenone present	Absorbance max above 580nm
	Operator 1	Operator 2	Operator 3		
A	Green	Green	Dark Green	20 mg/L	yes
B	Brown	Olive green	Dark Grey	Not Detected	no
C (dyed fuel)	Brown	Deep purple	Deep red	Not Detected	no
D	Brown	Khaki	Green	2 mg/L	yes
E	Green	Green	Dark Green	6 mg/L	yes
F	Dark blue-green	Green	Dark Green	28 mg/L	yes
G	Yellow	Khaki	Light Green	Not Detected	no
H	Brown	Khaki	Brown	Not Detected	no
J	Yellow	Yellow	Yellow	Not Detected	no
K dyed	Brown	Brown	Black	2 mg/L	yes
L	Dark Green	Dark Green	Dark Green-blue	40 mg/L	yes
M dyed	Brown	Brown	Dark Green	Not Detected	no

Table 2 Fuels tested for correlation of colorimetric test with ASTM D4625 (13 weeks at 43°C) total sediment

Source	Composition of samples tested
Refinery 1	2%, 8%,12%, 20% LCO in Gas Oil Blend 1
	Light Gas Oil (LGO)
	Heavy Gas Oil - 2 samples
	Medium Gas Oil
Refinery 2	2% LCO in Gas Oil Blend 2
	Low S Gas Oil
	High S Gas Oil
	Desulphurised Gas Oil
	Kerosine blend
	Heavy gas oil
Refinery 3	2%, 8%, 12%, 20% LCO in Gas Oil Blend 3
	Desulphurised Gas Oil - 2 samples
	Blending Kero - 2 samples
	Straight run gas oil
Refinery 4	2%, 8%, 12%, 20% LCO in LGO
	25%, 50% hydrofined product in LGO
Refinery 5	2%, 8%, 12%, 20% LCO in LGO (fresh components)
	2%, 8%, 12%, 20% LCO in LGO (components aged 5 years)
	Straight run gas oil
Refinery 6	Blending kerosine (straight run)
	Diesel (straight run)
	Automotive gas oils (NATO F-54) - 3 samples
	Gas Oil (NATO F-76) - 2 samples
	Marine gas oil - 2 samples

Table 3 Survey of marine gas oils using the colorimetric test to monitor storage stability

Source	Total MGO Samples	Total of unstable samples	No. over limit	No. border-line	some unstable product present, but below limit
USA	11	11	11		
S&C America	30	9	4	3	2
Europe	94	27	7	11	9
Middle East	18	4	2	1	1
Africa	15	0			
Asia	17	0			
Others	16	0			

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THERMAL STABILITY AND FILTERABILITY OF JET FUELS CONTAINING PDR ADDITIVES IN SMALL-SCALE TESTS AND REALISTIC RIG SIMULATIONS

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Specification, small-scale and realistic fuel simulation tests have addressed concerns about the impact of pipeline drag reducer (PDR) flow modifying additives on jet fuel handling and performance. A typical PDR additive tended to block filters which were similar to those used in the specification Jet Fuel Thermal Oxidation Tester (JFTOT) and other thermal stability test apparatus. Blockages reduced flow rates and PDR concentrations downstream of the filters. Consequently two PDR additives (A & B) were tested in JFTOT apparatus without the usual in-line pre-filters as part of a Ministry of Defence (MoD) co-ordinated Round Robin exercise. Some fuel/PDR additive combinations caused decreases in JFTOT breakpoints. Effects were additive- (type, concentration and degree of shear) and fuel-dependent; most failures were caused by filter blockages and not by a failing lacquer rating. In further work at Thornton, the thermal stability characteristics of similar fuel/additive combinations have been examined in non-specification tests. In Flask Oxidation Tests, PDR additives caused no significant increase in the liquid phase oxidation rates of the fuels. Additives were tested in the Single Tube Heat Transfer Rig (STHTR) which duplicates many of the conditions of a heat exchanger element in an engine's fuel supply system. B produced an average two-fold decrease in thermal stability in a Merox fuel; A had no significant effect. In hydrotreated fuel, B reduced the thermal stability up to five-fold. A had little effect below 205°C, while at higher temperatures there may have been a marginal improvement in thermal stability. Again, certain jet fuel/PDR combinations were seen to reduce thermal stability.

In the late 1980's NATO became interested in using pipeline drag reducer additives (PDR) in middle distillate fuels, particularly kerosine, that were being transported through strategic pipelines. Typically, PDR additives are exceptionally long chain polymers (homo- and co-polymers) derived from various α-olefin monomers. When additive/fuel blends pass through high shear regions, PDR average molecular weights (M_w) are degraded from about 20-30 million to about 1-2 million, and drag-reducing properties diminish. The manufacturers claim that these sheared PDR molecules are invisible to the end use of the fuel product. The additives are already approved in some instances for use in diesel and gasoline fuels; tested at 10-25 times their usual dose rates, the only specification test that registers a change is that for gum[1]. Used throughout the USA's extensive network of pipelines, they substantially reduce energy losses associated with fluid drag. One can increase product flowrate for a given amount of input energy (i.e. number of pumping stations[2]) or achieve the same flowrate with fewer pumping stations[3]. For jet fuel, however, there was concern that very high M_w PDR additives would affect fuel handling and filtration, as well as subsequent performance properties such as thermal stability and combustion spray patterns[4]. Increased local viscosity around the filter pores or pore blockages could affect the filterability of a PDR-doped fuel. Should the molecules, even in their sheared states, pass through the final stages of filtration (1 μm nominally, but there can be holes up to about 26 μm) before entering the aircraft fuel tanks, they might contribute to fuel thermal degradation products, being incorporated into lacquers or filterable deposits.

Thornton's research effort has addressed the related concerns of filterability and thermal stability and has involved specification, small-scale and realistic fuel rig simulation tests. Some of the work has been performed in a Round Robin exercise organised by the British Ministry of Defence (MoD) Thermal Stability Working group, involving five other independent laboratories[5-7] and using the Jet Fuel Thermal Oxidation Tester (JFTOT) to examine the behaviour of jet fuels doped with two PDR additives, A and B. (N.B. The JFTOT is used in the fuel certificate of quality test (ASTM D3241) and so ought to highlight any operational problems that might be expected from PDR introduction.) A necessary preamble to thermal stability tests was to investigate PDR filterability; all thermal stability rigs use a high degree of prefiltration (0.45 μm Millipore) to ensure that the system responds to fuel stability and not contamination. At a realistic doping rate, some PDR could fail to reach the JFTOT test section and 17 μm downstream filter if the pre-filter were to be used, so the impact of PDRs on lacquer formation could be underestimated. The sequence and aims of tests at Thornton were as follows: (1) measure the filterability properties of PDR-fuel blends and determine how these might affect specification (JFTOT) testing and other thermal stability systems; (2) explore the thermal stability of PDR-fuel blends within the MoD JFTOT Round Robin, making use of different fuel types and additive, and additive shear rate; (3) derive some chemical mechanistic information on PDR systems via the flask oxidation test, and (4) determine fuel fouling rates within a large scale realistic rig, using PDR-doped fuels. The mode of action of these additives suggests that their behaviour might differ between turbulent and laminar flow conditions. Thus, the results of large-scale testing in the Single-Tube Heat-Transfer Rig (STHTR) could differ markedly from JFTOT studies.

Other large-scale rig testing of PDR additives had been performed by Rolls-Royce, Derby and the USAF, at their Wright-Patterson laboratories. However, while Rolls-Royce had claimed an increase in lacquering in their "Catacomb" rig, Wright-Patterson had not reported a consistent effect. Thornton's use of the STHTR for testing PDR thus provided the opportunity to produce, if not a definitive statement of PDR behaviour, one which would allow confirmation of certain findings.

EXPERIMENTAL SECTION

Apparatus. Figure 1 shows the rig used to measure the filterability of PDR-containing fuels. Fuel is pressurised within a vessel by a compressed air system and then flows under a constant known pressure to the filter housing via an on/off fuel valve. It is discharged through a filter into a beaker placed on a balance. Data are recorded as profiles of cumulative flow weight (filtrate weight) versus time, typically for 0-200 g of filtrate. A filterability index (FI) can be defined as

$$\text{FI} = (\text{flow time of 100 g of base fuel})/(\text{flow time of 100g PDR-doped fuel}) \qquad 1)$$

The ASTM JFTOT[8] assesses the thermal stability of a fuel by its propensity to lacquer the test section or to block a downstream (17 μm) filter by decomposition products. The test fuel is drawn from a reservoir and passes through a 0.45 μm pre-filter before entering the test section region. Normal operation requires a fuel flowrate of 3 ml/minute. The highest temperature at which a fuel still passes the test is called the JFTOT breakpoint.

Flask Oxidation Tests (FOT)[9] are used to measure the liquid phase thermal oxidation rate of fuels and thereby determine their other oxidation characteristics. Perturbing the system with a radical initiator enables a fuel's intrinsic radical initiation rate to be determined. This rate has been found to be a good predictor of fuel deposition tendency.

The STHTR[10] is used to study the deposition tendencies of fuels. It duplicates the dimensions, fuel flow rates and metallurgy of an aircraft fuel-cooled oil-cooler element. The configuration used for the PDR studies is shown schematically in Figure 2; the additive injection system was reconfigured to bypass the prefiltration step and thus prevent any PDR loss due to filtration. There is a turbulent flow regime (i.e. Reynolds number >> 5,000) within the test element, the Test Heat Exchanger, T.H.E.; the JFTOT and many other rigs only produce laminar flow conditions. The temperatures are increased to ensure measurable deposition. Three heating stages are arranged in series: (1) a 20 litre glass tank in which the fuel is subjected to moderate heating (95-125°C) for about an hour (simulating the wing tank of a supersonic aircraft, in which the wing skin experiences frictional heating, or the collector tank of a military aircraft that has some form of recirculatory fuel system.), (2) a tubular pre-heater which heats the fuel to 165-210°C (simulating fuel heating due to the cabin air, avionics and hydraulic oil coolers), and (3) the Test Heat Exchanger (T.H.E.) which represents one element of a multi-element fuel-cooled engine oil cooler. The T.H.E. consists of a thin walled, dimpled stainless steel tube through which fuel is heated to 190-242.5°C. The fuel side heat-transfer coefficient (htc) decreases due to the insulating effect of any deposits laid down on the interior of the tube and is calculated from

$$\text{htc} = \{M\, C_p\, (T_2 - T_1)\}/\{A\, \Delta T_m\} \qquad 2)$$

where: T_1 and T_2 are, respectively, temperatures of fuel entering and leaving T.H.E., M = fuel mass flow rate, C_p = specific heat of fuel, A = surface area of T.H.E. and ΔT_m = arithmetic mean temperature difference across the T.H.E. Temperature and flow rate data are collated and sent to a computer. The rate of deposition on the inside of the T.H.E. is determined by measuring the change with time of the heat transfer coefficient across the tube. The % per hour loss of heat transfer efficiency, ΔHTC, for each test condition of the T.H.E. can then be determined by

$$\Delta HTC, \%/hour = \{d/dt(10000/htc)/(10000/htc)_{\infty}\} \times 100 \qquad 3)$$

where $(10000/htc)_{\infty}$ is the reference value of 10000/htc at the start of the test series, i.e. when the tube is clean, and d/dt(10000/htc) is the change in 10000/htc with time, obtained from the gradient of the post induction rate.

The initial period where there is slow and little deposition on a clean metal surface is termed the induction period. The period of running the rig to lay down deposits on the inside of a new T.H.E. until there is no more clean metal surface, and hence overcoming the induction period, is termed tube pre-conditioning. N.B. the T.H.E. surface is not accessible for polishing to a given finish. Pre-conditioning mimics practice with real engines, where fuel system components soon become lacquered in service. A lacquered surface also provides a more consistent surface finish and, unlike a virgin metal surface, one which does not over-respond to surface active species in the fuel; experience has shown such surfaces produce more repeatable and therefore more reliable results. The post-induction rate, when Δ htc becomes time invariant at that test temperature, measures the much greater rate of deposition that occurs on a fouled surface. As this rate is constant for a given fuel at a given temperature, it is the most useful parameter for comparing fuels' deposition tendencies.

Reagents. Filterability tests used a clean hydrotreated fuel (Y), low in polar species, while a Merox-treated fuel (AD) was used for oxidation tests. The large scale rig programme used three hydrotreated fuels (AM, AO and AQ), and two sweetened Merox fuels (AP and AN), with high polars contents; key analytical properties of all seven fuels are given in Table 1. Two additives types were tested, A and B, in unsheared and fully-sheared forms, and at final polymer concentrations up to 50 ppm by mass in the fuels. (A 100% sheared additive produces no increase in fuel flow in a flow loop rig). Only additive A (in sheared and unsheared forms) was supplied in sufficient quantity for the large-scale fuel blending needed to perform filterability trials, oxidation studies and preliminary thermal stability rig work.

Procedures. 1) JFTOT filterability: A drop count method was used to measure flowrates for fuel Y in the JFTOT as a function of time rather depending on a calculated average flowrate at the end of test. The JFTOT method uses 8 μm coarse filtration (Whatman No. 2) when loading the fuel reservoir and a 0.45 μm prefilter (Millipore) when leaving the reservoir. In some experiments only the base fuel was subjected to the coarse filtration prior to the addition of PDR. In others, the entire finished blend was coarse filtered.

2) STHTR. Apart from base fuel characterisations, preliminary STHTR tests used a single rig condition, a T.H.E fuel exit temperature of 225°C. Later studies adopted a generalised test sequence of: i) full temperature characterisation of base fuel, ii) full temperature characterisation of fuel + 20 ppm additive, iii) single point (225°C fuel outlet) determination of fuel + 5 ppm additive, and iv) repeat one temperature (225°C fuel outlet) of the base fuel, to further improve repeatability. Where possible, the full sequence was performed using the same T.H.E..

3) Particulates analysis. Effluent samples for tests involving fuels AO and AP were collected from two locations within the STHTR (points S1 and S2, Figure 2), to clarify whether PDR was having an effect on the generation of insolubles. Particulate contamination was determined by passing samples through 0.22 μm filters, in a scaled down version of IP 216/ASTM D2276: single rather than duplicate measurements were made, and 1 rather than 5 litre samples were used.

RESULTS AND DISCUSSION

Filterability experiments - JFTOT and FI rig: Figure 3 shows results for unsheared PDR blends in fuel Y tested with a 5 μm rather than a standard 0.45 μm pre-filter. Up to 100 minutes, flowrate profiles are constant with time; higher PDR concentrations produce lower flowrates because of the local viscosity increase as fuel passes through the filter. At longer times and higher doping rates (beyond 100 minutes and 40 ppm PDR), flowrates progressively decline, indicating filter blocking.

All concentrations of unsheared additive show a decline in flowrate with time (see Figure 4) when the finer pre-filter (0.45 μm) is used, i.e. there is steady blocking of the pre-filter. Coarse filtration of the entire blend, however, reduces the filter plugging considerably; for instance, 40 ppm coarse filtered blend produces similar plugging to 20 ppm of unfiltered additive blend. The coarse Whatman No. 2 paper filter (nominally 8 μm) affects particles in a range similar to that of 0.45 μm Millipore membrane filter. Similarly, Whatman No. 1 (nominally 11 μm) is effective in a range similar to 0.8 μm Millipore. The sheared additive is only 60% as effective as the unsheared additive in terms of filter plugging, i.e. 50 ppm sheared additive blend behaves like 30 ppm unsheared additive blend.

Clearly, a number of PDR/fuel combinations were capable of blocking the standard JFTOT pre-filter. The above results suggest that the PDR molecules themselves are responsible for filter blocking as opposed to poor cleanliness of the additive, by-products of synthesis or chance contamination. In addition, the fact that the filter plugging is more evident for the 0.45 μm than the 5 μm Millipore filter leads to the conclusion that many of the particles which cause plugging are in the range ≈ 0.45 to 5 μm. It is possible that large (fuel solvated) PDR molecules align themselves with the flow in fast flow systems whereas in the JFTOT the extremely slow flow prevents this alignment and thus aids filter plugging by such large molecules. Order of magnitude calculations of the length of the unsheared PDR molecules yield figures around 40 μm, thus only a well-aligned molecule will pass through a 0.45 μm filter.

FI can be used as a guide to the concentration of PDR in a system assuming no shear (or constant level of shear) within the samples. A series of flowrate versus time lines (see Figure 5) show slight but significant curvature, indicating that the flowrate is not only impeded by a local viscosity increase in the pores but also that there is some measure of filter blockage. Fuel flow times were measured under a number of different rig conditions. The best discrimination among the blends was achieved at the lower pressures (0.0524 bar, 21" water) and finer filter size, i.e. Whatman No.1. Figure 6 is the PDR calibration graph for this most discriminating system. PDR-FI calibration graph and flowrate profiles (Figures 5 and 6) were applied to samples derived from the JFTOT rig before and after the prefiltration step. One can estimate that the 0.45 μm prefiltration will reduce a PDR concentration of 40 ppm down to 25 ppm, i.e. by 37%. This means that JFTOT and other thermal stability rigs using the same high degree of filtration could be testing significantly lower levels of additive than anticipated and thus, if used unmodified, would underestimate the performance of similarly doped fuels in real situations.

FOT. These experiments required a fuel, Merox-treated AD, that yielded a repeatable and inhibited oxidation trace. With 5ppm additive A, a non-polar species, in AD there was no tendency to increase the fuel's radical initiation rate. It was assumed that the same would be true for additive B.

JFTOT Round Robin. The MoD wished to investigate a "worst case" of a pipeline with ten pumping stations, additive injection at each station and no loss of additive. For these reasons JFTOT testing was performed with doping rates of 50 ppm and 15 ppm (by mass) active matter, to reflect 10x old and new recommended in-service dope rates. The MoD-sponsored Round-Robin exercise used the JFTOT without the usual pre-filter in place. Instead, fuels were pre-filtered externally to the JFTOT and then the PDR additive concentrates were doped into the filtered fuel. Breakpoint temperatures were determined for various fuel/additive combinations. The results from the six laboratories involved are reported in detail elsewhere[5-7]. Briefly, they showed that PDRs could reduce breakpoints significantly (by up to 50°C in one case), with sheared additives tending to have more effect than unsheared additives. The magnitude of the breakpoint reduction also depended on fuel (hydrotreated or Merox) and additive type. Most JFTOT failures were caused by excessive pressure drops (a result of post test section filter blockage) and not by lacquer formation.

STHTR - Preliminary tests. The object of these rig studies was to compare and contrast the behaviours of two different fuel types, in particular to identify whether they responded similarly to the presence of two different types of PDR additives. Because only small samples were available, preliminary STHTR work was restricted to the additive A. The additive injection pump was able to provide a final concentration in the fuel of 20 ppm PDR, but not the 50 ppm level of the JFTOT Round Robin. Unsheared A was studied in both hydrotreated (AM) and Merox-treated (AN) fuels at 5 and 20 ppm, and in sheared form in AM. Within the repeatability of the STHTR, unsheared A had no propensity to increase lacquering in either fuel (see Table 2); in fact, the evidence might have suggested a reduction of lacquering at the higher dope rate in the Merox fuel. Tests with the fully-sheared additive in AM failed to produce any lacquer on the test section.

Full STHTR characterisations - a) base fuels. Displaying $\log_{10}(\Delta HTC)$ results as a function of temperature produces pseudo Arrhenius plots. These will be referred to as Arrhenius plots hereafter although, strictly, true Arrhenius plots are for single mechanism systems; past work at Thornton[10] has shown that limited treatment of STHTR data with such plots can be informative. The lower the rate of loss of heat-transfer efficiency at a given fuel outlet temperature, the more thermally stable the fuel. Figure 7 displays results for base fuels used in the STHTR studies. As expected, results for the Merox-treated and hydrotreated fuels occupy different areas of the plot. Linear regression fits for data for the three hydrotreated fuels indicate fuels of comparable stability while the two Merox fuels are 10 to 15 times less stable.

The rate of deposition for some hydrotreated fuels can be too low to be measured easily or with any great precision at lower rig operating temperatures. Unfortunately, the logarithmic scale of the Arrhenius plot accentuates the problem and low temperature data can have undue influence on the regression lines of Figure 7. The larger supply of fuel AQ allowed testing in an order that would highlight if any of the results were affected by the pre-conditioning Merox fuel lacquer. Improved confidence in the regression data for the last test on AQ was achieved by testing at two additional, intermediate, temperatures where reliable lacquer measurements were possible. The results, shown in Figure 7, were similar to those of fuel AO.

Experiments with the Merox fuel, AP, produced significantly higher fouling rates and probably benefited from the better pre-conditioning possible with Merox fuels. Fuel AP produced a good fit and was more stable than the Merox fuel, AN, used in the earlier PDR studies.

Full STHTR characterisations - b) additivated fuels. In later studies, only fully sheared additives were tested. Additive B at 20 ppm in fuel AO produced a plot almost parallel to that of the base fuel but shifted to lower stabilities (Figure 8). This shift represents an average 5-fold increase in fouling across the range of test temperatures. There was also a shift when B was doped into fuel AP, corresponding to a 2-fold increase in fouling rates across much of the temperature range (see Figure 8). This is a smaller increase than seen with hydrotreated fuel; the PDR's contribution is less significant in the naturally "dirtier" (i.e. more polars), less stable fuel. The single point determination for 5 ppm B in AP produced an increase on the base fuel figure of 1.7-fold. This is only slightly smaller than the effect for 20 ppm; the difference between the 20 and 5 ppm cases probably is not significant within the repeatability of the rig. (STHTR repeatability has been estimated to be, at best, ±25%.) This lack of sensitivity to the 4-fold increase in PDR concentration, seen also with the hydrotreated fuel, may indicate that a critical threshold for PDR additives to have an effect is at or below the 5 ppm level.

Figure 9 shows the best line through the three measurable results for fuel AO plus 20 ppm additive A. The gradient seemed much too shallow, with the 0.005% intercept suggesting an extremely unstable fuel. At the time, the results were discounted. There was insufficient fuel to repeat the experiment, except with another hydrotreated fuel, AQ. The experimental 10,000/htc trace at the 207.5°C condition was not clear, i.e. the gradients that could be measured after the first few hours were very varied and no single value seemed more reasonable than another. Figure 9 indicates (with *) extremes of values (i.e. upper and lower plausible gradients) that could be computed from the trace. As with fuel AO results, extrapolation to lower temperatures using the higher 207.5 °C value produces a totally unrealistic gradient and 0.005% intercept, consistent with a relatively unstable fuel. If the lower value at 207.5°C is to be believed, the inference is that A's presence has produced a real improvement in fuel stability at all temperatures. The two point fit to the data, although undesirable, is more realistic and suggests that at temperatures above about 205°C additive A perhaps improves the fuel thermal stability (by a factor of about 2 at 225°C). Below 205°C, there is no convincing conclusion to be drawn about the fuel's performance.

The odd behaviour appears to occur for both hydrotreated fuels suggesting that it is not an anomaly. The kinetic analysis and software for the STHTR experiment assume a one-way reaction, or an overall process with a single rate determining step (RDS) throughout the temperature regime being investigated. For additive-free systems, in particular, this assumption has proved reasonable in the past. If, however, there are a series of finely balanced equilibria that produce, for instance, a change in the overall RDS over the temperature regime studied, artefacts could be produced and a single Arrhenius plot treatment of the data would be misleading.

Addition of 20 ppm A to Merox-treated fuel AP produced no significant change to the fouling rate (Figure 10). Likewise, the 5 ppm result at 225°C was not significantly different.

Particulates measurements. Table 4 summarises data obtained for samples taken during STHTR testing of fuels AO and AP. The ambient temperature contaminants levels seem to increase in AO when 20 ppm additive B is introduced to the base fuel. However, there is no obvious effect of higher T.H.E. temperatures on the contaminants levels in the additivated fuel. If the base fuel particulates levels (not measured) at non-ambient temperatures were to be temperature independent, this would mean that all of the contaminant level increase could be ascribed to the presence of the additive, and not to normal fuel lacquer precursors.

At a given temperature and in either fuel, contaminants levels appear to be greater when additive B rather than A is used, by up to as much as 90%. This agrees with the STHTR results which suggest that additive B reduces fuel thermal stability. It is also consistent with most of the JFTOT Round Robin results, where the majority of failures were due to fuel insolubles (causing pressure failures) rather than due to excessive lacquer deposition[6,7], and which found that additive B tended to produce larger breakpoint depressions than additive A. With the Merox fuel, unlike with fuel AO, there is evidence for an increase in contaminants levels with increasing temperature; the particulates more than double on changing from the 190°C to 242.5°C conditions. This may, however, be more of a reflection on the inherent poorer stability of this fuel than a PDR effect; again, particulates levels were not measured for base fuel which had passed through the rig. The 5 ppm and 20 ppm results are not very different.

General STHTR Discussion. Tables 2 and 3 summarise the STHTR results at 225°C for unsheared and sheared additives, respectively. Data are normalised to the base fuel's result, using the "best straight line" value wherever possible rather than the actual 225°C result (the base fuel figures for fuel AM and AN are from single point (225°C) determinations, not linear regression fits). Data for unsheared A had shown no deterioration in thermal stability, with a possible improvement in performance suggested by data for 20 ppm loadings in both the hydrotreated and Merox fuels.

In sheared form, additive A was only tested in fuel AM. For this test, base fuel both with and without PDR gave "negative" fouling rates (i.e. a clean-up effect, with 10,000/htc decreasing throughout); these data have not been tabulated since no meaningful conclusions regarding thermal stability performance could be drawn. The later data (Table 3) for fully sheared A show an improvement in thermal stability in the hydrotreated fuel but show no significant effect in the Merox fuel.

Tabulated and graphical results (Figure 8) confirm that in certain cases, low levels of additive B reduce the thermal stability of both hydrotreated and Merox fuels in a realistic high temperature rig. Problems manifest themselves as increased lacquers and increased levels of particulate contamination, though not increased filter blockage, with the PDR contribution being more noticeable in hydrotreated fuels. Previously, data from the Working Group Round Robin[6,7] had indicated that PDR additives were likely to increase fuel filter insolubles rather than cause surface lacquers in the JFTOT apparatus; JFTOT failures were caused by pressure drop failures rather than by higher lacquer ratings.

Also obvious from the tables and graphs is that 5 ppm and 20 ppm loadings of a given additive in a given fuel produce similar results. This may suggest that there is a critical concentration of PDR above which no further deposit formation can be produced; this may provide a route to conjecturing on the deposition mechanism.

The rig data do not warrant detailed mechanistic discussion but provide scope for conjecture. They resolve some of the apparent differences between earlier results generated by Rolls-Royce and Wright-Patterson laboratory. The interim Rolls-Royce results[11] had related to a Merox fuel, with 50 ppm of fully sheared additives. There was possibly an improvement in thermal stability caused by A. B, however, had caused significant increase in deposit rates in both temperature regimes studied and more pressure build up across filters. Neither fuel had indicated any problems when JFTOT breakpoints were measured. Fuel and additives details of the Wright-Patterson work are not available, but USAF claimed that the PDRs did not worsen thermal stability performance. The STHTR results provide convincing proof that additive B can produce more lacquer in realistic rigs, as Rolls-Royce had claimed, and that the effect may be more dramatic in a hydrotreated than in a Merox fuel. The additive A data are in general agreement with those from Rolls-Royce. Any effect for this additive is negligible or slightly beneficial, and there may be a different temperature dependence for such behaviour than that seen with unadditivated fuels.

CONCLUSIONS

PDR filterability experiments have confirmed that the concentrations of PDR additives reaching test sections of unmodified thermal stability test rigs could be significantly reduced by the pre-filters. Flowrates of PDR-doped fuels are retarded by two mechanisms: (i) an increase in local viscosity in the test filter pores and (ii) trapping of additive molecules in the test filter pores producing partial blockage. The Filterability Index method would suggest that up to about 40% of PDR additive concentration could be held back by a JFTOT prefilter.

A comprehensive set of tests looking at a matrix of a) fuel processing type, b) additive type, c) additive concentration and d) temperature has been performed in a reliable, established turbulent flow rig (STHTR), modified to allow for filtration effects. Data from the STHTR show that addition of low levels of fully sheared additive B (< 20 ppm) to jet fuels can cause up to a 5-fold reduction in the thermal stability of the fuel. The effect is more pronounced with a hydrotreated fuel than with a Merox treated fuel. Similar levels of fully sheared additive A added to a Merox treated fuel cause no significant change to the fuel's thermal stability but in a hydrotreated fuel cause, if anything, a slight improvement in the fuel's thermal stability above about 205°C. The effect of PDR additives on STHTR behaviour appears independent of additive concentration, suggesting that there may be a critical concentration level, about or below 5 ppm, above which further PDR addition has no further impact.

These rig experiments confirm the MoD working group's JFTOT studies, i.e. with certain jet fuel/PDR combinations, the PDR additive can reduce the fuel's thermal stability. It is not invisible to end use. The STHTR data do not show the same additive concentration dependence as the JFTOT studies but are in broad agreement with those from the Rolls-Royce "Catacomb" rig, i.e. some fuel/PDR additive combinations are less thermally stable than the base fuel alone. Both sets of rig data support the view of the JFTOT Round Robin exercise that current generation PDRs should not be used in jet fuel systems. Should any PDR material manage to pass the final stages of fuel-handlers' filtration, it could produce early component blockages as well as more rapid lacquer build-up and consequent reduction in component lifetimes.

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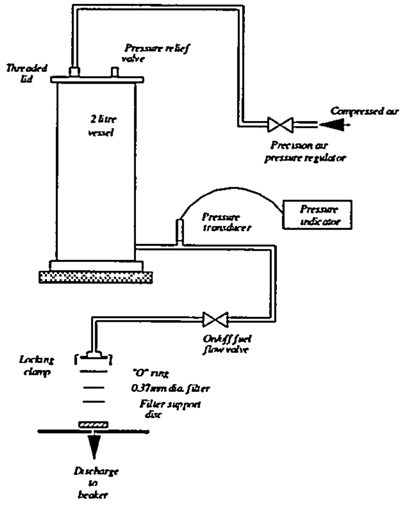


FIG. 1 - Schematic of filterability index rig

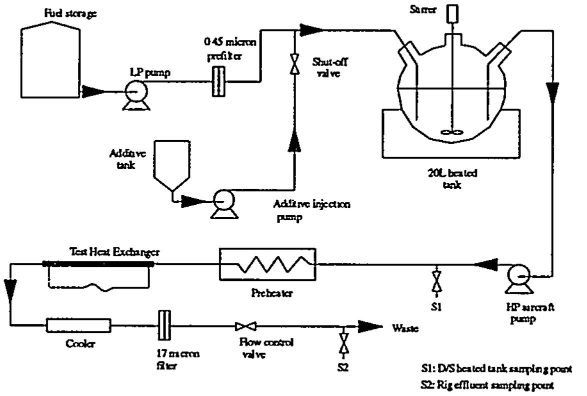


FIG. 2 - Schematic of STHTR rig showing main heating elements and sampling positions (S1 and S2)

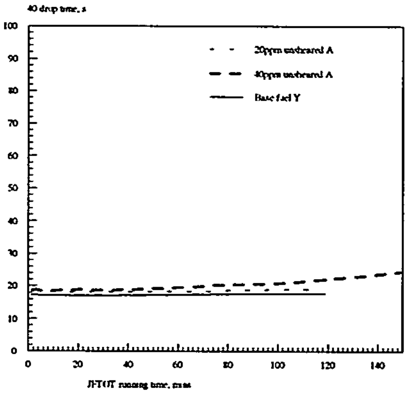


FIG. 3 - PDR-JFTOT flow-rate effects for fuel Y and unsheared additive A with 5 micron pre-filter in place

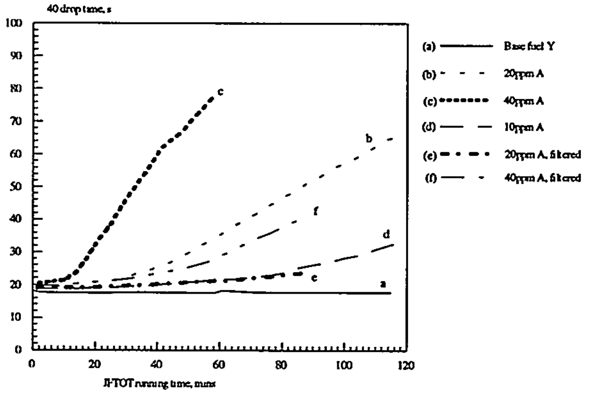


FIG. 4 - PDR-JFTOT flow-rate effects for fuel Y and unsheared additive A with 0.45 micron pre-filter in place

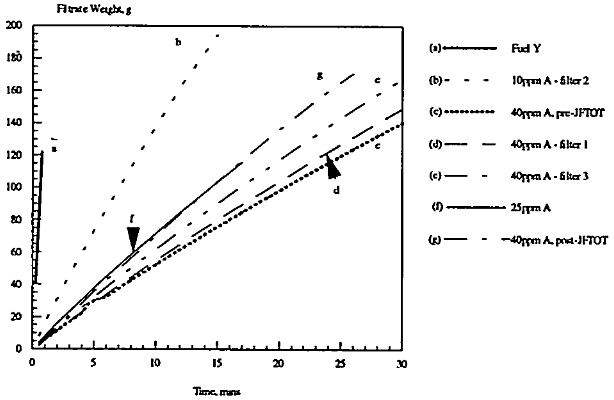


FIG. 5 - Filterability of unsheared A in FI rig

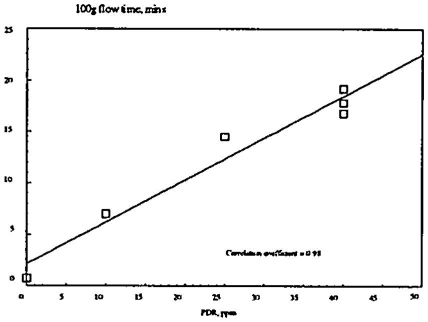
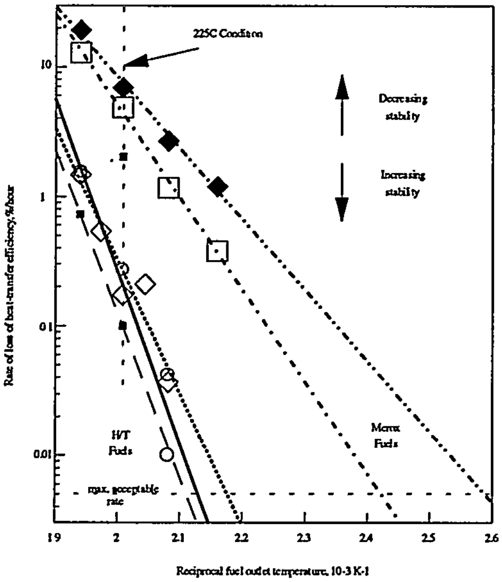
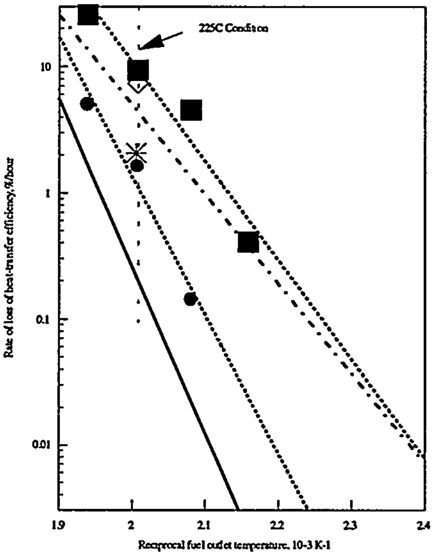


FIG. 6 - 100g flow time as function of unsheared additive A concentration in fuel Y



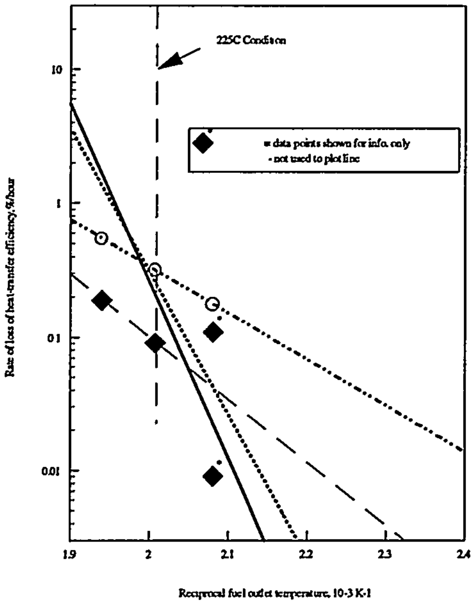
Fuel	AM	AN	AO	AP	AQ
	—■—	--◆--	—○—	-▣-	···◇···

FIG. 7 - Base fuel lacquering rates in the STHTR as a function of fuel outlet temperature



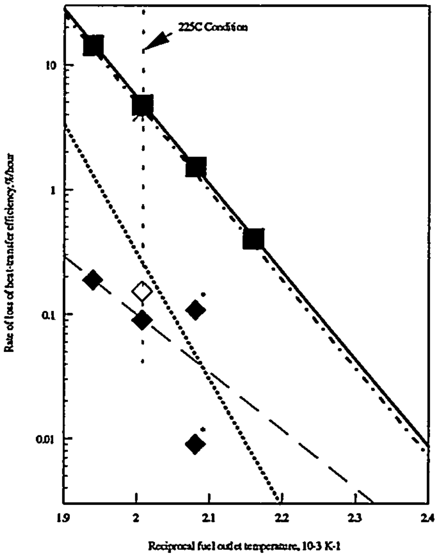
Fuel	AO	AO + 20ppm sheared B	AO + 5 ppm sheared B
	—	··●··	✳
Fuel	AP	AP + 20 ppm sheared B	AP + 5 ppm sheared B
	-·-·	··■··	◇

FIG. 8 - Effect of additive B on lacquering rates of fuels in the STHTR



Fuel	AO	AO + 20 ppm sheared A	AQ	AQ + 20 ppm sheared A
	—	··○··	········	— ◆ —

FIG. 9 - Effect of additive A on lacquering rates of hydrotreated fuels in the STHTR. Points marked * not fitted



Fuel	AP	AP + 20ppm sheared	AP + 5ppm sheared
	-·-·	—■—	✳
Fuel	AQ	AQ + 20ppm sheared A	AQ + 5ppm sheared A
	········	—◆—	◇

FIG. 10 - Effect of additive A on lacquering rates of fuels in the STHTR. Points marked * not fitted

Table 1. Properties of Hydrotreated (HT) and Merox-treated (M) fuels used in study.

	Fuel code:	AD	Y	AM	AN	AO	AP	AQ
	Treatment:	M	HT	HT	M	HT	M	HT
PROPERTY	Method							
Aromatics, %v	D1319	18.0	16.0	13.5	17.7	17	17.6	17.4
Olefins, %v	D1319	0.5	<1.0	<1.0	0.3	<1.0	0.5	0.4
Total sulphur, ppm m/m	D2622		17		200	200	500	
	D1266	720		<1				100
Mercaptan S -Doctor test	D235		Neg	Neg		Neg		Neg
ppm m/m	D3227	11			12	<3	<6	2
Acidity, mg/KOH	D3242	0.005	0.004	0.005	0.006	0.005	0.005	<0.001
JFTOT Breakpoint, °C		275	285	285	275	285	280	295
Radical initiation rate								
10^{-7} mole/Ls		8.26	0.93	0.72	5.25	0.71	5.43	0.58
Induction period, min				46		52.3		53.1
STHTR, %/h at 225°C		0.68	0.19	0.1	7.46	0.2	4.37	0.26
Distillation, C	D86							
IBP		165.0	155.0	155.0	154.5	159.5	147.0	153.0
50%		192.5	200.0	198.5	195.5	200.0	193.0	197.0
FBP		254.0	259.0	251.0	255.5	256.5	252.5	256.0
Density at 15 C, kg/m^3	D4052	798.0			800.6		796.5	
	D1298		796.0	789.1		794.7		788.8
WSIM (MSEP)	D3948	76	95	97	97	92	78	95
Copper, microg/L = ppb	ICP-MS	12	<2	<2	18	<3	<3	<2

ADDITIVES	Class							
Hitec 4733, mg/L	AntiOxid			20				
RDE/A/609, mg/L	AntiOxid					23		19.0
Ionol J65, mg/L	AntiOxid		19.0					
ASA-3, mg/L	AntiStatic		0.7	0.7				
Stadis 450, mg/L	AntiStatic	1.89			0.45	1.3	1.13	1.1

Table 2. STHTR fouling rates at 225°C normalised to base fuel rate for unsheared PDR

Test fuel	ΔHTC at 225°C (normalised)		
	AM	AN	
		1st Test	2nd Test
Base fuel	1	1	1
+ 5 ppm A	1.2	0.96	-
+ 20 ppm A	0.87	0.78	0.83

Table 3. STHTR fouling rates at 225°C normalised to base fuel rate for sheared PDR

Test fuel	ΔHTC at 225°C (normalised)		
	AO	AQ	AP
Base fuel	1	1	1
+ 5 ppm B	9.2	-	1.7
+ 20 ppm B	5.6	-	2.1
+ 5 ppm A	-	0.8	1
+ 20 ppm A	-	0.5	1.1

Table 4. Filtration studies on STHTR effluent samples of sheared PDR fuel blends

Fuel / T.H.E. fuel outlet temperature	Particulate contaminants, mg/l	
AO at ambient	0.38 (base fuel)	
	with B	with A
AO + 20 ppm PDR: at ambient	0.90	-
at 207.5°C	0.55	0.50
at 225.0°C	1.40	0.80
at 242.5°C	1.09	0.67
AP + 5 ppm PDR at 225.0°C	2.29	2.10
+ 20ppm PDR at 190.0°C	1.10	0.82
at 207.5°C	1.73	0.91
at 225.0°C	2.30	1.70
at 242.5°C	2.70	2.38

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SYSTEM EVALUATION OF IMPROVED THERMAL STABILITY JET FUELS

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Abstract: A single-pass, single-tube heat exchanger device called the Phoenix rig and a single-pass, dual-heat exchanger system called the Extended Duration Thermal Stability Test system are specific devices/systems developed for evaluating jet fuel thermal stability. They have been used extensively in the evaluation of various jet fuels and thermal stability additives. The test results have indicated that additives can substantially improve the thermal stability of conventional jet fuels. Relationships of oxygen consumption, residence time, bulk, and wetted wall temperatures on coking deposits that form in the heated tubes have also been investigated.

1. Introduction: Thermal management is a major factor in designing today's high-performance aircraft. The trends are towards larger and higher power avionics, higher power hydraulic and electrical systems, and more efficient, higher-temperature engines. Fuel is used as the primary heat sink for cooling of the aircraft and engine systems. Fuel operating temperatures will increase to accommodate the higher loads. Laboratory systems have been developed and tests conducted to establish the temperature limits for JP-8 fuels and to provide a baseline for evaluating improved thermal stability fuels (JP-8+100). JP-8+100 fuel is being developed by the U.S. Air Force to provide a 100°F (56°C) improvement in thermal stability. This paper covers laboratory test systems being used to evaluate JP-8 thermal stability limits and the test results with conventional JP-8 and JP-8+100 fuel candidates.

Temperature limits for engine fuel systems using conventional JP fuels were basically established by field experience. There are many tests, such as Jet Fuel Thermal Oxidation Tester (JFTOT) for evaluating the thermal stability of fuels. However, these tests do not provide data appropriate for system design considerations. These tests are normally conducted at high temperatures and for short durations to accelerate the test, and at low flow rates to conserve the amount of fuel required for the test. These tests emphasize the fuel's tendency to make deposits at the higher temperatures. For example, the minimum acceptable temperature for JP-8 fuel in

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the JFTOT is 260°C (500°F); whereas the general temperature limits that are used for engine design are 163°C (325°F) for bulk fuel and wetted wall temperatures of 205°C (400°F) in engine fuel injector nozzles. The systems and tests covered in this paper were directed toward developing an improved research device for evaluating fuel thermal stability and establishing fuel thermal degradation criteria for JP-8 fuels that can be used for aircraft system designers. These criteria are also required to evaluate the increased thermal stability temperature capability of the JP-8+100 fuel candidates.

2. **Increased Fuel Thermal Stability Requirements:** Advanced fighters that will be produced late in this decade will require increased cooling resources. Fuel will be subjected to higher temperatures, higher heat fluxes, and multiple heating and cooling cycles due to increased heat loads imposed by the aircraft and engine systems. Integrated aircraft thermal management is becoming a significant driver in the balance between providing sufficient cooling resources to maintain component integrity and life and the aircraft performance capabilities. Fuel is the primary heat sink for aircraft thermal management. Most current fighter aircraft recirculate the fuel on the airframe to maintain proper aircraft cooling and to maintain the aircraft/engine interface temperature to between 80°C (176°F) and 120°C (248°F). The fuel is cooled before it is returned to the main fuel tanks to prevent the bulk fuel from exceeding 66°C (150°F). The fuel is cooled via either ram air or natural convective/conductive cooling available in the metal wing tanks (Fig. 1).

The burn fuel flow for the engines now being developed will be too low during most of the flight mission to satisfy the increased system heat loads. To provide the require fuel cooling flow, fuel will be bypassed from the engine back to the aircraft fuel tanks by way of a ram air/fuel cooler. From a thermal management standpoint it is desirable for the aircraft and engine fuel systems to operate at higher temperatures to eliminate or reduce the size of the ram air/ fuel heat exchanger by reducing the required bypassed fuel flow and increasing the effectiveness of the heat exchanger. Bypassed flow with current fuels at low engine power settings can exceed 2.5 times the flow required to provide the engine thrust. In addition, it is anticipated that these aircraft using current fuel such as JP-8 will require increased fuel system maintenance to replace fouled engine components. The JP-8+100 fuel discussed later in this paper is being developed to provide the additional heat sink capability and to eliminate the fuel fouling of fuel system components.

Looking ahead toward the beginning of the next century, the Integrated High Performance Engine Technology (IHPTET) program is developing technology that will potentially double the turbopropulsion capability of current engines. To achieve these goals, fuels will be stressed to considerably higher temperatures than present aircraft applications. New lubricants being developed under the IHPTET program will operate at temperatures of 316°C (600°F) for the next generation engines and 385°C (725°F) for the following generation. Present-day lubricants are limited to temperatures of 177°C (350°F). Future fuels must have a similar temperature capability increase to avoid fouling problems in the fuel/lube oil coolers. In addition, studies have shown[1] that the wetted wall temperature in main burner nozzles will be in the range of 260°C (500°F) to 300°C (572°F) compared to the maximum allowed wetted wall temperature of 204°C (400°F) for use with current fuels such as JP-8. The bulk fuel temperatures projected for the higher wetted wall temperature range from 204°C (400°F) to 218°C 425°F).

3. JP-8+100 Fuel Development: The United States Air Force embarked on a program in 1989 to improve the thermal stability of JP-8 fuel[1]. Two approaches were initially explored. The first approach was to develop a new refinery specification for a more thermally stable JP-8 fuel. This approach was discarded early since a new fuel would be costly to obtain and would offer logistics penalties contrary to a single fuel for the battlefield. The second and preferred approach was to develop a thermal-stability-improving additive package that could be added to the JP-8 kerosene base fuel and increase its thermal stability by 100°F (56°C). Currently, the improved fuel is referred to as JP-8+100, but when the development is complete it is anticipated that the additive package will be listed in a Qualified Products List (QPL) for use in the JP-8 specification, Mil-T-83133. The cost goal for the additive package is $0.001 per gallon of fuel.

Current research indicates that the additive package will contain four main ingredients: antioxidants, metal deactivators, detergents, and dispersants. The Air Force contacted major additive manufacturers and oil companies to provide thermal-stability-improving additives for evaluation. To date, more than 300 additives have been screened, and several show promise for meeting the thermal stability goals. A number of test devices have been developed or refined for screening additives[2]. The Phoenix rig and the Extended Duration Thermal Stability Test (EDTST) system are the primary flowing type test systems for evaluating the most promising additives identified by the other screening tests.

The Phoenix test rig was established as a research device for evaluating a fuel's tendency to form deposits at elevated temperatures. It is primarily used for short tests (under 24 hours) at accelerated temperature conditions. The EDTST system was established for longer duration tests (96 hours or higher) at aircraft fuel system simulated heat load, residence time, and temperature conditions.

4. Phoenix Test Rig: The Phoenix test rig is a single pass fuel flow system that heats fuel in a single steel tube. Fig. 2 is a flow schematic diagram of this rig which consists of a preconditioning tank, a positive displacement diaphragm pump, two copper blocks (one for heating, the other for cooling), a fuel supply system, filters, and instrumentation. Small-bore stainless-steel tubes (0.3175 cm o.d., 0.216 cm i.d., and 55.9 cm in length) are used as the test sections in the copper blocks. The internal surface of the tube has an roughness range of 0.2 to 0.38 cm. The heating block is a 45.7 cm long copper cylinder with an o.d. of 7.6 cm. The copper cylinder is split lengthwise into two halves, with each section containing a full-length cartridge heater. A lengthwise groove in the flat face of each cylinder surface was provided for clamping the 0.3175 cm diameter tube in between the cylinder halves. The cooling block is designed similarly, except that it is not provided with cartridge heaters.

5. Phoenix Test and Test Results: The Phoenix test rig is used to measure various aspects of fuel thermal stability, such as carbon deposition versus temperature, oxygen consumption, and methane production. The carbon deposition testing has been conducted primarily at three copper block temperatures (227°C (441°F), 270°C (518°F), and 300°C (572°F)). The flow rate for the 270°C (518°F) and 300°C (572°F) tests is 16 ml/min, and the 227°C (441°F) test is conducted at 4 ml/min. The test duration is 12 hours at 227°C (441°F) block temperature, and six hours for the other test temperatures. The residence time in the heater tube is about 25 sec at 4 ml/min and 6.2 sec at 16 ml/min. The 227°C (441°F) and 270°C (518°F) block temperature test results only are covered in this paper. The 300°C (572°F) block test is not considered to be applicable to JP-8+100 requirements.

At the conclusion of the tests, the test sections are removed, drained, cut into 50 mm segments, rinsed with hexane, dried in a vacuum oven, and analyzed for carbon deposits by a LECO RC-412 multiphase carbon analyzer.

Evaluation of the JP-8+100 additives has been accomplished by running repetitive tests with and without the additives in various Jet A and JP-8 fuels. Tests were run with a variety of fuels to ensure that the additive is effective in fuels from different base stocks and processing methods. Tests were also conducted with a JPTS fuel, which was established as a baseline fuel for the JP-8+100 overall program. Three Jet A fuels were primarily used as baseline fuels for evaluating the JP-8+100 additives: POSF-2926[**], POSF-2980, and POSF-2827. Since JP-8 is the baseline fuel for this overall program, the fuels were doped with the standard additive package (corrosion inhibitor, anti-icing additive, and static dissipater additive) to make them into JP-8 type fuels.

POSF-2926 was considered to be the best (from a thermal stability standpoint) of the three baseline Jet A fuels. The refinery method for this fuel was not known. Comparisons of the carbon deposits of this fuel with and without a potential JP-8+100 additive package (JP-8+100 additive #1) for 227°C (441°F) and 270°C (518°F) block temperaturesare shown in Figs. 3 and 4. JP-8 additive #1 consisted of 100 mg/ml of a proprietary dispersant (Betz 8Q405) and 25 mg/l of butylated hydroxy toluene (BHT) antioxidant. At the lower temperatures, the deposits for the fuel without the additive package reached a peak in the middle of the heater tube. Fuel deposits with this fuel at the 270°C (518F) block temperature were increasing at the end of the heater tube. At the lower temperature, the deposit peak occurs where the oxygen is being consumed in the middle of the heater tube. At the higher temperature, the oxygen is not completely consumed in the heater tube. The oxygen consumption difference between the two temperature tests is caused by lower flow and associated longer residence time of the lower temperature test. At both temperatures, the deposits for the fuel with the JP-8+100 additive package were almost identical to each other and considerably lower than the fuel without the additive package.

The second Jet A fuel tested was designated as POSF-2980. This fuel was Merox treated during its refining process. The comparisons of the carbon deposits of this fuel with and without

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[**] Each fuel acquired by the Air Force has been assigned a four-digit number (e.g., POSF-xxxx). POSF is indicative of the Air Force Branch which catalogued the fuel. These numbers are used for identification here to be consistent with other reports and tests which have been performed on these fuels.

the potential JP-8+100 additive #1 package are shown in Figs. 5 and 6. The deposits for this fuel with the JP8+100 additive package at both temperatures were considerably lower than for the fuel without the additive package. This fuel without the additive package had carbon deposit patterns similar to POSF-2926. A peak was reached at the lower temperature; at the higher temperature, the deposit continued to rise at the end of the heater tube.

The third Jet-A fuel tested was designated as POSF-2827. This fuel was refined by a straight-run process with no hydrotreating. The comparisons of carbon deposits with and without a potential JP-8+100 additive #2 package are shown in Figs. 7 and 8. This was not the same package as tested with the other Jet A fuels. Additive #2 consisted of 300 mg/l of a proprietary dispersant (MCP477), 100 mg/l Betz 8Q405, and 25 mg/l BHT. The other additive package has not been tested in this fuel. The deposits for this fuel without the additive package were considerably less than the deposits with the additive package. The deposits of the fuel with the additive package reached a peak in the heater tube at both block temperatures. This additive package is no longer a candidate for JP-8+100 fuel.

Tests were conducted with JPTS fuel at the same block temperatures. A comparison of the carbon deposit is shown in Fig. 9. The deposits on the heater tubes at both block temperatures were very low and significantly less than the other fuels tested.

An oxygen consumption test is another test that is conducted on the Phoenix test rig. This test is performed by increasing the tube wall heater temperatures in 5°C (9°F) or 10°C (18°F) increments while maintaining a flow of 4 or 16 ml/min. After the flow and temperature changes stabilize, the fuel upstream and downstream of the heated tube is analyzed for dissolved gases using a modified HP-5890 Series II gas chromatograph[3].

Thermal stressing of the fuel causes the dissolved oxygen to react with the fuel to form both bulk and wall deposits, as well as trace quantities of methane gas. The oxygen consumption test is used to examine the effects of candidate additives on fuel oxidation rates. For example, an antioxidant additive may significantly increase the temperature at which the dissolved oxygen reacts with the fuel. Also, the amount of methane produced appears to correlate with the amount of deposit formed[4].

Fig. 10 is a plot of oxygen consumption versus temperature characteristics of the four baseline fuels. The hydrotreated JP-TS fuel reacts with oxygen at the lowest bulk temperatures. POSF-2827 reacts with oxygen at the highest temperature and its slope is very gradual, significantly extending the oxygen-consumption temperature range. The higher oxygen-reaction temperatures for POSF-2827 are attributed to significant quantities of natural antioxidants in the fuel after refining. Fig. 11 shows the oxygen consumption comparison of the JP-8 and JP-8+100 additive #1 in POSF-2926 and POSF-2980. Here the oxygen-consumption temperatures were increased by the JP-8+100 additive for both fuels. Fig. 11 also shows the effect of oxygen consumption of JP-8+100 additive # 2 in POSF-2827. This additive produced the high hot tube deposits and is no longer a JP-8+100 candidate, as discussed previously.

6. EDTST System: The EDTST system was established by modifying an existing facility that was originally a "hydrotreater" for processing fuels. A schematic of the EDTST system is shown in Fig. 12. The system consists of a 60-gallon feed tank, an electrical motor-driven gear pump, two clam shell furnace heaters, and a scrap tank. Normally, fuel makes only one pass through the system. The first furnace heater (preheater) in the system is used to establish the desired fuel bulk temperature in the second heater. The fuel bulk temperature is representative of the fuel temperatures that are experienced due to aircraft and engine heat loads. Temperature is established in the second furnace heater (main heater) to represent the wetted wall temperatures associated with engine injection nozzles. Bulk fuel and wetted wall temperatures have been established because they are used to define limits for engine fuel systems design. The present bulk fuel temperature limit for engine control systems is 163°C (325°F). Engine fuel injectors are normally limited to wetted wall temperatures of 204°C (400°F) to avoid coking problems with conventional JP-type fuels. The desired capability for JP-8+100 fuel is to provide fuels that are thermally stable at wetted wall temperatures of 260°C (500°F) and bulk temperatures of 218°C (425°F).

Both furnace heaters are 0.81 meters long and resistively heated. Each has five heating element zones that are independently controlled. The fuel flows upward through a single stainless-steel tube in each heater. The tube in the preheater has a diameter of 0.96 cm and a wall thickness of 0.0889 cm. The tube in the main heater has a diameter of 0.32 cm and a wall thickness of 0.0889 cm. Each tube is assembled inside a thick-walled furnace tube that has an i.d. of 2.54 cm and an o.d. of 5.08 cm. The tubes have thermocouples attached to the outer wall for establishing wetted wall temperature. The annular space between the furnace tube and heater tubes is filled with sand. A typical main heater assembly is shown in Fig. 13. Both furnaces have two sets of thermocouples in each heater element zone to control temperature. One set of thermocouples is used to control the heat input from the clam shell heaters; the other set is used for a safety shutoff control system.

During tests, the temperature of the heating zones of the preheater is increased to establish the desired bulk outlet temperature. Similarly, the temperature of the heating zones of the main heater is established to provide the desired wetted wall temperature as measured on the tube outer wall. The middle heating zone is set at the highest temperature to ensure that the desired wetted wall temperature occurs in this zone. A typical temperature profile for the main heater tube is shown in Fig. 14. A flow rate of 1 gallon per hour (gph) and a duration of 96 hours have been used for most tests. At the 1 gph flow rate, the residence time from the inlet of the preheater to the outlet of the main heater is 50 seconds. Similarly, the residence time from the inlet to the outlet of the main heater is 1.6 seconds. The Reynolds number in the heater tube is approximately 2500 at the 1 gph flow rate. The EDTST system is computer controlled and can run unattended for long periods.

7. EDTST Test and Test Results: POSF-2926 with the standard JP-8 additive package was tested with and without candidate JP-8+100 additive #1 at a wetted wall temperature of 260°C (500°F) and a bulk inlet temperature of 177°C (350°F). A comparison of carbon deposits for these tests is shown in Fig. 15. The segment numbers correspond to 5.1 cm segments that the heater tubes are cut into for carbon analysis. Segments 13 and 14 are in the middle zone of the heater where the maximum wetted wall temperature occurs. Total carbon is measured by burning off the carbon from the tubes in the LECO Carbon Analyzer. A test duration of 96 hours was used for these tests and for all the tests discussed later in this paper. There were essentially no deposits with the JP-8+100 additive added to this fuel for these temperature conditions. The deposits for the fuel without the additive were significant and peaked in the middle section of the tube. This same fuel with the additive was then tested at a wetted wall temperature of 288°C

(550°F) and a bulk inlet temperature of 177°C (350°F) to establish how much temperature improvement the additive provides. A comparison of the carbon deposits for this test and the previous two tests is shown in Fig. 16. Based on these results, the additive provides approximately a 28°C (50°F) wetted wall temperature improvement for this fuel. However, the additive in this fuel provided a margin of 28°C (50°F) in regards to the 260°C (500°F) wetted wall temperature goal. A test was also conducted on the JP-8+100 additive #2 candidate in this fuel at a wetted wall temperature of 260°C (500°F) and a bulk inlet temperature of 177°C (350°F). A comparison of the carbon deposits with this additive and the baseline fuel in both the preheater and heater is shown in Fig. 17. This additive resulted in significant deposits in the preheater tube and deposits thoughout the heater tube with no peak. This result correlates with the Phoenix test rig findings that this additive reduces the temperature at which oxygen is consumed in this fuel.

Similar tests were conducted on POSF-2980 with and without the standard JP-8 additive package plus the JP-8+100 additive #1 candidate at the same conditions as run with POSF-2926. A comparison of carbon deposits for these tests with POSF-2980 is shown in Fig. 18. The deposits were approximately 50 percent higher with this fuel as compared with POSF-2926 and indicated that the JP-8+100 additive provided about the same wetted wall temperature improvement.

Tests were then conducted on the third Jet A fuel (POSF-2827) with and without the standard JP-8 additive package plus the JP-8+100 additive #1 package at the same wetted wall temperatures and bulk inlet temperatures as used for the other two fuels. A comparison of carbon deposits for these tests is shown in Fig. 19. The results of these tests indicate that the deposits from this fuel were similar to POSF-2980. The deposits with the JP-8+100 additive were higher than with the other two fuels. However, this deposit quantity is considered to be acceptable for meeting the JP-8+100 goals. The maximum thickness of the deposit is estimated to be 0.0002 inch. At this rate, it would take 5000 hours at these conditions to obtain a 0.010 inch deposit.

Tests were also conducted on JPTS fuel at a wetted wall temperature of 260°C (500°F) with a bulk inlet temperature of 177°C (350°F) and a wetted wall temperature of 288°C(550°F) with bulk inlet temperatures of 177°C (350°F) and 218°C (425°F). A comparison of the results of these tests is shown in Fig. 20. This figure shows that the fuel formed significant deposits at 288°C (550°F) wetted wall temperatures at the higher bulk inlet temperature (218°C (425°F)) but did not have any deposits at the same wetted wall temperature at the lower bulk inlet (177°C (350°F)) condition. A comparison of the tube deposits in the preheater for these 288°C (550°F) wetted wall temperature tests are shown in Fig. 21. This figure indicates that the fuel forms deposits in the preheater at the 218°C (425°F) bulk inlet temperature. Therefore, the allowable bulk temperature (218°C (425°F)) for engine fuel system design desired by this overall program could not be met by the JPTS fuel tested. The result of this test also indicates that there is a definite induction time involved with deposits being formed on the hot tube walls, since significant deposits were not obtained for this fuel at higher bulk and wetted wall temperatures during the shorter duration Phoenix tests.

POSF-2980 with the standard JP-8 additive package plus the JP-8+100 additive was also tested at a 288°C (550°F) wetted wall temperature and bulk inlet temperatures of 177°C (350°F) and 218°C (425°F). A comparison of the carbon deposits from both the preheater and heater for these tests is shown in Fig. 22. Similar to JPTS, this fuel also formed deposits in the preheater at the 218°C (425°F) bulk inlet temperature. This fuel had higher heater deposits at the lower bulk inlet temperature condition. These higher deposits appear to have occurred because the fuel formed the deposit in the preheater instead of the heater at the higher bulk inlet temperature condition. Phoenix oxygen consumption tests suggest that the deposits formed as a result of the oxygen being depleted in the preheater with this fuel at these conditions. The JP-8 +100 additive candidate in this fuel also did not meet the desired bulk temperature requirement for this overall program. Other additive candidates and increased concentrations of the additive tested are to be evaluated to determine their potential to provide the desired capability. More tests of this additive package will also be conducted to determine its maximum allowable bulk operating temperature.

8. Summary: The development of an improved JP-8 fuel (JP-8+100) offers a significant payoff to the Air Force. The trends towards higher heat loads and their associated increase in fuel system temperatures are the main stimulus for this new fuel development. In addition to the higher thermal stability fuel, a need was also identified for improved test apparatus and/or test techniques to evaluate the fuel. To date, tests conducted using the Phoenix test rig and EDTST have verified that additives can improve the thermal stability of JP-8 fuels. The goal for operating at wetted wall temperatures of 260°C (500°F) has been achieved. The goal for bulk fuel temperatures of 218°C (425°F) with no deposits has not been achieved. Further tests will be conducted on the most promising additives to determine their allowable temperature operating limits. Additional additive candidates will also be evaluated in both the Phoenix test rig and EDTST to identify potential additives to meet the wetted wall and bulk fuel temperature goals of this program. However, if the bulk temperature goal cannot be totally achieved, the JP-8 fuel specification will most probably be changed to take advantage of the wetted wall temperature improvement already demonstrated by a JP-8+100 additive candidate.

9. Acknowledgments: This work was supported by the U.S. Air Force, Wright Laboratory, Fuels and Lubrication Division, Aero-Propulsion and Power Directorate, Wright-Patterson Air Force Base, Dayton, Ohio, under contract No. F33615-92-C-2207, with Mr. Charles W. Frayne serving as the Air Force Technical Monitor.

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3) T. F. Williams, C. R. Martel, and H. L. Imwalle, “Studies of Jet Fuel Thermal Stability in a Flowing System”, Volume I: Experimental Work and Volume II: Data Set, August 1992, University of Dayton Research Institute Report No. UDR-TR-92-98 and UDR-TR-92-99.

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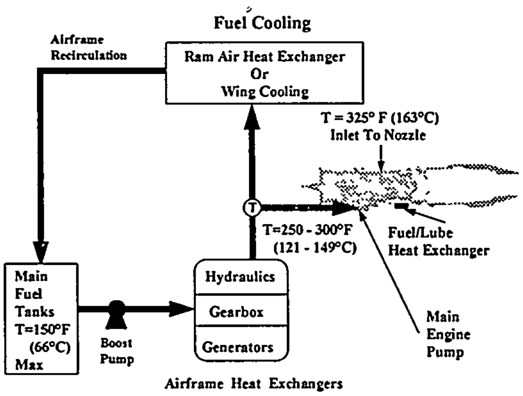

Fig. 1: Current Fighter Aircraft Thermal Management System

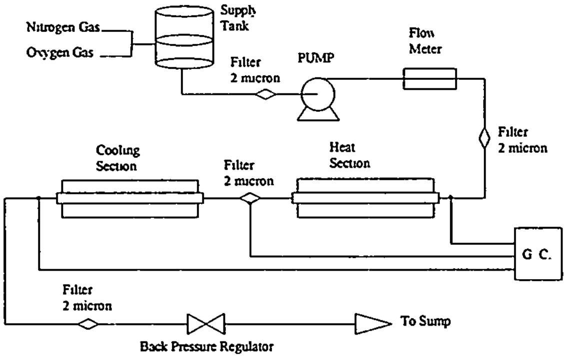

Fig. 2: Phoenix Rig Schematic

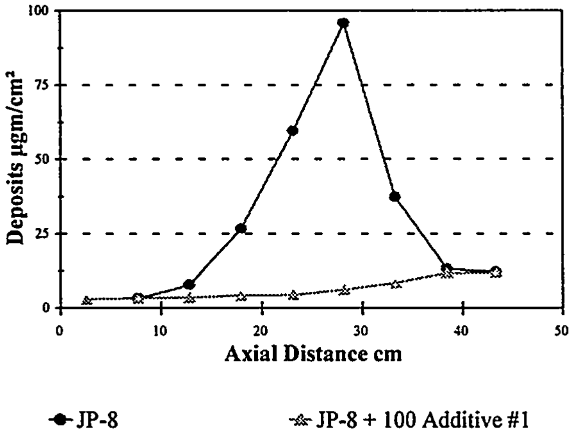

Fig. 3: JP-8+100 Additive Effects in POSF-2926 at 227°C Block Temperature

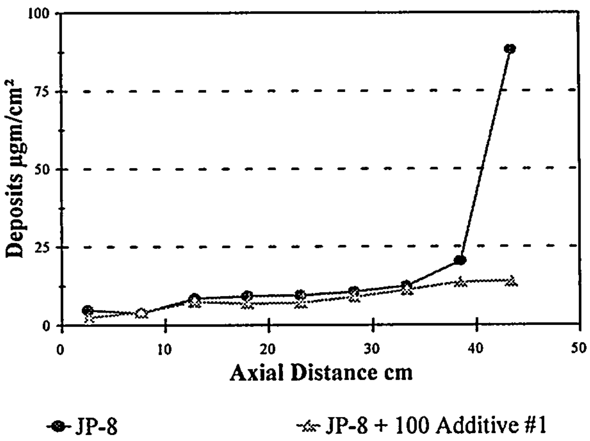

Fig. 4: JP-8+100 Additive Effects in POSF-2926 at 270°C Block Temperature

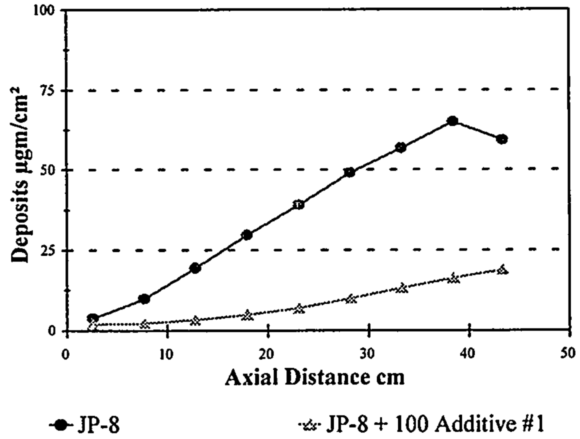

Fig. 5: JP-8+100 Additive Effects in POSF-2980 at 227°C Block Temperature

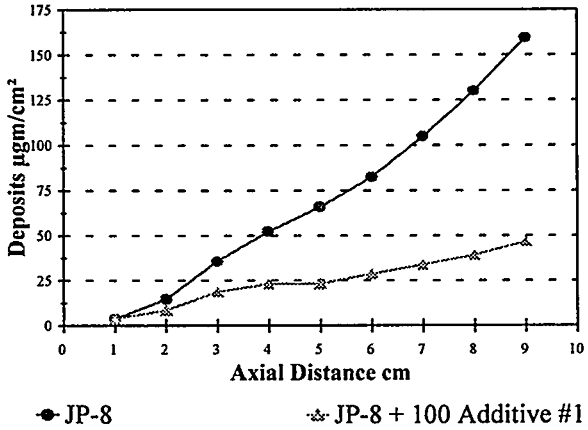

Fig. 6: JP-8+100 Additive Effects in POSF-2980 at 270°C Block Temperature

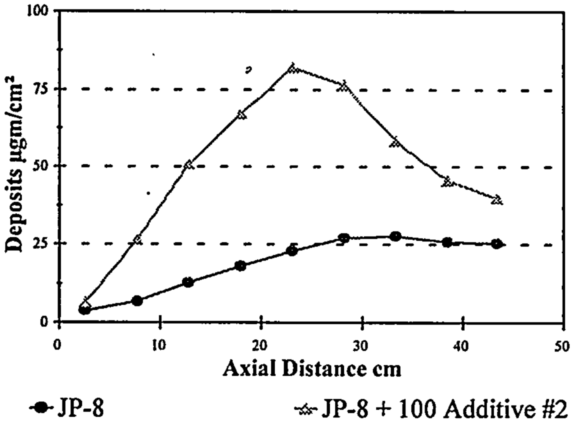

Fig. 7: JP-8+100 Additive Effects in POSF-2827 at 227°C Block Temperature

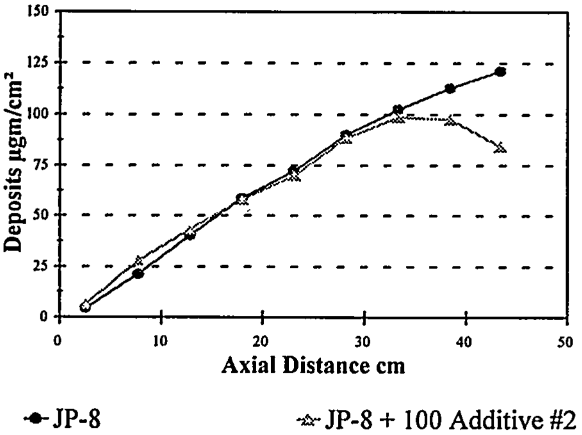

Fig. 8: JP-8+100 Additive Effects in POSF-2827 at 270°C Block Temperature

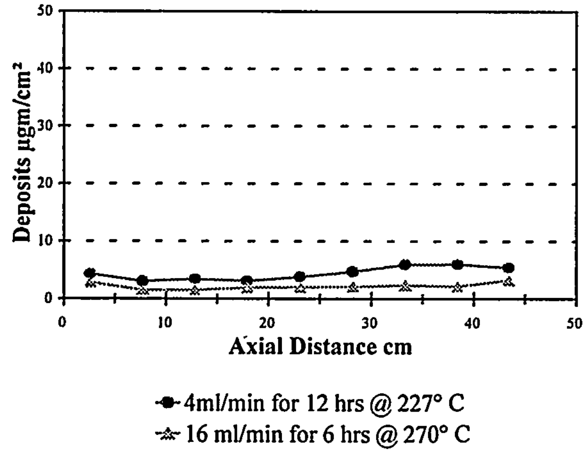

Fig. 9: Effects of POSF-2976 (JPTS) at 227°C and 270°C Block Temperatures

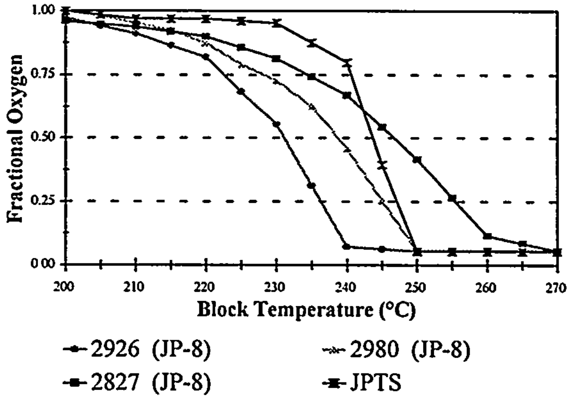

Fig. 10: Oxygen Consumption versus Temperature for Baseline Fuel

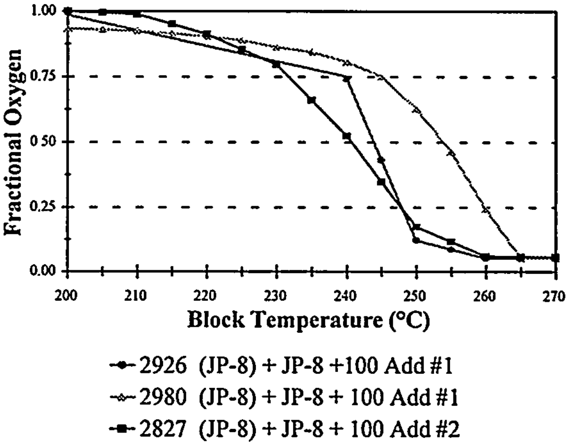

Fig. 11: Oxygen Consumption versus Temperature for Baseline Fuel With JP-8+100 Additives

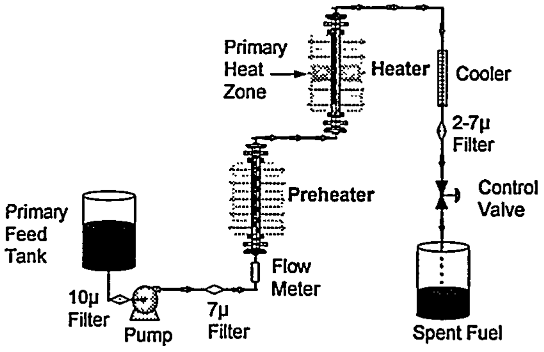

Fig. 12: Schematic of EDTST

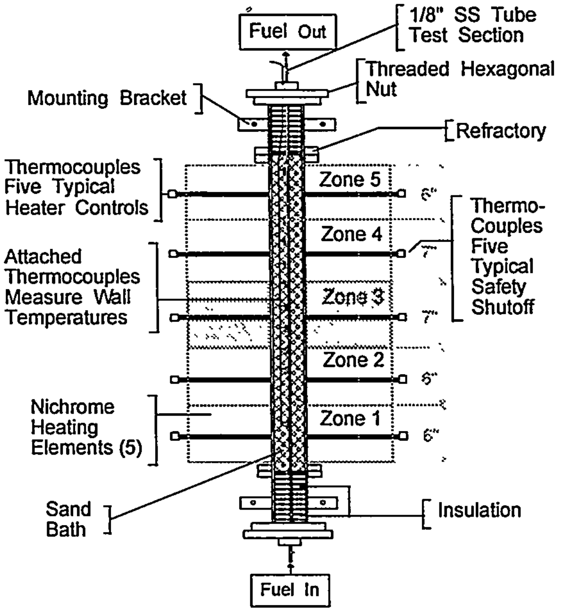

Fig. 13: EDTST Heater Diagram

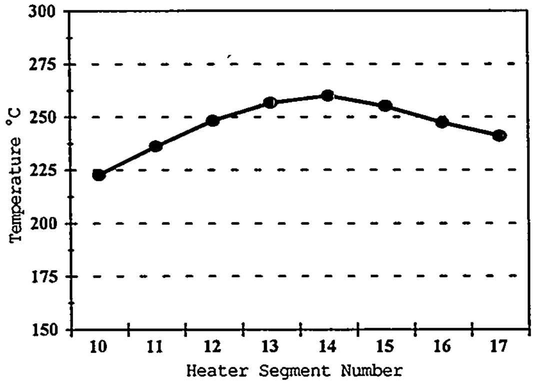

Fig. 14: Temperature Profile of Main Heater (260°C WWT)

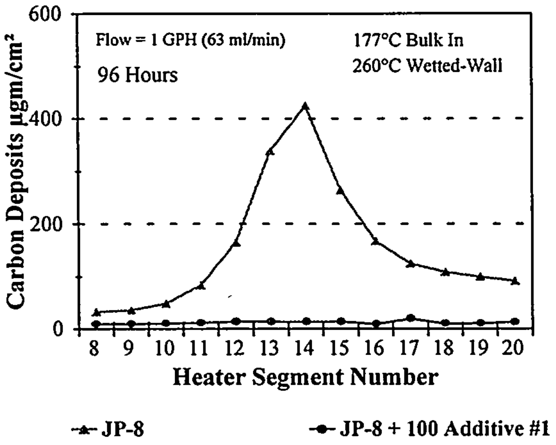

Fig. 15: Carbon Deposits for POSF-2926 with and without the JP-8+100 Additive Package

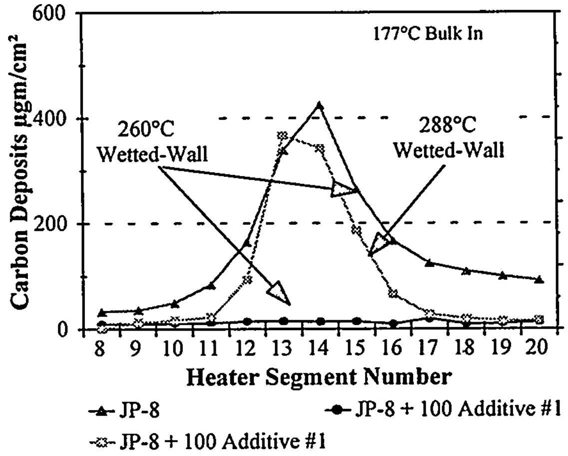

Fig. 16: Carbon Deposits of JP-8+100 Additive #1 Compared to JP-8 at Various Temperatures

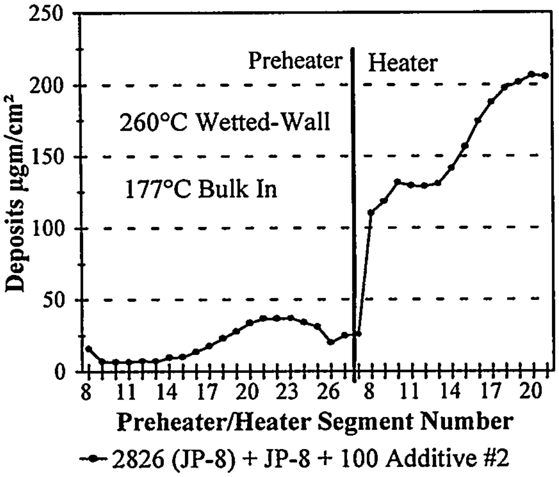

Fig. 17: Carbon Deposits with JP-8+100 Additive #2 in POSF-2926

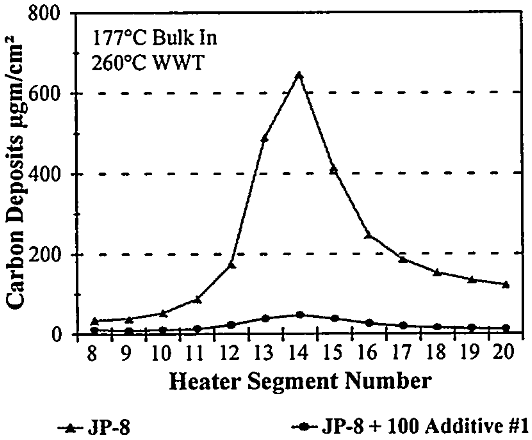

Fig. 18: Carbon Deposits for POSF-2980 with and without the JP-8+100 Additives

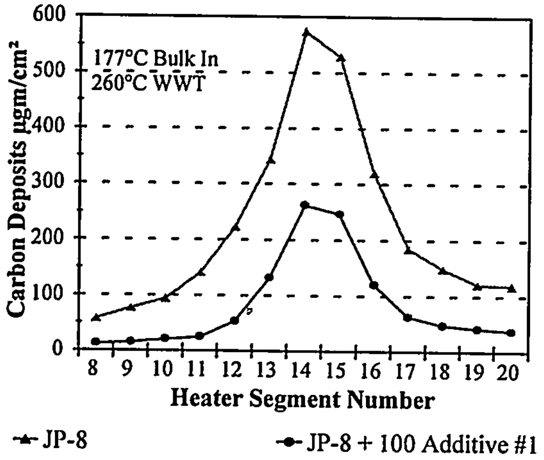

Fig. 19: Carbon Deposits for POSF-2827 with and without JP-8+100 Additives

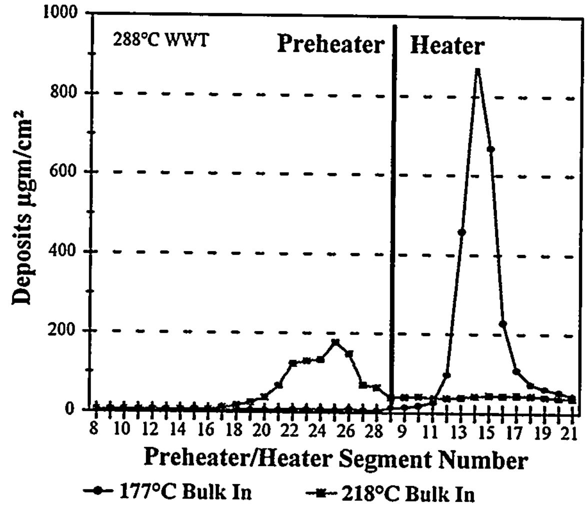

Fig. 22: Carbon Deposits for POSF-2980 with JP-8+100 Additives at Different Bulk Inlet Temperatures

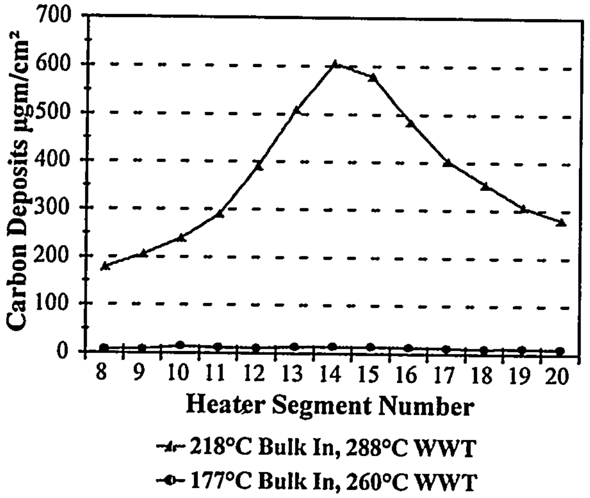

Fig. 20: Carbon Deposits for JPTS Fuels

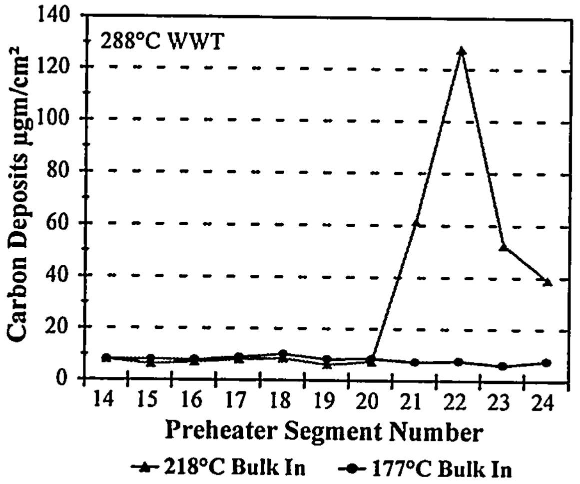

Fig. 21: Carbon Deposits for JPTS Fuels

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IMPROVEMENT OF TEST METHODOLOGY FOR EVALUATING DIESEL FUEL STABILITY

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The storage stability of diesel fuel has been extensively investigated for many years under laboratory conditions. Although continuous efforts have been made to improve testing techniques, there does not yet exist a generally accepted correlation between laboratory methods (such as chemical analysis of the fuel) and actual diesel engine tests. A testing method was developed by the Technion Internal Combustion Engines Laboratory (TICEL), in order to address this problem. The test procedure was designed to simulate diesel engine operation under field conditions. It is based on running a laboratory-modified single cylinder diesel engine for 50 h under cycling operating conditions. The overall rating of each test is based on individual evaluation of the deposits and residue formation in the fuel filter, nozzle body and needle, piston head, piston rings, exhaust valve, and combustion chamber (six parameters). Two methods for analyzing the test results were used: objective, based on measured data, and subjective, based on visual evaluation results of these deposits by a group of experts. Only the residual level in the fuel filter was evaluated quantitatively by measured results. In order to achieve higher accuracy of the method, the test procedure was improved by introducing the measured results of nozzle fouling as an additional objective evaluating (seventh) parameter. This factor is evaluated on the basis of the change in the air flow rate through the nozzle before and after the complete engine test. Other improvements in the method include the use of the nozzle assemby photograph in the test evaluation, and representation of all seven parameters on a continuous scale instead of the discrete scale used anteriorly, in order to achieve higher accuracy. This paper also contains the results obtained by application of this improved fuel stability test for a diesel fuel stored for a five-year period.

Introduction

A number of stability tests have been suggested for the evaluation of long-term storage of gas oil. Most of these tests are conventional, and can be performed in a reasonable time. It seems that the most important accelerated aging test is the ASTM-D-2274 Stability of distillate fuel oil by an accelerated oxidation test. This technique is also currently specified in the VV-F800C specification[1] for gas oil, and in the MIL-F-16884G specification[2]. Another alternative method used for diesel fuel stability testing during a prolonged storage period is ASTM-D-4625.

Stavinoha et al.[3] reported field problems caused by unstable diesel fuels in military applications. Some of the reported problems were: fuel injection pump seizure, filter plugging, corrosion of vehicle fuel tanks, fuel tank sludge, and accumulation of fuel deterioration by microbial contamination.

Despite the intensive work devoted to the improvement of storage stability tests, little has been achieved to establish correlations between the above-mentioned tests and actual diesel engine field tests. For this reason, a testing method was developed by the Technion Internal Combustion Engines Laboratory (TICEL)[4]. The test procedure was designed to simulate diesel engine operation under field conditions. It is based on running a single cylinder diesel engine for 50 h at 1500 rpm, under cycling operating conditions. The method has been implemented successfully to test diesel fuel stability after long-term storage.

In order to improve the method's accuracy, some modifications have been made, including the additional objective measurement of the injector nozzle fouling. This paper describes the modified method, and presents the results of its application for testing the stability of diesel fuel after five years of storage.

Original Test Method

The test method developed by TICEL[4], to evaluate diesel fuel stability, is based on running a laboratory-modified Petter AV-1 single cylinder diesel engine with the tested fuel 50 hours at engine constant speed (1500 rpm), completing three full cycles (45 h) at three different loads, according to the following schedule:

Cycle Mode	Time (h)	Engine Power (kw)
a	5	2.22
b	5	2.95
c	5	3.69

and an additional short cycle 1 2/3 h at each of these loads.

An engine running-in before every test has to be performed for 8 hours with the tested fuel, as specified by IP standards[5]. The test (including the engine running-in), is carried out during a 6-day period, and the daily fuel tank temperature is maintained constant for the length of this period.

The lubricating oil used was MIL-L-21040, and the fuel filter was the conventional type in the Petter AV-1 diesel engine tests employed.

The overall rating of each test is based on the individual evaluation of the deposits in residual formation in the following engine components: fuel filter, nozzle body and injection needle, piston head, rings (ring sticking), exhaust valve and combustion chamber. Our previous paper[4] outlined the procedure for evaluating the amount of residue in the fuel filter. The codes of the final evaluation are given at the bottom of Table III

Two methods for analyzing the test results were used: objective, based on measured data, and subjective, based on visual evaluation results of these deposits by a group of experts. Most of the fuel stability evaluations have been performed so far by using the subjective method. Only the residue level in the fuel filter was evaluated quantitatively by measured results.

Improved Methodology

In order to achieve higher accuracy of the method, the test procedure was modified by introducing the test results of checking the nozzle fouling, as an additional objective evaluating factor. This measurement is performed in an air-flow test bench, designed specifically for this purpose, according to IS0 standard 4010 (see Appendix A). The nozzle fouling level is evaluated on the basis of the change in the air flow rate through the nozzle before and after the complete engine test. This supplementary information enables the consideration of additional quantitative data regarding the influence of fuel aging on deposit formation in the injector.

During the tests performed since introducing the method for evaluating diesel fuel stability, it has been observed that when the needle was removed from the nozzle body to obtain the photograph in Fig. 1, some parts of the deposit were detached. Therefore, the photograph of nozzle assembly was added, in order to permit a better visual evaluation of deposit formation on the nozzle frontal surface.

Another improvement of the methodology is the evaluation on the basis of a continuous scale. Originally, five of the first six parameters in Table III (column 2), were marked on a discrete basis, while only the residue in the fuel filter was the result of a measured quantity. Since the objective measurement of the nozzle fouling (by air flow) has been added, it was decided to represent all seven parameters on a continuous basis. Linear scales were chosen, as shown at the bottom of Table III. The scale for the fuel filter residue was determined such that it agrees with the previous discrete scale. The one for the nozzle air flow is based on a perfect mark (10) for a new injector, and zero for a totally clogged nozzle. The Total Achievement is calculated, as previously, by summing the average marks given by the experts and the two objective ones. The Relative Achievement is then obtained by dividing this value by the maximum possible score of 70.

Application of the Improved Method: Evaluation of Diesel-Fuel Stability After Long-Term Storage

Fuel. The diesel fuel tested in this work by TICEL was military gas-oil, with pour point - 15°C. The fuel was stored for five years in a tank without any additives.

Test Procedure. The present test was carried out according to the above procedure, including the nozzle air flow test.

Test Results. Figures 1 - 3 represent the nozzle body and injection needle, nozzle assembly and piston head, respectively, and Tables I and II present the results of the fuel filter weighing and the nozzle air-flow test, respectively.

Analysis of the Results. In order to compare the present findings with those obtained with the original test procedure[4], on the same basis, columns 2 and 3 in Table III do not contain the evaluation of the nozzle fouling, but only of the six parameters used before. A group of experts graded each parameter. Column 2 in this Table includes grades on a discrete level basis determined unanimously by the group. Column 3 In Table III contains averages of grades given individually by the experts on the basis of a continuous scale (except for the residue in fuel filter, see code at the bottom of the Table). In both columns (2 and 3), the grades are summed to yield the Total Achievement, and the Relative Achievement is calculated as percent of the maximum (60 points).

Column 4 in Table III includes the evaluation based on seven parameters: the previous six and the nozzle air flow test as explained above. This evaluation is new, and is introduced here for the first time as an improvement of the method developed earlier to check diesel fuel stability.

The Relative Achievement of the tested fuel was found to be 70%, as can be seen in Table III. This result is compared to the Relative Achievement of 80% obtained [6] for the same fuel, stored four years with stabilizer and biocyde additives.

Conclusions

The method developed earlier by TICEL to test the stability of diesel fuel was modified to include evaluation of injector fouling by measuring the air flow through it. These objective quantitative data improve the accuracy of the method.

The modified method has been used to test the stability of non-additized diesel fuel after five-year storage[5], and of the same fuel after four-year storage with stabilizer and biocycle additives[6]. The Relative Achievement was found to be higher in the latter case (8O%, compared to 7O% in the former case).

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(1) VV-F-800 C, Fuel Oil Diesel, U.S. Federal Specification.

(2) Mil-F-16884 G Specification, Fuel Oil, Diesel.

(3) Stavinoha, L.L; Westbrook, S.R; Le Pera, M.E. Army Need for Diesel Fuel Stability and Cleanliness. ASTM STP 751, 1981; pp. 103-126.

(4) Luria, D; Stotter, A; Gutman, M; Shavit, A.B. The Evaluation of Storage Stability of Gas Oil by Engine Test. J. of the Institute of Energy, 1986. 440. pp. 142-147.

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Acknowledgment

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Figure 1: Nozzle body and injection needle

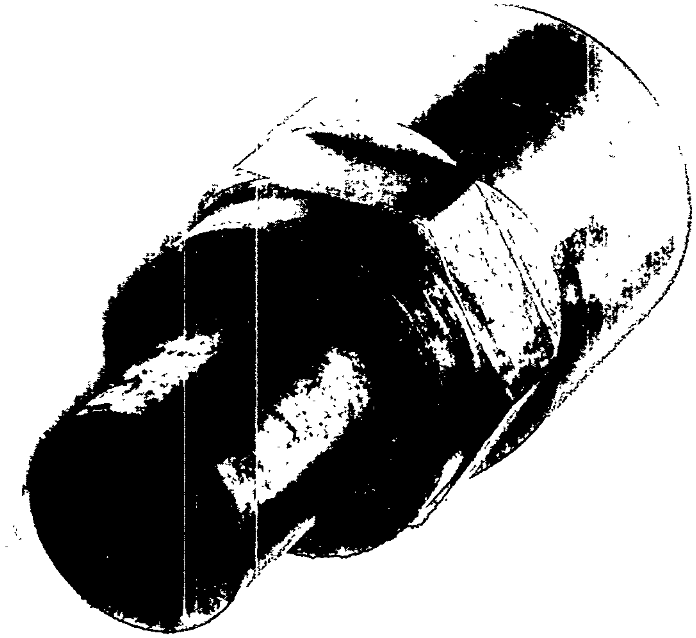

Figure 2: Nozzle assembly

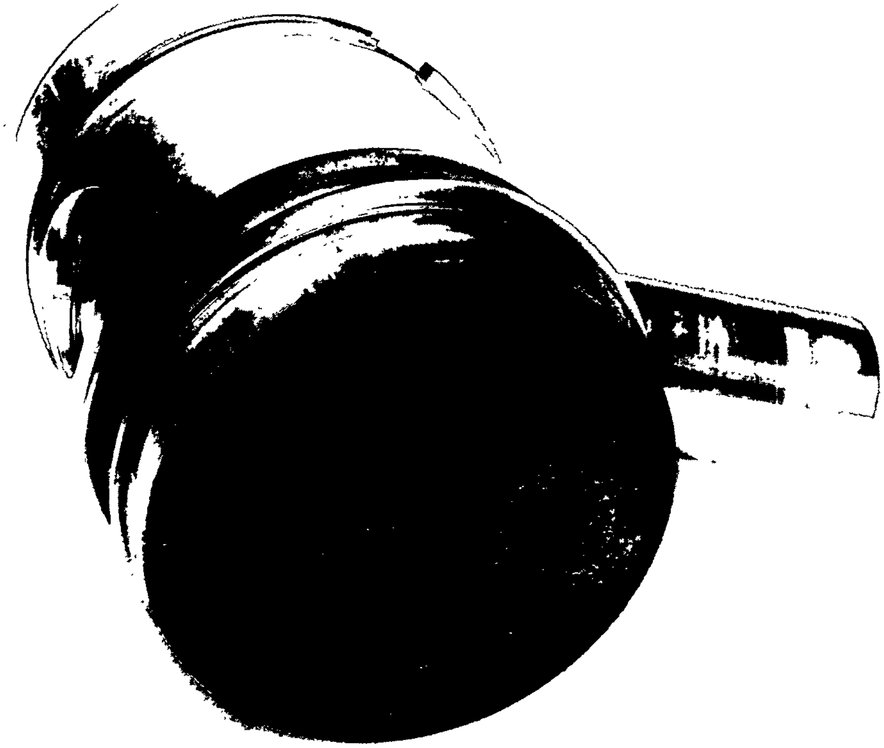

Figure 3. Piston Head

Table I. Results of fuel filter weighing

Weight of fuel filter, g.		
Before test, after drying, G_1	After test, after drying, G_2	G_2 - G_1 (difference)
36.6505	38.1014	1.4509

Table II. Results of nozzle air flow test

Needle lift, mm.	Flow rate, l/min		Flow rate change, %
	Before test	After test	
0.05	0.65	0.36	45
0.10	1.71	1.35	21
0.15	1.86	1.66	11
0.20	1.90	1.73	9

Table III. Achievements Results

Item	Discrete Basis	Continuous Basis	
	6 parameters	6 parameters	7 parameters
	Experts Group Marks *	Average Experts' Marks **	***
1	2	3	4
Injector	5	6.6	6.6
Piston Head	5	6.5	6.5
Ring Sticking	10	10	10
Exhaust Valve	7.5	7.6	7.6
Combustion Chamber	7.5	7.6	7.6
Residue in Fuel Filter	5	5	5.2
Nozzle Air Flow Test	-	-	5.5
Total Achievement	40	43.3	49
Relative Achievement	67%	72%	70%

Discrete Scale

Code 1 - Engine Components:

good -	10
good-moderate -	7.5
moderate -	5
moderate-poor -	2.5
poor -	0

Code 2 - Residue in Fuel Filter:

residue ≤ 0.5g -	good -	10
0.5g ≤ residue ≤ 1.0g -	good-moderate -	7.5
1.0g ≤ residue ≤ 2.0g -	moderate -	5
residue ≥ 2.0g -	poor -	0

Continuous Scale

Code 1 - Engine Components:

Continuous rating between the grades of Code 1 for the Discrete Scale.

Code 2 - Residue in Filter:

Linear Scale:

0g - 10

≥ 3g - 0

Code 3 - Nozzle Air Flow Test:

Difference in air flow rate before and after engine test:

Linear Scale:

0% - 10

100% (zero flow) - 0

* According to the discrete scale.

** According to the continuous scale for 5 parameters and the discrete scale for the residue in fuel filter.

*** According to the continuous scale.

Appendix A: Procedure of Nozzle Fouling Evaluation by air-flow test

Purpose

This procedure is for checking the air-flow rate through a nozzle in order to evaluate its fouling grade.

Test System

The test system was designed according to Standard ISO-4010 requirements. A schematic description of the test bench is given in Figure A1.

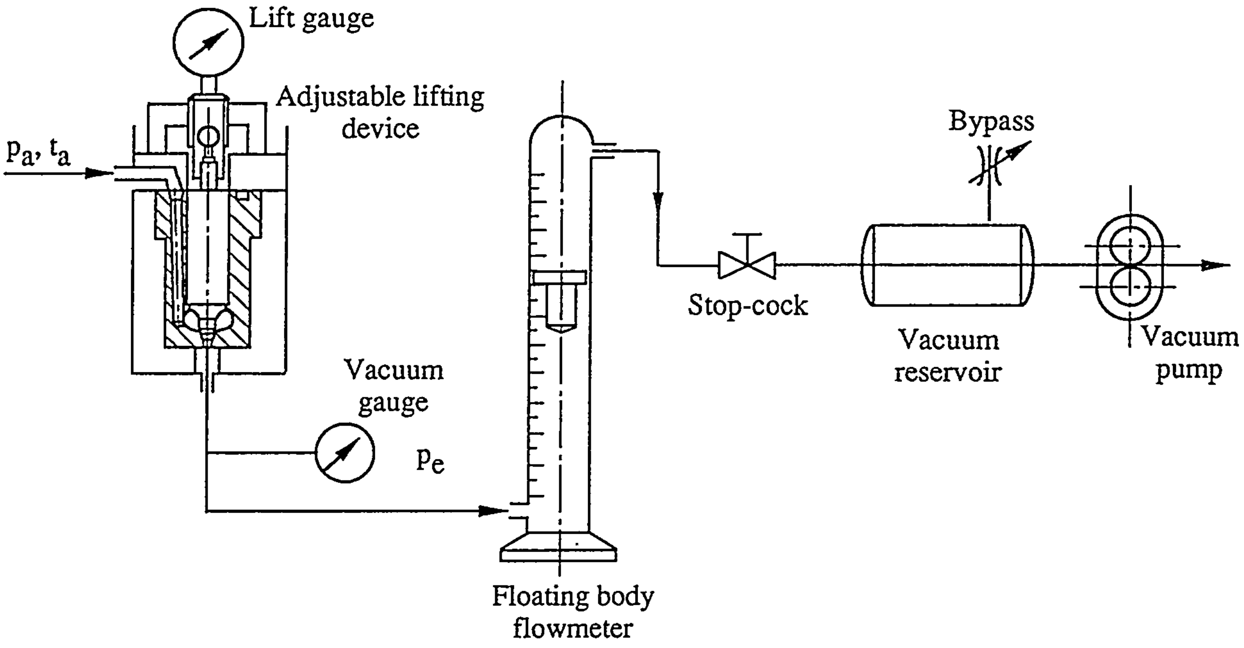

Figure A1: Test bench (schematic) for measuring the air-flow through a fuel injector nozzle.