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# STUDIES OF THE BEHAVIOR OF THE TBP-KEROSENE SOLVENT IN URANIUM REFINING: DEGRADATION OF THE KEROSENE DILUENT

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# DISCLAIMER

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## ABSTRACT

Extensive studies have been conducted of kerosene-type diluents for the tri-n-butyl phosphate (TBP)-kerosene solvent used in uranium extraction. Wide variations have been shown in the paraffinic, isoparaffinic, aromatic, and olefinic hydrocarbon contents of these diluents. Such diluents have been shown to be unstable in the presence of high nitric acid concentrations, and in the presence of small amounts of nitrous acid. This instability is primarily a function of the non-paraffinic hydrocarbon content of the diluent and of the nitrous acid concentration of the contacting medium. Degradation of a diluent has been shown to discolor a diluent, increase its density and viscosity, and influence uranium distribution during re-extraction operations. Solvent treatment with $Na_2CO_3$, followed by $H_2O$ and nitric acid washes, has been shown to be only partially effective in removing diluent degradation products. The diluent degradation products have been characterized, chemically and spectrally, as carboxylic acids, organic nitrates, organic nitro compounds, and nitroso compounds.

# INTRODUCTION

At the National Lead Company of Ohio, uranium is separated from its ores and concentrates by a liquid-liquid extraction operation.[1] Continued use of the organic extractant (a 33 volume per cent tri-n-butyl phosphate (TBP)-67 volume per cent kerosene solvent) leads to degradation of the solvent and inefficient operations. Ordinarily, a sodium carbonate-nitric acid solvent treatment is expected to restore used solvent to good condition. In December, 1956, however, excessive degradation and loss of efficiency of the solvent necessitated replacement of the entire solvent inventory with fresh material.[2]

This precipitated an intensive study of the TBP-kerosene solvent. Early studies were designed to develop a modified solvent treatment system which would prevent extremes of degradation, and to determine the feasibility of incorporating the discarded solvent back into the Refinery system.

The studies were successful. The Refinery now uses a sodium carbonate-water-nitric acid solvent treatment system,[3] and results have indicated increased treatment efficiency from this modification. Further, inefficient uranium refining has been attributed to three different phenomena present in, produced in, or introduced into the solvent;[4]

1. Di-n-butyl phosphate (DBP), the first degradation product of TBP,
2. An unknown agent, or agents, which inhibit uranium mass transfer during re-extraction operations, and
3. Unknown complexing agents which prevent total re-extraction of uranium from the solvent stream.

It has been shown that normal solvent treatment (i.e., sodium carbonate-water-nitric acid) will effectively control or eliminate both the DBP and the agents affecting mass transfer.[5] This solvent treatment is, however, relatively ineffective in removing the unknown complexing agents.

The latter situation resulted in an intensive search of the literature and intensive studies of the kerosene diluent. The literature search[6] covered TBP degradation, kerosene degradation, and solvent treatment techniques as they were reported in both the classified and unclassified literature.

The studies of the kerosene diluent and its stability are the subject of this report.

# LABORATORY STUDIES OF THE KEROSENE DILUENT

## INITIAL EVIDENCE OF DILUENT INSTABILITY

The stability of the kerosene diluent to nitric acid was investigated briefly under various conditions of time, temperature, and concentration of acid. These tests all resulted in discoloration of the kerosene, indicating that some reaction had taken place. The colors ranged from pale yellow to red, deepening as the acid concentration, temperature, or duration of contact was increased. It was known that purely paraffinic hydrocarbon fractions should be relatively unreactive toward nitric acid at temperatures below 150°F, at acid concentrations below 5$\underline{N}$, and in contacts of less than one hour (conditions similar to those the diluent might encounter in the Refinery). However, any aromatic and/or olefinic hydrocarbons present in the kerosene would be distinctly more reactive to the same set of conditions.[7] Obviously, the purely paraffinic nature of the kerosene used as a diluent in the Refinery was doubtful. Therefore, the then-current Refinery diluent,* as well as a number of other diluents supplied to National Lead Company of Ohio by petroleum processors, were subjected to chemical and infrared analyses to establish their contents of paraffinic, aromatic, and olefinic hydrocarbons. Some of these same diluents were subjected to extensive tests of their stability in the presence of acids.

## ANALYSES OF KEROSENE DILUENTS

### Chemical Analyses

Three different chemical analyses were employed, as well as two qualitative tests for olefinic hydrocarbons. The analytical procedures were the chromyl chloride ($CrO_2Cl_2$) determination for unstable constituents in a hydrocarbon mixture,[8] the American Society for Testing Materials (ASTM) test for total aromatic and olefinic hydrocarbon content,[9] and the ASTM test for olefinic hydrocarbon content.[10] The qualitative spot tests for olefins utilized potassium permanganate solution[11] and a solution of bromine in carbon tetrachloride.[12] The results of these analyses and spot tests, as they were applied to a large number of kerosene diluents, are summarized in Table I. The procedures employed for each analysis are detailed in Appendix A.

Several comments are apropos of the results presented in Table I. The aromatic contents were determined by the difference of the sulfonation and olefin number tests. It has been stated[13] that a kerosene diluent having a $CrO_2Cl_2$ number of 0.02 meq/ml or less is suitable for use in a TBP-kerosene system. Table I reveals that none of the diluents analyzed fulfills this specification. The $CrO_2Cl_2$ tests was not exploited further because it was time-consuming, produced a result of questionable interpretation, and involved the use of a rather nebulous concept — i.e., "zero time."

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* *At this time, the Refinery diluent was Shell 140 Solvent.*

TABLE I Summary of Chemical Analyses of Kerosene Diluent

| Diluent | Chemical Analyses | | | | Qualitative Spot Tests for Olefins | |
|---|---|---|---|---|---|---|
| | Sulfonation Number[9] (vol %) | Olefin Number[10] (vol %) | Aromatic Content (vol %) | $CrO_2Cl_2$ Test for Total Unstable Constituents | Spot Test[11] (Acidic $KMnO_4$ Solution) | Spot Test[12] ($Br_2$ in $CCl_4$ Solution) |
| Amsco Base H Solvents | 0 | Not Measured | 0 | Not Tested | Negative | Negative |
| Amsco Kerosene Diluent No. 1 | 13.2 | 0.53 | 12.67 | 0.256 meq/ml | Positive | Positive |
| Amsco Kerosene Diluent No. 2 | 14.4 | 0.11 | 14.29 | 0.250 meq/ml | Positive | Positive |
| Amsco Odorless Mineral Spirits | 0 | Not Measured | 0 | Not Tested | Negative | Positive |
| Apco Deodorized 125 | 2.6 | 0.16 | 2.44 | 0.190 meq/ml | Weakly Positive | Weakly Positive |
| Apco Deodorized 467 | 1.2 | 0.03 | 1.17 | Not Tested | Weakly Positive | Weakly Positive |
| Apco 125- Wetage Spirits | 11.2 | 0.47 | 10.73 | Not Tested | Positive | Positive |
| Apco 140 | 9.46 | 1.19 | 8.27 | 0.281 meq/ml | Positive | Positive |
| Apco 467 | 9.2 | 0.64 | 8.56 | Not Tested | Positive | Positive |
| Atlantic Odorless Mineral Spirits | 4.6 | 0.48 | 4.12 | 0.279 meq/ml | Negative | Positive |
| Bronoco 140 Solvent | 13.95 | 0.27 | 13.68 | 0.275 meq/ml | Positive | Positive |
| Bronoco Deodorized Base No. 3800 | 2.7 | Not Measured | — | Not Tested | Not Tested | Not Tested |
| Bronoco Deodorized Base No. 3850 | 11.2 | Not Measured | — | Not Tested | Not Tested | Not Tested |
| Shell Dispersol | 1.1 | 0.16 | 0.94 | 0.036 meq/ml | Positive | Positive |
| Shell Insecticide Base | 1.0 | 0.04 | 0.96 | Not Tested | Weakly Positive | Positive |
| Shell 140 Solvent | 6.23 | 0.29 | 5.94 | 0.266 meq/ml | Positive | Positive |
| Shell Sol 75 | 7.2 | 0.32 | 6.88 | Not Tested | Negative | Positive |
| Sinclair Odorless Solvent, Heavy | 15.2 | 15.8 | −0.60 | Not Tested | Negative | Positive |
| Sinclair Odorless Solvent, Light | 3.2 | 3.0 | 0.20 | Not Tested | Negative | Positive |
| Suntide Odorless Mineral Spirits | 0.2 | 0.04 | 0.16 | Not Tested | Negative | Positive |

The more nearly universally accepted ASTM tests were exploited more fully. The test for combined aromatic and olefinic hydrocarbons (ASTM designation D-1019-57T) proved to be quite useful when applied to a kerosene, although results for isoparaffinic diluents were questionable, as will be seen later. Attempts to use this analysis on solvent (that is on the TBP-kerosene mixture) revealed first, that the TBP was solubilized by the sulphuric acid-phosphorous pentoxide reagent along with the aromatic and olefinic hydrocarbons and second, that the reproducibility and accuracy of the analysis decreased as the TBP content of the solvent increased.

The ASTM test for olefins (D-1158-57T), basically a bromine number test, produced less suitable results. This was especially true in the tests of Sinclair Odorless Solvent, Heavy and Sinclair Odorless Solvent, Light. In these two tests, the ASTM analyses showed a volume per cent of olefins essentially equal to or greater than the total aromatic and olefin content.

Comparison of these analyses with the results of the qualitative spot tests conducted for a total of 18 diluents gives some insight into the problem and its explanation. The $Br_2$-in-$CCl_4$ spot test was positive for all diluents except Amsco Base H Solvents, and essentially corroborated the results of the ASTM test.[10] However, the $KMnO_4$ test was negative for a total of seven of the diluents tested, including both Sinclair solvents (there being six discrepancies). An explanation of the conflicting results lies in the basic flaw in the olefin number test. Bromine is, of course, capable of adding across the double bond of an olefin, but it is also capable of replacing a tertiary hydrogen atom of an isoparaffinic hydrocarbon. In the latter case, there is usually a noticeable evolution of HBr gas. Such was the case during the spot testing of all six of the diluents which showed negative results to $KMnO_4$ solution, but strong positive results to $Br_2$ in $CCl_4$. As will be seen later (in the discussion of the infrared spectral studies of the diluents), olefinic absorption bands were never identified in the spectra in any of the diluents. Furthermore, the spectral studies characterized all six of the disputed diluents as being isoparaffinic rather than paraffinic. Thus, although olefin number measurements for paraffinic diluents are considered valid, the same measurement for an isoparaffinic diluent must be considered questionable.

As an immediate result of this work, the ASTM test for combined aromatics and olefins became an integral part of the specification and testing of incoming kerosene diluent. Also, the purchase specification for kerosene diluent was modified; it was required that the kerosene contain no more than a nominal 1 volume per cent of combined aromatic and olefinic hydrocarbons, with a maximum of 2 volume per cent, as determined by ASTM D-1019-56T.

## Infrared Spectral Analyses

A Beckman Model IR-4 infrared spectrophotometer was used in these and all subsequent spectral studies. This instrument contains a single-pass, double-monochromater optical system. For this work, cells fitted with KBr plates were used; the reference cell was also a KBr plate. Operations and specifications for the instrument have been described elsewhere.[14]

Infrared spectra were determined for each of the 20 kerosene diluents previously mentioned. The spectra were first determined using cells of 0.05-mm path length. The paraffinic versus isoparaffinic nature of the diluents was evaluated from these spectra on the basis of the presence or absence of several absorption bands in the vicinity of 8 to 9 microns, due to possible tertiary butyl $[(CH_3)_3\text{-}C\text{-}R)]$ and/or isopropyl $[(CH_3)_2\text{-}CH\text{-}R]$ branchings.

Spectra were then determined using cells with a path length of 0.25 mm. In this case, the spectrograms covered only the 6.0 to 6.5$\mu$ range and were used to establish the relative aromatic hydrocarbon contents of the diluents. Aromatic hydrocarbons have an absorption band at 6.25$\mu$ (1600 $cm^{-1}$) characteristic of the C = C stretching vibration of the benzene ring.

Table II summarizes the findings of the infrared spectral analyses of the various diluents. In general, these analyses were in good agreement with the chemical analyses. As mentioned previously, olefinic absorption peaks were not located in any of the spectra, an expected result

TABLE II Summary of Infrared Spectral Analyses of Kerosene Diluents

| Diluent | Paraffinic Nature (8.0 - 9.0$\mu$) | Aromatics* (Absorbance at 6.25$\mu$) | Olefins (6.1$\mu$) |
|---|---|---|---|
| Amsco Base H Solvents | Some Isoparaffins | 0.011 | Never Identified In Any Tested Diluent |
| Amsco Kerosene Diluent No. 1 | Paraffinic | 0.430 | |
| Amsco Kerosene Diluent No. 2 | Paraffinic | 0.498 | |
| Amsco Odorless Mineral Spirits | Isoparaffinic | 0.000 | |
| Apco Deodorized 125 | Paraffinic | 0.088 | |
| Apco Deodorized 467 | Paraffinic | 0.063 | |
| Apco 125 - Wetage Spirits | Paraffinic | 0.343 | |
| Apco 140 | Paraffinic | 0.222 | |
| Apco 467 | Paraffinic | 0.142 | |
| Atlantic Odorless Mineral Spirits | Isoparaffinic | 0.000 | |
| Bronoco 140 Solvent | Paraffinic | 0.402 | |
| Bronoco Deodorized Base No. 3800 | Paraffinic | 0.059 | |
| Bronoco Deodorized Base No. 3850 | Paraffinic | 0.171 | |
| Shell Dispersol | Paraffinic | 0.000 | |
| Shell Insecticide Base | Some Isoparaffins | 0.010 | |
| Shell 140 Solvent | Paraffinic | 0.148 | |
| Shell Sol 75 | Isoparaffinic | 0.000 | |
| Sinclair Odorless Solvent, Heavy | Isoparaffinic | 0.000 | |
| Sinclair Odorless Solvent, Light | Isoparaffinic | 0.000 | |
| Suntide Odorless Mineral Spirits | Isoparaffinic | 0.000 | |

* Aromatic hydrocarbon content is expressed as absorbance at 6.25$\mu$, where absorbance = $\text{Log}\frac{I_0}{I}$

since all the ASTM olefin analyses[10] indicated olefin contents of less than one volume per cent (excluding those for the two Sinclair Solvents, which were of doubtful validity).

Comparison of the data in Tables I and II reveals a number of anomalies. Olefin numbers do not agree with infrared analyses for olefins in two cases. This is, of course, due to the isoparaffinic nature of some of the diluents, as explained previously. Another inconsistency is evident when one compares sulfonation numbers with relative absorbances at 6.25$\mu$ in the infrared. The sulfonation number is, of course, expected to be a measure of the combined aromatic and olefinic hydrocarbon content of a diluent. Thus, in theory the aromatic content of a diluent should be represented by the sulfonation number less the olefin number. Earlier discussion has shown that olefin numbers are valid only for paraffinic diluents. This being the case, the actual aromatic content can be determined for only 12 of the diluents investigated (i.e., those which are paraffinic and for which olefin numbers were measured. Figure 1 represents an attempt to correlate aromatic content and absorbance for these 12 diluents.

The best line for the data was determined by the least-squares method, using first the aromatic content and then the absorbance as the independent variable. The average of the two lines developed in this manner, is represented by the following equation:

$$\text{Absorbance} = 0.0330\,(\text{aromatic content}) - 0.0224$$

The correlation coefficient, r, for this line = 0.975.

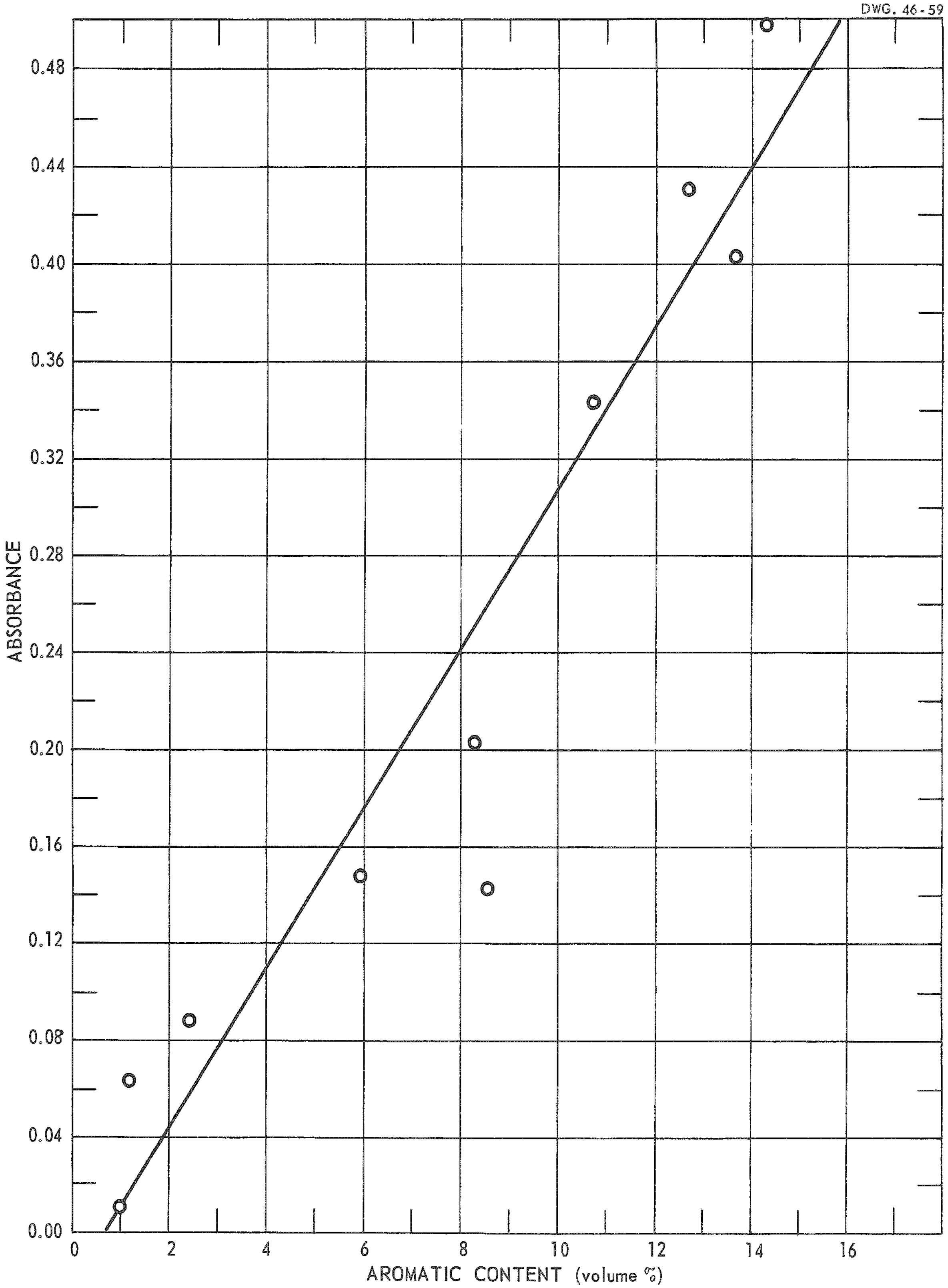

FIGURE 1 Correlation of Infrared and Chemical Analyses for Aromatic Hydrocarbons

The correlation is good, but it should be noted that one of the 12 points is far out of line (Apco 467, Absorbance = 0.142, Aromatic Content = 8.56 volume per cent).

The correlation was recalculated, using the other 11 points, and the equation of this line was:

$$\text{Absorbance} = 0.0331 \text{ (aromatic contant)} - 0.013.$$

In this case, the correlation was excellent. The correlation coefficient, r, was 0.9966. Unfortunately, no Apco 467 was available for rechecking the sulfonation and olefin numbers. The improvement in the correlation as a result of disregarding the analyses of Apco 467 is a strong indication of error in the analysis of that diluent.

The wide variations (in several cases) between sulfonation numbers and the appropriate absorbances are also of interest. Here again, as was the case for questionable olefin numbers, the explanation lies in the isoparaffinic character of some of the diluents. All of the wide variations occurred in the analyses of isoparaffinic diluents. Infrared analyses consistently indicated the absence of any significant quantities of aromatic hydrocarbons, while sulfonation numbers varied from 0 volume per cent to 15.2 volume per cent.

The doubtful sulfonation numbers must be a function of the availability of tertiary hydrogen atoms on isoparaffinic hydrocarbons. Sulfonation and solubilization of aromatic and olefinic hydrocarbons are the bases for the sulfonation number test, but sulfonation can also take place on tertiary hydrogen atoms. Therefore, although there is no reason to question the sulfonation numbers of paraffinic diluents, the sulfonation numbers of isoparaffinic diluents cannot be considered entirely valid.

## ACID STABILITY OF THE DILUENT

The literature indicated that, under extreme conditions of time, temperature, and concentration, nitric acid would react deleteriously with a kerosene diluent.[15] At the same time, the literature also stated that the presence of even small concentrations of nitrous acid in the aqueous phase in contact with the diluent would greatly enhance the degradation of the diluent.[16] To evaluate this diluent reactivity in the presence of acids, seven diluents were subjected to degradation tests. The diluents used, and their original analyses, are summarized in Table III.

To differentiate the effects of nitric and nitrous acids in degrading a diluent, parallel tests were conducted. The diluents were contacted with equal volumes of $5\underline{N}$ $HNO_3$ and of a $5\underline{N}$ $HNO_3$-$0.1\underline{N}$ $HNO_2$ mixture. The test mixtures were maintained at a temperature of 150°F and were thoroughly agitated for six hours. (These conditions were chosen to be slightly in excess of any which might reasonably be encountered during Refinery operation.) The degradation tests were first evaluated visually, on the basis of the intensity of the color of the diluent after treatment. Then the degraded diluents were evaluated on the basis of changes in their infrared spectra and in various physical properties. Those diluents which evaluations showed to be markedly degraded were further evaluated by determining the amount of uranium held in an apparently thoroughly re-extracted solvent containing 33 per cent TBP and 67 per cent of the degraded diluent. Ultimately, the effects of a degraded diluent on uranium distribution during both extraction and re-extraction were determined for three of the degraded diluents.

TABLE III Diluents Employed in Degradation Tests

| Diluent | Sulfonation Number[9] (vol %) | Paraffinic Nature Indicated by Infrared Spectrum |
|---|---|---|
| Suntide Odorless Mineral Spirits | 0.20 | Isoparaffinic |
| Shell Dispersol | 1.00 | Paraffinic |
| Shell Insecticide Base | 1.10 | Some Isoparaffinic |
| Apco Deodorized 125 | 2.6 | Paraffinic |
| Shell 140 Solvent | 6.23 | Paraffinic |
| Apco 140 | 9.46 | Paraffinic |
| Bronoco 140 Solvent | 13.95 | Paraffinic |

## Color Evaluation of Diluent Degradation Tests

Comparison of the diluent color between parallel tests (i.e., treatment with 5N $HNO_3$ and with 5N $HNO_3$ - 0.1N $HNO_2$) gave an immediate indication of a difference in attack by the acids. The diluent contacted with the nitric-nitrous acid mixture always had the darker color. In the absence of $HNO_2$, the colors ranged from essentially colorless to a light red-yellow, following the order of increasing sulfonation number. When $HNO_2$ was present, the colors ranged from light yellow to a moderate red-brown, again following the order of increasing sulfonation numbers.

## Infrared Spectral Evaluation of Diluent Degradation Tests

Comparisons of the infrared spectra of these diluents, before and after acid treatment* showed that in the absence of $HNO_2$, no noticeable attack had taken place. On the other hand, treatment of the diluents with the nitric-nitrous acid mixture resulted in the appearance of an absorption band at 6.42 microns, indicating that a chemical reaction had taken place. At this time, accurate characterization of this band was not made; however, it was later attributed to the presence of organic nitro-compounds.

The relative intensity of this degradation band was compared with the sulfonation number of the various diluents (Table III). The correlation was fair; the intensities of the degradation bands for Shell Insecticide Base and Suntide Odorless Mineral Spirits were slightly greater than those of Shell Dispersol and Apco Deodorized 125, but the other diluents fell in the proper order. The inconsistency in the cases of Suntide Odorless Mineral Spirits and Shell Insecticide Base was due to the isoparaffinic nature of these diluents and to the attendant presence (and susceptibility to reaction) of tertiary hydrogens. As will be seen later, diluent degradation actually involved several reactions, and the 6.42-micron band represented the product of only one of these reactions. Thus, a good correlation of the intensity of this single band with the sulfonation number of a diluent would be only a fortunate coincidence. Furthermore, as indicated earlier, the sulfonation number does not always accurately represent the total unstable constituent content of a diluent – that is, the total aromatic, olefinic and isoparaffinic contents.

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* *The spectra of these treated diluents were determined, using cells with 0.05-mm path lengths.*

## Physical Property Evaluations of Diluent Degradation Tests

The density and viscosity were measured for each diluent before treatment and after treatment with acid (or acids). Surface tension measurements were also made in some cases, but their relative inaccuracy and their small variations made them useless.

As was observed in the infrared spectral evaluations, physical property measurements indicated no detectable change in the diluents as a result of treatment with nitric acid alone. However, diluents treated with the nitric-nitrous acid mixture showed a consistent increase in both density and viscosity — a definite indication of change in the diluent. Results of all of the physical measurements are included in Appendix B, while Table IV summarizes the significant changes in density and viscosity.

Here again, attempts were made to correlate physical property changes with unstable constituent content. As in the case of the infrared evaluations, such a correlation was not entirely consistent. The density changes increased in exactly the same order as the intensity of the 6.42-micron degradation band, but not in the order of increasing sulfonation numbers. Viscosity changes followed both correlations poorly. These discrepancies, which seemed serious, became less significant when the extreme complexity of diluent degradation was subsequently determined.

## Uranium Hold-Up Evaluation of Diluent Degradation Tests

Since all previous evaluations of the diluent degradation tests indicated that significant attack had taken place only when nitrous acid was present, the nitric acid treated diluents were not subjected to this evaluation of uranium hold-up. The diluents which had been degraded by the nitric-nitrous acid mixture were used to prepare 33 per cent TBP-67 per cent kerosene solvents. These solvents were used to perform batch shakeout re-extraction tests.* The re-extraction

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* *Batch shakeout re-extraction tests are a standard means of evaluating TBP-kerosene solvents at National Lead Company of Ohio. A portion of the solvent under test is equilibrated with a 200 g/l U, 3N $HNO_3$ solution of uranyl nitrate hexahydrate at an organic to aqueous ratio of 20/11. This produces a uranium-laden solvent (about 95 g/l U, 0.2N $HNO_3$). This uranium-laden solvent is then equilibrated with successive equal volumes of distilled water to re-extract the uranium. Normally, fresh solvent will be totally re-extracted after six equivolume re-extractions (i.e., the uranium content of the solvent will be reduced to less than 0.0005 g/l).*

TABLE IV Physical Property Changes Due to Degradation of Diluents

| Diluent | Change in Density as a Result of Degradation (%) | Change in Viscosity as a Result of Degradation (%) |
|---|---|---|
| Suntide Odorless Mineral Spirits | +0.62 | +6.0 |
| Shell Dispersol | +0.30 | +0.7 |
| Shell Insecticide Base | +0.71 | +3.3 |
| Apco Deodorized 125 | +0.33 | +2.0 |
| Shell 140 Solvent | +0.79 | +2.5 |
| Apco 140 | +1.35 | +7.4 |
| Bronoco 140 Solvent | +1.34 | +6.1 |

TABLE V **Comparative Uranium Hold-Ups for Solvents Containing Various Degraded Diluents**

Organic Phase: 33% TBP-67% Degraded Diluent, ~97 g/l U, ~0.2N $HNO_3$.
Aqueous Phase: Distilled Water.
Room Temperature

| Diluent | Uranium Hold-Up (g/l) | |
|---|---|---|
| | <15 Days After Treatment | >50 Days After Treatment |
| Suntide Odorless Mineral Spirits | <0.0005 | 0.050 |
| Shell Dispersol | 0.003 | 0.022 |
| Shell Insecticide Base | 0.001 | 0.031 |
| Apco Deodorized 125 | 0.002 | 0.014 |
| Shell 140 Solvent | 0.008 | 0.033 |
| Apco 140 | 0.024 | 0.031 |
| Bronoco 140 Solvent | 0.032 | 0.62 |

phase of these tests was continued through one equilibration more than was known to be sufficient to re-extract a fresh solvent to <0.0005 g/l U, after which the uranium hold-up in the solvents was determined. These tests were conducted twice, once within 15 days of the degradation treatment and again, more than 50 days after the treatment. The results of these tests are presented in Table V.

The significance of these results lay not in the obvious lack of correlation between uranium hold-up and either the sulfonation numbers or the intensities of the 6.42 micron degradation band, but first, in the definite ability of a degraded diluent to retain uranium in the solvent phase in a non-water-soluble form, and second, in the significant increase in this uranium hold-up attendant to the aging of a degraded diluent. The latter situation was attributed to changes in the nature of the degradation products subsequent to their original formation, a situation which has been postulated by other workers.[17] At the same time, the slow formation of DBP from TBP might account for some of this uranium retention, but at normal temperature, the amount of DBP formed in ~40 days would be almost negligible. Consideration of these results led to the belief that degraded diluents were responsible for part or all of the hold-up of non-water-soluble uranium previously attributed to some unknown complexing agent or agents.

## Uranium Distribution Evaluation of Diluent Degradation Tests

Uranium distribution curves for both extraction and re-extraction (Fig. 2 to 5) were determined for the solvents containing degraded diluents representing low, medium, and high degrees of degradation,* and for one solvent containing fresh diluent. In the case of extraction distribution curves, the aqueous phase was adjusted to 3N nitric acid after equilibration with the organic phase. The re-extraction distribution curves utilized distilled water as the aqueous phase.

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* *At this time, the intensity of the infrared spectral band at 6.42 microns was used to gauge the extent of degradation.*

The standard or reference solvent for the extraction distribution curves was 33 per cent TBP-67 per cent fresh Shell 140 Solvent.

The test solvents were: 32.2 per cent TBP-67.8 per cent degraded* Suntide Odorless Mineral Spirits (low degree of degradation); 32.2 per cent TBP-67.8 per cent degraded Shell 140 Solvent (medium degree of degradation); and 33 per cent TBP-67 per cent degraded Apco 140 (high degree of degradation). The extraction distribution curves are presented in Figures 2 and 3, while the analytical results from which these curves were plotted are included in Appendix C. Examination of these curves showed that, within the limits of analytical error (see Appendix D) there was essentially no difference in the distribution of uranium between $3\underline{N}$ $HNO_3$ and solvents containing either fresh or degraded diluent.

For the re-extraction distribution curves, the reference solvent was again 33 per cent TBP-67 per cent fresh Shell Bronoco 140 Solvent. In this case, the test solvents were: 32.2 per cent TBP-67.8 per cent degraded Suntide Odorless Mineral Spirits (low degree of degradation); 32.2 per cent TBP-67.8 per cent degraded Shell 140 Solvent (medium degree of degradation); and 33 per cent TBP-67 per cent degraded Bronoco 140 Solvent (high degree of degradation). The distribution curves are presented in Figures 4 and 5, while the analytical results are included in

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* *Diluents referred to as degraded were treated for 6 hours at 150°F with* $5\underline{N}$ $HNO_3$ *-* $0.1\underline{N}$ $HNO_2$.

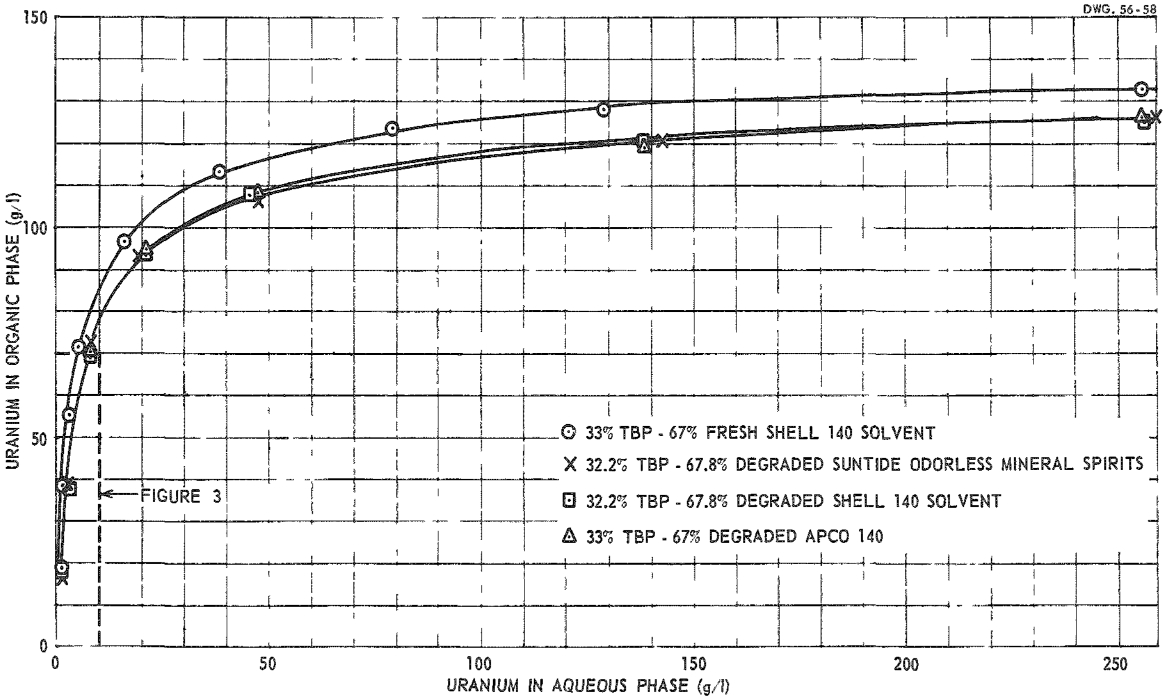

FIGURE 2 Uranium Distribution in the $3\underline{N}$ $HNO_3$ vs 33 Per Cent TBP - 67 Per Cent Kerosene System (Extraction)

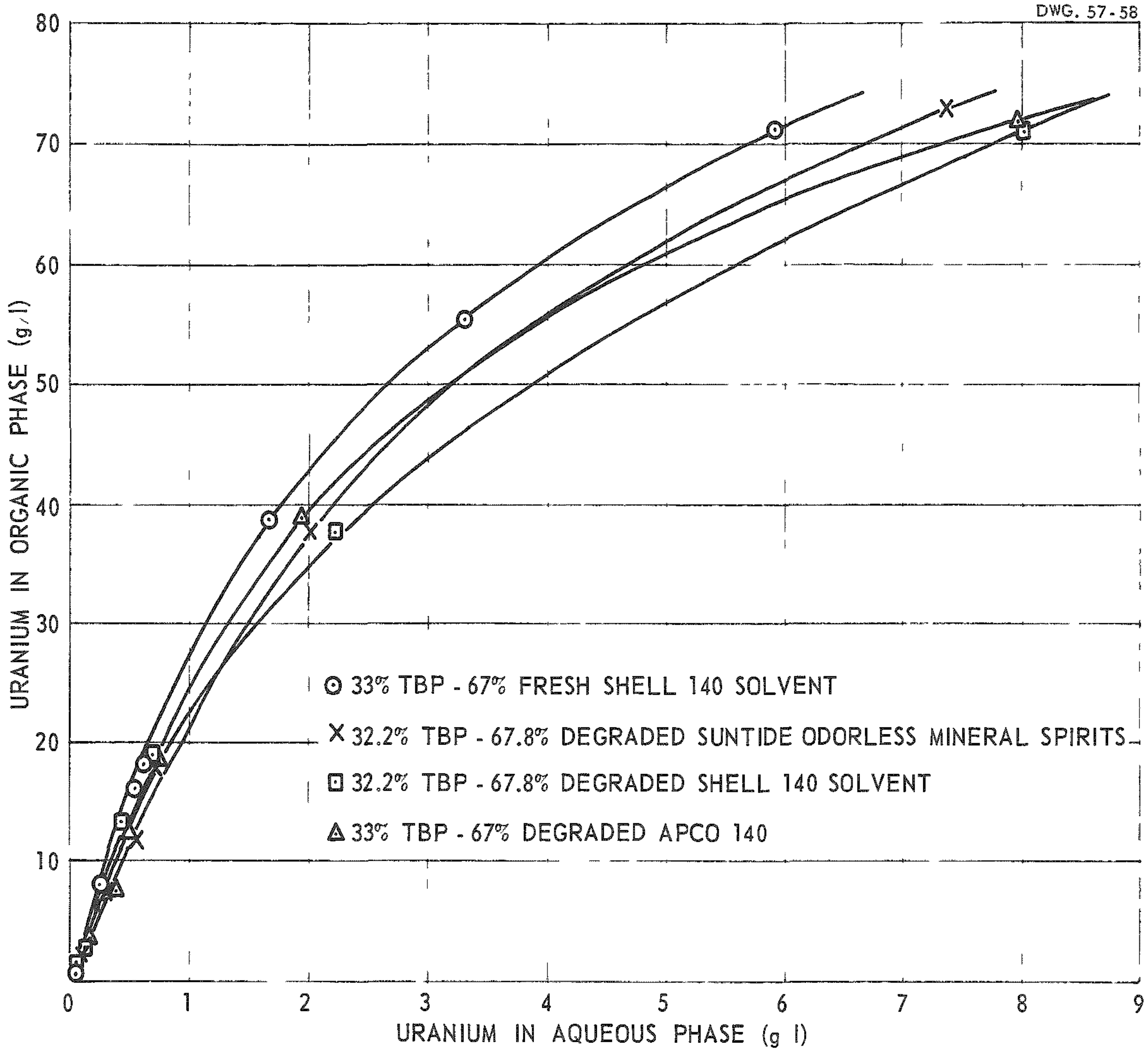

FIGURE 3 Uranium Distribution in the 3$\underline{N}$ $HNO_3$ vs 33 Per Cent TBP - 67 Per Cent Kerosene System (Extraction)

Appendix C. Examination of Figure 4 revealed that (as was the case during extraction) the presence of a degraded diluent had virtually no effect on uranium distribution during the initial stages of re-extraction. Figure 5, however, revealed a startling difference in uranium distribution when the uranium concentration in the organic phase was less than 1 g/l. Under this circumstance, the distribution was shifted more and more toward the solvent phase, as the extent of the diluent degradation increased from solvent to solvent. This shift was most dramatic in the case of the degraded Bronoco 140 Solvent (a highly degraded diluent), for which the uranium concentration in the solvent phase could not be reduced below 0.5 g/l.

These distribution curves supported the contention that the presence of a degraded diluent was responsible for at least part of the water-insoluble-uranium hold-up previously attributed to unknown complexing agents.

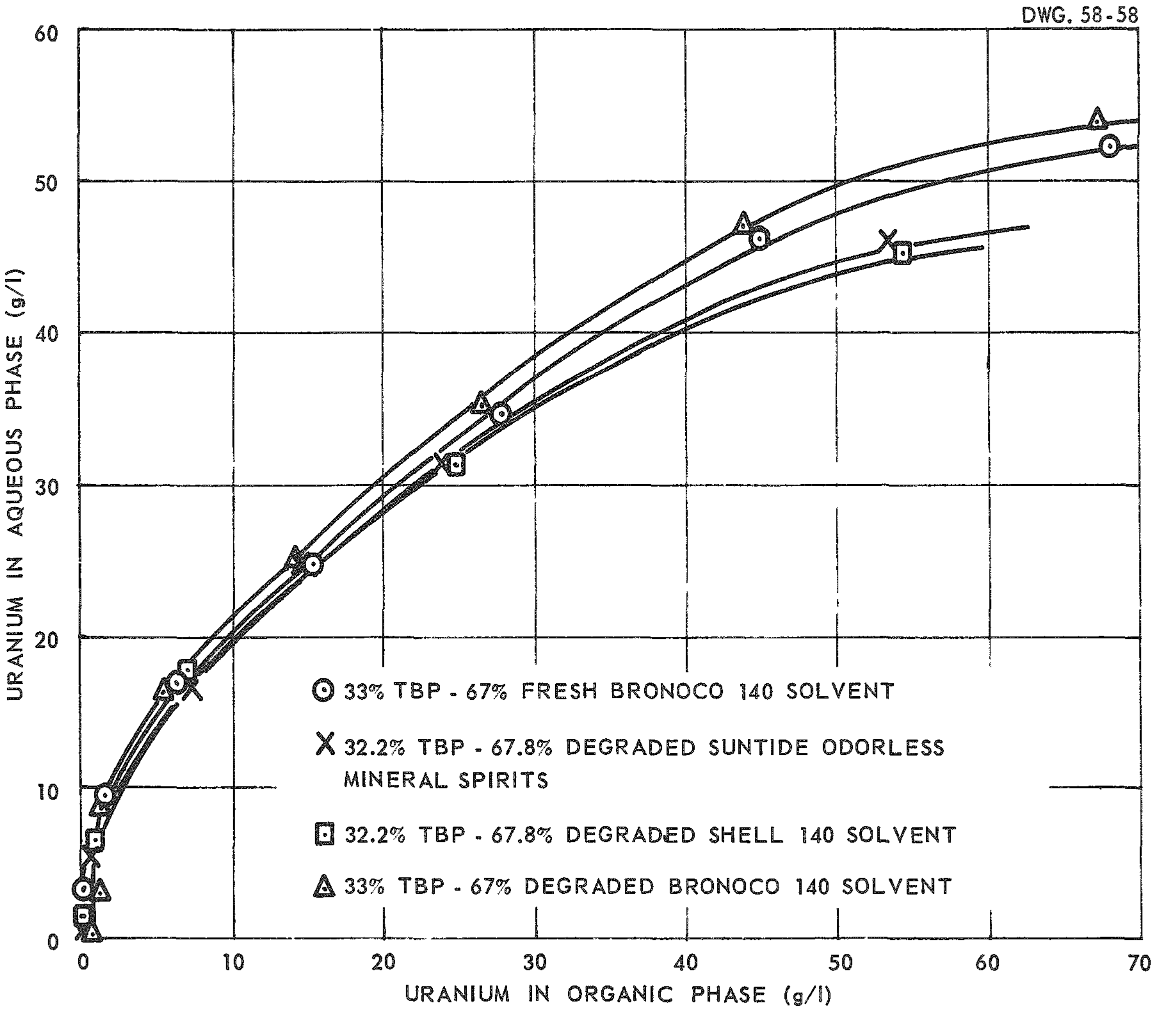

FIGURE 4 Uranium Distribution in the 33 Per Cent TBP - 67 Per Cent Kerosene Distilled Water System (Re-extraction)

## EFFECT OF NITROUS ACID CONCENTRATION ON DILUENT DEGRADATION

A series of degradation tests was conducted, using Bronoco 140 Solvent and nitric-nitrous acid mixtures containing varying amounts of nitrous acid. These were designed to correlate nitrous acid concentration with the extent of degradation, and were evaluated on the basis of infrared spectra and uranium hold-ups. Four tests were made, using nitrous acid contents of 0.05, 0.10, 0.25, and 0.50$\underline{N}$. As in previous tests, 5$\underline{N}$ $HNO_3$ was used, the temperature was maintained at 150°F, and the solutions were agitated for six hours. Infrared spectral evaluation of these tests, based on the relative intensity of the band at 6.42 microns, showed approximately equivalent attack when 0.10, 0.25, or 0.50$\underline{N}$ $HNO_2$ was present, but approximately half this attack when 0.05$\underline{N}$ $HNO_2$ was present. The uranium hold-ups were determined within five days of the degradation treatment, and again more than 40 days after treatment.

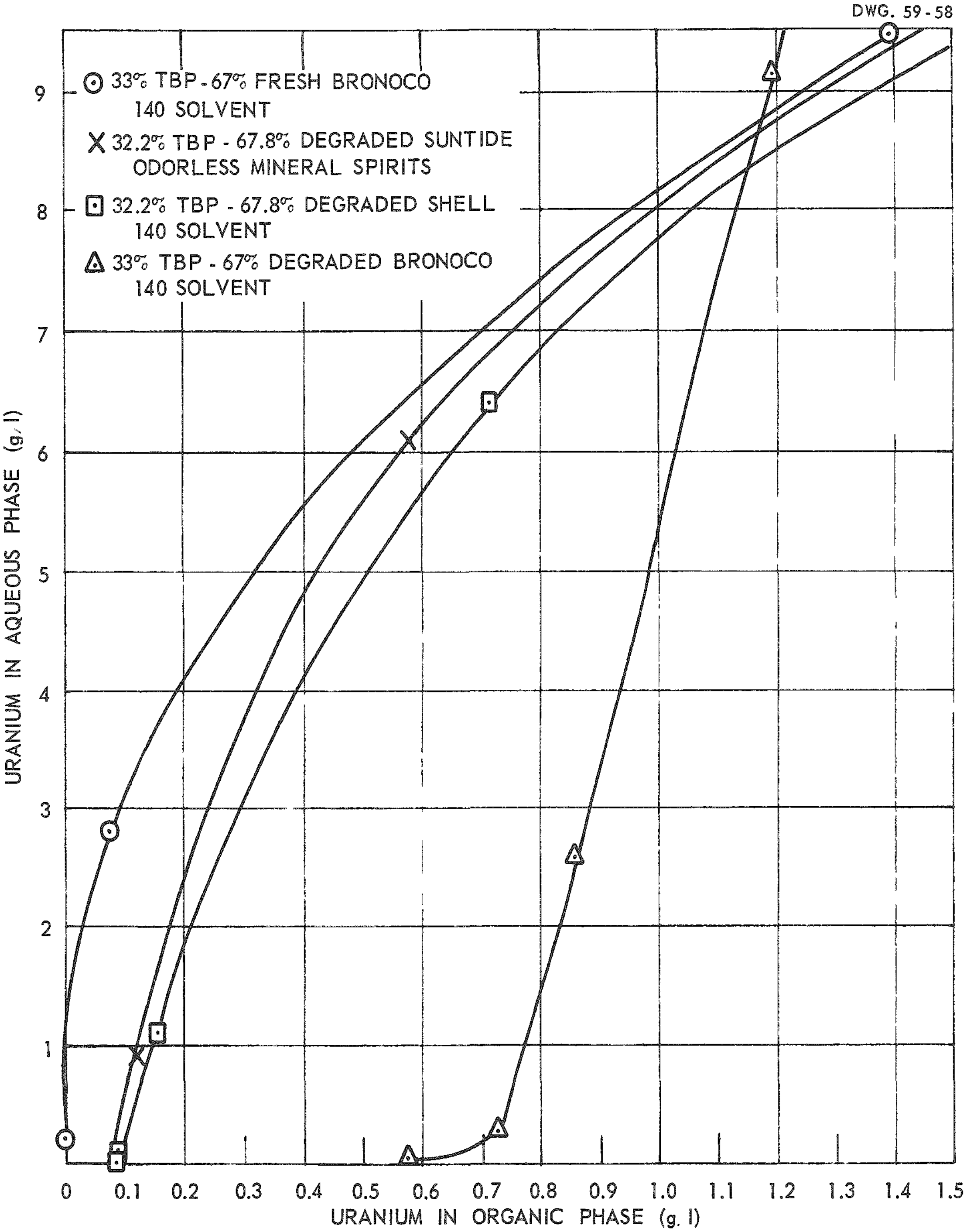

FIGURE 5 Uranium Distribution in the 33 Per Cent TBP - 67 Per Cent Kerosene Distilled Water System (Re-extraction). This is an enlargement of the lower end of the curves in Figure 4.

The results are presented in Table VI. These results indicate that at first, degradation increased with increasing nitrous acid concentration; after aging and probable rearrangement of the degrada-

TABLE VI Comparative Uranium Hold-Ups for Solvents Containing Bronoco 140 Degraded By Varying Concentrations of Nitrous Acid

Organic: 33% TBP-67% Degraded Bronoco 140 Solvent, 95 g/l U, 0.2N $HNO_3$.
Aqueous: Distilled Water.
Room Temperature

| $HNO_2$ Conc. During Degradation (N) | Uranium Hold-Up* (g/l) | Uranium Hold-Up** (g/l) |
|---|---|---|
| 0.05 | 0.019 | 0.16 |
| 0.10 | 0.026 | 0.13 |
| 0.25 | 0.034 | 0.14 |
| 0.50 | 0.042 | 0.14 |

* Re-extraction tests conducted less than 5 days after degradation of the diluent.

** Re-extraction tests conducted more than 40 days after degradation of the diluent.

tion products, there was an approximately equivalent degradation for all four solvents. Thus, in the range of concentrations tested, degradation is only partly dependent on nitrous acid concentration.

## ANALYSIS FOR NITROUS ACID IN REFINERY FEED SLURRIES

At the conditions tested, diluent degradation and the attendant uranium hold-up in a solvent containing a degraded diluent were apparently partially a function of the nitrous acid content of the degrading medium. Thus, it was necessary to establish the presence of nitrous acid in the feed slurries with which Refinery solvent came in contact. After some experimentation, an electrometric titration using standard potassium permanganate solution was developed to about 90 per cent precision. Analyses were then made of two chemical concentrate feed slurry samples, and of two slurry samples prepared from Q-11 ore concentrate (a highly reactive feed material whose nitric acid slurry would be expected to contain a fair amount of nitrous acid). The samples analyzed were not fresh (about 5 days old), and at least some of the nitrous acid originally present would certainly have been lost. Nevertheless, the first pair of samples contained about 0.005N $HNO_2$, and the second pair (the Q-11 samples) contained about 0.05N $HNO_2$. Thus, the presence of nitrous acid in the feed slurries was adequately demonstrated, and the environment necessary for diluent degradation was known to be present in the Refinery.

## EFFECT OF NORMAL SOLVENT TREATMENT ON DEGRADED DILUENTS

Refinery experience indicated that a sodium carbonate-water and/or acid solvent treatment system would not return a used TBP-kerosene solvent to "like-new" condition. Such a system would, of course, remove DBP, but it might not completely remove diluent degradation products. To evaluate the removal of such products, samples of several of the diluents treated with nitric acid, and the nitric-nitrous acid mixture (see the Section of this report titled Acid Stability of the Diluents) were subjected to exhaustive treatment with 5 per cent $Na_2CO_3$, distilled water, and 1N $HNO_3$. These treatments were continued until the aqueous phases from two successive cycles of carbonate, water, and acid were colorless. These cleaned solvent samples were then evaluated on the basis of color, physical property changes, infrared spectral changes, and uranium hold-ups during re-extraction. The last evaluation was only partial (i.e., only two diluents were tested).

## Color Evaluation of Degraded Diluent Clean-up

The results of this evaluation were essentially identical with the results of the color evaluations of the original degraded diluents. When $HNO_2$ had been present originally, the colors were always darker after treatment than were those of the corresponding diluents that originally had been treated with nitric acid alone. Variations in color followed the same order (i.e., increasing color with increasing sulfonation numbers), but the solvent treatment resulted in a universal reduction in this color intensity. Thus, this clean-up apparently removed some, but not all, of the diluent degradation products.

## Physical Property Evaluation of Degraded Diluent Clean-up

Densities, viscosities, and surface tensions were measured. (As mentioned previously, surface tention measurements were too inaccurate to be of use.) As had been noted during the initial evaluation of these degraded diluents, for diluents that had been treated with $HNO_3$ alone, clean-up caused no physical property changes. However, for diluents that had been treated with the nitric-nitrous acid mixture, the density and viscosity were always less after clean-up than before clean-up, but never as low as for the fresh, untreated diluent. The results of these measurements are presented in Appendix B, while the significant changes are summarized in Table VII. These results again indicate that part, but not all, of the diluent degradation products are removed during a carbonate-water-nitric acid treatment.

**TABLE VII Physical Property Changes Due to Clean-Up of Degraded Diluents**

| Diluent | Density Change Obtained by Cleaning Degraded Diluent (%) | Viscosity Change Obtained by Cleaning Degraded Diluent (%) |
|---|---|---|
| Shell Dispersol | −0.08 | −0.6 |
| Apco Deodorized 125 | −0.67 | − .1 |
| Shell 140 Solvent | −0.35 | −1.1 |
| Apco 140 | −0.70 | −1.6 |
| Bronoco 140 Solvent | −0.63 | −1.9 |

## Infrared Spectral Evaluation of Degraded Diluent Clean-up

Infrared spectral analysis of cleaned-up diluents originally treated with nitric acid alone showed no change, supporting all previous indications of no significant change in a diluent treated with nitric acid alone, at the test conditions. For diluents that had been treated with the nitric-nitrous acid mixture, the carbonate-water-acid clean-up led to a universal but inconsistent slight reduction in the intensity of the 6.42-micron absorption band previously attributed to diluent degradation products. Again, indications were that only a part of the diluent degradation products had been removed by the clean-up procedure.

## Uranium Hold-up Evaluation of Degraded Diluent Clean-up

This evaluation was limited to the testing of two diluents, one slightly degraded (Suntide Odorless Mineral Spirits) and the other highly degraded (Bronoco 140 Solvent). Both diluents were used to prepare 33 per cent TBP-67 per cent kerosene solvents. These solvents were then used for batch shakeout re-extraction tests. After sufficient stripping equilibrations to completely re-extract uranium from a fresh solvent, both test solvents were analyzed, given a single pass with 5 per cent $Na_2CO_3$, water, 1N $HNO_3$ clean-up treatment, and used for a second batch shakeout re-extraction test. Results of these tests are presented in Table VIII.

These tests showed: first, the more extensive degradation in the case of Bronoco 140 Solvent; second, the positive presence of agents capable of retaining uranium in the organic phase; and finally, the reduction but not elimination of these agents, as a result of a carbonate-water-acid solvent clean-up.

## IDENTIFICATION OF THE DILUENT DEGRADATION PRODUCTS

As was stated previously, there is a tentative identification of a number of diluent degradation products in the literature.[18] These are mostly nitrogen-containing substances, but also include

TABLE VIII Effect of Solvent Treatment On Uranium Hold-Up of Solvents Containing Degraded Diluent

| Treatment | U (g/l)<br>33% TBP-67% Degraded<br>Suntide Odorless Mineral Spirits | U (g/l)<br>33% TBP-67% Degraded<br>Bronoco 140 Solvent |
|---|---|---|
| Synthetic BP* | 95 | 95 |
| Re-extraction | 0.017 | 0.13 |
| Solvent Clean-up | 0.0039 | 0.002 |
| Synthetic BP | 95 | 95 |
| Re-extraction | 0.004 | 0.029 |

* Uranium-containing solvent stream.

organic acids and possibly aldehydes and ketones. Infrared spectral analyses of the degraded diluents investigated to this point had shown one absorption peak (at 6.42 microns) due to degradation products, but no positive characterization of this peak had been made. As a result, a more intensive study of degraded diluents was undertaken in the hope that the degradation products might be accurately characterized. Knowledge of their exact character was expected to materially aid any studies of means for their removal.

Two independent approaches were used to finally identify the diluent degradation products. These were: organic qualitative spot tests and expanded infrared spectral analyses.

## Organic Qualitative Spot Tests of Degraded Diluents

The spot tests employed were all standard qualitative organic tests. They were for:

a. Organic acids:[19] Neutralization with alcoholic NaOH.

b. Nitro or Nitrate Compounds:[20] Alkaline oxidation of ferrous sulfate.

c. Carbonyl Compounds:[21] Reaction with 2-4 dinitrophenylhydrazine.

d. Alcohols:[22] Reaction with ceric nitrate.

e. Nitroso Compounds:[23] Liebermann's nitroso reaction; phenol and sulfuric acid, followed by NaOH.

f. Nitrite Compounds:[24] Reaction with sulfanilic acid and $\alpha$-naphthylamine in HCl medium.

These tests were used on all available degraded diluents, as well as on those which had been cleaned up after degradation. The results of these spot tests are presented in Table IX. In every case, the tests for alcohols, carbonyl compounds, and nitrite compounds were negative. All of the diluents treated with nitric acid alone, or treated with nitric acid, and then solvent-cleaned were also negative to the tests for organic acids, nitro or nitrate compounds, and nitroso compounds. On the other hand, all diluents treated with the nitric-nitrous acid mixture gave positive tests for organic acids, nitro or nitrate compounds, and nitroso compounds. After solvent clean-up, these diluents tested positive again in all three cases; there was, however, a marked decrease in the acid content, indicating at least partial removal of the acid degradation products.

Thus, the qualitative organic spot tests characterized diluent degradation products as organic acids, nitro or nitrate compounds, and nitroso compounds. Here was further indication of the complexity of the degradation of a kerosene-type diluent.

## Infrared Spectral Identification of Diluent Degradation Products

To facilitate these infrared studies, a fresh diluent degradation test was conducted, using Amsco Kerosene Diluent No. 1 (13.2 volume per cent aromatic and olefinic hydrocarbons, as shown in Table I), 5N $HNO_3$-0.1N $HNO_2$, 150°F, and six hours of agitation. This diluent was

TABLE IX Qualitative Organic Spot Tests* of Acid-Treated Diluents

| Treatment | Diluent | Organic Acids | Nitro or Nitrate | Carbonyl Compounds | Alcohol | Nitroso | Nitrite |
|---|---|---|---|---|---|---|---|
| 5$\underline{N}$ $HNO_3$ at 150°F for six hours. | Shell Dispersol | – | – | – | – | – | – |
| | Shell 140 Solv. | – | – | – | – | – | – |
| | Apco 140 | – | – | – | – | – | – |
| | Apco Deodorized 125 | – | – | – | – | – | – |
| | Bronoco 140 Solv. | – | – | – | – | – | – |
| 5$\underline{N}$ $HNO_3$ at 150°F fox six hours, followed by exhaustive solvent treatment | Shell Dispersol | – | – | – | – | – | – |
| | Shell 140 Solv. | – | – | – | – | – | – |
| | Apco 140 | – | – | – | – | – | – |
| | Apco Deodorized 125 | – | – | – | – | – | – |
| | Bronoco 140 Solv. | – | – | – | – | – | – |
| 5$\underline{N}$ $HNO_3$ - 0.1$\underline{N}$ $HNO_2$ at 150°F for six hours | Shell Dispersol | + | + | – | – | + | – |
| | Shell 140 Solv. | + | + | – | – | + | – |
| | Apco 140 | + | + | – | – | + | – |
| | Apco Deodorized 125 | + | + | – | – | + | – |
| | Bronoco 140 Solv. | + | + | – | – | + | – |
| | Suntide Orderless Mineral Spirits | + | + | – | – | + | – |
| | Shell Insecticide Base | + | + | – | – | + | – |
| | Amsco Kerosene Diluent #1 | + | + | – | – | + | – |
| 5$\underline{N}$ $HNO_3$ - 0.1$\underline{N}$ $HNO_2$ at 150°F for six hours, followed by exhaustive solvent treatment | Shell Dispersol | Weak + | + | – | – | + | – |
| | Shell 140 Solv. | Weak + | + | – | – | + | – |
| | Apco 140 | Weak + | + | – | – | + | – |
| | Apco Deodorized 125 | Weak + | + | – | – | + | – |
| | Bronoco 140 Solv. | Weak + | + | – | – | + | – |
| | Suntide Odorless Mineral Spirits | Weak + | + | – | – | + | – |
| | Shell Insecticide Base | Weak + | + | – | – | + | – |
| | Amsco Kerosene Diluent #1 | Weak + | + | – | – | + | – |

* For references to the specific tests employed, see the text of this report

used in determining infrared spectra at several cell path lengths (0.05 mm, 0.10 mm, and 0.25 mm). These studies revealed several absorption bands (at 5.85, 6.06, 6.42, and 7.78 microns) due to the degradation products. These bands were attributed to carboxylic acids, organic nitrates, organic nitro-compounds, and organic nitrates, respectively.

An attempt was made to increase the concentrations of the various degradation products by refluxing a diluent with 15.8$\underline{N}$ $HNO_3$ for one hour. The result was a dark-red diluent whose infrared spectrum showed the four previously discussed absorption bands, as well as a band at 11.75 microns also due to the presence of organic nitrates.

Final characterization of the diluent degradation products was the result of one further test.

Since a $Na_2CO_3$ solution removed part of the diluent degradation products, a large volume of degraded diluent was extensively washed with sodium carbonate solution. This carbonate solution was then neutralized with nitric acid, and the degradation products were extracted with ethyl ether. After evaporation of the ether, a small amount of red, oily liquid remained. This was apparently a sample of the degradation products. The infrared spectrum of this sample contained all of the previously mentioned absorption-bands, as well as bands at 3.75, 7.05, 7.38, and 10.70 microns. A summary of the bands due to diluent degradation products, and their assignments is presented in Table X.

Thus, through infrared analyses, the diluent degradation products were characterized as carboxylic acids, organic nitrates (i.e., esters), organic nitro compounds, and nitroso compounds. There was no evidence for nitrites, aldehydes, ketones, or alcohols. These results corroborated and amplified the results of the qualitative organic spot tests.

TABLE X Spectra-Compound Type Correlation for Diluent Degradation Products

| Wavelength (microns) | Assignment | | Compound Type |
|---|---|---|---|
| 3.75 | O-H | st | Carboxylic Acids |
| 5.85 | C=O | st | Carboxylic Acids |
| 6.06 | $NO_2$ | st-asym | Organic Nitrates |
| 6.42 | $NO_2$ | st-asym | Organic Nitro Compounds |
| 7.05 | N=O | st | Nitroso Compounds |
| 7.38 | $NO_2$ | st-sym | Organic Nitro Compounds |
| 7.78 | $NO_2$ | st-sym | Organic Nitrates |
| 10.70 | O-H | w | Carboxylic Acids |
| 11.75 | O-N | st | Organic Nitrates |

st = stretching vibration
w = wagging vibration
asym = asymmetric
sym = symmetric

## DISCUSSION AND CONCLUSIONS

These studies of the kerosene diluents have produced a number of beneficial results. Chemical and infrared spectral analyses of fresh diluents have shown that there is considerable variation in the paraffinic, isoparaffinic, aromatic, and olefinic hydrocarbon contents of outwardly similar solvents. This has led to more thorough testing of incoming diluent intended for Refinery use.

In connection with these characterizations of kerosene diluents, correlation of chemical and infrared analyses has shown that the ASTM sulfonation numbers and olefin number tests are quite valid when applied to essentially paraffinic hydrocarbon mixtures. These same tests are, however, less valid when applied to isoparaffinic hydrocarbon mixtures.

Degradation tests have firmly established the instability of a kerosene-type diluent to nitric acid at high concentrations or high temperatures. These tests have also amply demonstrated the dependence of diluent degradation on the presence of nitrous acid and/or aromatic olefinic, and isoparaffinic hydrocarbons at the temperatures and nitric acid concentrations encountered during Refinery operations (i.e., $<5\underline{N}$ $HNO_3$ and $<150°F$).

The presence of small amounts of nitrous acid in the Refinery feed slurries has been established.

Thus, although diluent specifications have been adjusted to eliminate almost all unstable constituents, the requirements for diluent degradation are all met during normal Refinery operations. Diluent degradation tests have further demonstrated that an essentially paraffinic diluent is more stable than is an essentially isoparaffinic diluent.

The ability of a degraded diluent to cause a hold-up of non-water-soluble uranium in an apparently thoroughly re-extracted solvent has been shown. Further, aging of a degraded diluent, undoubtedly leading to the chemical rearrangement of some of the degradation products, results in even greater uranium hold-up. It has been shown that a degraded diluent has little or no effect on uranium distribution during extraction operations, but does shift the distribution toward the organic phase during re-extraction at low uranium concentrations.

The normal carbonate-water-acid solvent-treatment procedure removes part, but not all, of the diluent degradation products.

The diluent degradation products have been identified, by chemical and infrared spectral means, as carboxylic acids, organic nitrates (i.e., esters), organic nitro compounds, and nitroso compounds. During these studies, there was no evidence to support the presence of alcohols, aldehydes, or ketones in a degraded diluent.

From these results, it may be concluded that the ideal diluent would be a 100 per cent paraffinic hydrocarbon mixture, and that such a diluent should be used only in a nitrous acid-free system and at temperatures below 150°F. Economic, chemical, and operating factors make such a set of conditions impossible. Therefore, it must be accepted that:

1. The diluent will contain some aromatic, olefinic and isoparaffinic constituents.
2. Some nitrous acid will be present in the aqueous feed slurries.
3. Some diluent degradation will take place.
4. Such degradation will be a function of both the nitrous acid content of the feed slurries, and the unstable constituent content of the diluent.
5. This diluent degradation will discolor the solvent, and more important, will contribute to losses in efficiency during re-extraction operations.
6. The diluent degradation products, being acids and nitrogenous compounds, cannot be completely removed by a carbonate-water-nitric acid solvent treatment system.

All of these conclusions are in agreement with results obtained by other workers who have studied kerosene-type diluents.

## ACKNOWLEDGMENTS

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Acknowledgment is also made to the personnel of the National Lead Company of Ohio Analytical Department for the many and varied analyses provided during the course of this work, and to M. M. Smith for the typing of the manuscript of this report.

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# APPENDIX A – ANALYTICAL PROCEDURES FOR KEROSENE DILUENTS

## DETERMINATION OF UNSTABLE CONSTITUENTS IN HYDROCARBON MIXTURES BY CHROMYL CHLORIDE OXIDATION[8]

This test is designed to yield the milliequivalents of unstable constituents per milliliter of hydrocarbon mixture.

### Reagents

1. 0.1N $K_2Cr_2O_7$, primary standard.
2. 0.2N $FeSO_4$.
3. 0.7 to 1.0N $CrO_2Cl_2$ in $CCl_4$.
4. 1, 10 orthophenanthroline ferrous sulfate (Ferroin) indicator.

### Equipment

1. Two 50-ml burettes.
2. Three-ml and five-ml pipettes.
3. 250-ml glass-stoppered Erlenmeyer flasks.

### Procedure

1. Pipette 5 ml of the hydrocarbon mixture to be tested into the 250-ml Erlenmeyer flasks.
2. Carefully add 3 ml $CrO_2Cl_2$ via pipette, with no unnecessary mixing.
3. Prepare 4 identical samples; after preparation, shake all samples, starting at the same time ("0" time) to insure simultaneous reaction.
4. At time intervals of 10, 20, 30, and 40 minutes, stop further reaction by adding 10 ml standard $FeSO_4$ solution. Shake to insure complete reaction of the unused $CrO_2Cl_2$.
5. Add 5 to 7 ml conc. $H_2SO_4$, and wash down the sides of the flask with distilled water.
6. Add 5 drops of Ferroin indicator, and titrate past the brown-to-green color change with standard $K_2Cr_2O_7$.
7. Determine the actual endpoint by back-titrating with $FeSO_4$ to the green-to-brown color change.
   *NOTE: In the back-titrating, the color change fades rapidly back to the green.*

## Calculations

1. Determine the milliequivalents of $CrO_2Cl_2$ remaining at each time interval.
2. Plot, on semilog paper, the milliequivalents of $CrO_2Cl_2$ versus time. Draw the most representative line through the available points, and extrapolate to "0" time to determine the milliequivalents of $CrO_2Cl_2$ present at "0" time.
3. meq. $CrO_2Cl_2$ added - meq. $CrO_2Cl_2$, present at zero time = meq. $CrO_2Cl_2$ used.
4. $\frac{\text{meq. } CrO_2Cl_2 \text{ used}}{\text{ml in sample}}$ = meq. unstable constituents per ml of sample.

## DETERMINATION OF AROMATIC AND OLEFINIC HYDROCARBONS IN PETROLEUM DISTILLATES[9]

### Reagents

1. Sulfonation Acid: 70 per cent (wt basis) CP $H_2SO_4$ + 30 per cent (wt basis) CP $P_2O_5$
2. CP Sulfuric Acid (95 to 96 per cent by wt)

### Procedure

1. Measure 25 ml of the $H_2SO_4$-$P_2O_5$ mixture into a graduate, and transfer to the sulfonation flask.
2. Place the flask in the ice bath, and maintain it at a temperature of $0^\circ$ to $5^\circ C$ for 5 minutes.
3. Pipette 10 ml of sample down the side of the sulfonation bottle, keeping the two layers separate.
4. Cool for an additional 5 minutes.
5. Shake the mixture for 2 minutes without removing from the ice bath.
6. Shake the mixture for 20 seconds above the ice bath.
7. Place the mixture in the bath, and shake for 40 seconds.
8. Repeat the shaking procedure in 6 and 7 until 10 minutes of shaking has elapsed.
9. Remove the sample from the ice bath, and centrifuge for 3 minutes at approximately 1000 rpm.
10. Add $H_2SO_4$ (Sp.Gr.: 1.84) until the hydrocarbon layer is all within the calibrated portion of the flask neck.
11. Centrifuge for 3 minutes more.

12. Adjust the temperature of the acid-hydrocarbon mixture to within 1°C of that of the original test sample.
13. Allow to stand for five minutes.
14. Read the upper and lower levels of the hydrocarbon layer to the nearest 0.05 ml.

## Calculation

$$A = \frac{(V-R)100}{V} - \frac{10C}{V}$$

A = percentage by volume of aromatics plus olefins.

V = volume of sample in milliliters.

R = volume of hydrocarbons remaining after reaction in milliliters.

C = correction for solubility of hydrocarbons in the acid.

## PROCEDURE FOR OLEFIN DETERMINATION BY BROMINE NUMBER[10]

### Reagents

1. Carbon tetrachloride
2. Acetic acid, glacial
3. 0.5N bromide-bromate solution
4. Potassium iodide solution (150 g/l)
5. 0.1N sodium thiosulfate solution
6. Starch solution

### Procedure

1. Weigh a 5-ml aliquot of the sample.
2. Add this aliquot to 10 ml $CCl_4$ in a 50-ml volumetric flask, dilute to the mark with $CCl_4$, and mix well.
3. Pipette a 5-ml portion of this solution into a 500-ml Erlenmeyer flask containing 50 ml glacial acetic acid.
4. Maintain a temperature of 25° ± 5°C. Do not expose to direct sunlight.
5. Add the bromide-bromate reagent from a burette at a rate of 1 to 2 drops/second until a distinct yellow color forms and remains for at least 5 seconds. Keep the solution well agitated.

6. Add an additional 1 ml of the reagent, stopper the flask, and agitate for an additional 40 ± 5 seconds.
7. Add 5 ml KI solution, allowing the solution to flow slowly down the sides of the flask.
8. Stopper again, and shake vigorously.
9. Add 100 ml $H_2O$, and shake again for 1 minute.
10. Titrate with the $Na_2S_2O_3$ solution. Near the end of the titration, add 1 ml of starch indicator solution, and titrate slowly to the disappearance of the blue color. This back-titration should be made with 5 to 10 ml of $Na_2S_2O_3$ solution.

Calculations

$$\text{Bromine number} = \frac{(VN - vn) \times 7.99}{W}$$

$V$ = milliliters of bromide-bromate solution used.

$N$ = normality of bromide-bromate solution.

$v$ = milliliters of $Na_2S_2O_3$ solution used.

$n$ = normality of $Na_2S_2O_3$ solution.

$W$ = weight (in grams) of sample.

$$\%\ \text{olefins by volume} = \frac{B \times M}{160} = \text{Olefin Number}$$

$B$ = Bromine number

$M$ = Average Molecular weight of olefins (determined by ASTM 50 per cent boiling point)[25]

# APPENDIX B – PHYSICAL PROPERTY MEASUREMENTS OF ACID TREATED DILUENTS

Densities were determined by the use of pycnometers, viscosity by the use of Ostwald viscometers; and surface tensions by the use of a Cenco 70535 Tensiometer, all at 30°C.

Samples referred to as "cleaned" were subjected to exhautive sodium carbonate-water-nitric acid washing.

The error in density is thought to be no more than ±0.0002 g/ml; that of viscosity, no more than ±0.04 millipoise; and that of surface tension no less than ±0.5 dyne/cm. As a result, the surface tension measurements made are of little value.

| | No. | Treatment | Density (g/ml) | Viscosity (Millipoises) | Surface Tension (dynes/cm) |
|---|---|---|---|---|---|
| TABLE XIa<br>Shell Dispersol | 1 | As Received | 0.7785 | 13.54 | 22.9 |
| | 2 | $HNO_3$ | 0.7784 | 13.55 | 22.8 |
| | 3 | No. 2 Cleaned | 0.7786 | 13.48 | 23.1 |
| | 4 | $HNO_3$-$HNO_2$ | 0.7808 | 13.63 | 23.1 |
| | 5 | No. 4 Cleaned | 0.7802 | 13.55 | 23.0 |
| TABLE XIb<br>Shell 140 Solvent | 1 | As Received | 0.7737 | 10.74 | 22.4 |
| | 2 | $HNO_3$ | 0.7739 | 10.73 | 22.5 |
| | 3 | No. 2 Cleaned | 0.7732 | 10.70 | 22.5 |
| | 4 | $HNO_3$-$HNO_2$ | 0.7798 | 11.01 | 22.9 |
| | 5 | No. 4 Cleaned | 0.7771 | 10.93 | 22.9 |
| TABLE XIc<br>Apco 140 | 1 | As Received | 0.7783 | 10.71 | 22.5 |
| | 2 | $HNO_3$ | 0.7785 | 10.66 | 22.8 |
| | 3 | No. 2 Cleaned | 0.7786 | 10.63 | 22.8 |
| | 4 | $HNO_3$-$HNO_2$ | 0.7892 | 11.50 | 22.9 |
| | 5 | No. 4 Cleaned | 0.7837 | 11.04 | 22.7 |
| TABLE XId<br>Apco Deodorized 125 | 1 | As Received | 0.7644 | 9.15 | 21.6 |
| | 2 | $HNO_3$ | 0.7644 | 9.21 | 21.8 |
| | 3 | No. 2 Cleaned | 0.7646 | 9.27 | 21.6 |
| | 4 | $HNO_3$-$HNO_2$ | 0.7669 | 9.33 | 21.9 |
| | 5 | No. 4 Cleaned | 0.7664 | 9.32 | 21.9 |
| TABLE XIe<br>Bronoco 140 Solvent | 1 | As Received | 0.7684 | 10.28 | 22.1 |
| | 2 | $HNO_3$ | 0.7686 | 10.18 | 22.3 |
| | 3 | No. 2 Cleaned | 0.7686 | 10.20 | 22.4 |
| | 4 | $HNO_3$-$HNO_2$ | 0.7787 | 10.91 | 22.6 |
| | 5 | No. 4 Cleaned | 0.7738 | 10.70 | 22.5 |
| TABLE XIf<br>Shell Insecticide Base | 1 | As Received | 0.7788 | 13.49 | Not Measured |
| | 2 | $HNO_3$-$HNO_2$ | 0.7843 | 13.93 | Not Measured |
| TABLE XIg<br>Suntide Odorless Mineral Spirits | 1 | As Received | 0.7470 | 11.93 | Not Measured |
| | 2 | $HNO_3$-$HNO_2$ | 0.7516 | 12.64 | Not Measured |

# APPENDIX C – CHEMICAL ANALYSES FOR URANIUM DISTRIBUTION CURVES

## TABLE XIIa Uranium Distribution Between $3\underline{N}$ $HNO_3$ and 33 Per Cent TBP-67 Per Cent Fresh Shell 140 Solvent (Extraction)

Aqueous Phase: UNH Solutions, $\geq 3\underline{N}$ $HNO_3$.
Organic Phase: 33% TBP-67% Shell 140, nonacidified.
Room Temperature

| Solution No. | Organic Phase | | Aqueous Phase | |
|---|---|---|---|---|
| | U (g/l) | $HNO_3$ ($\underline{N}$) | U (g/l) | $HNO_3$ ($\underline{N}$) |
| 1 | 0.26 | 0.71 | 0.010 | 2.92 |
| 2 | 0.70 | 0.72 | 0.024 | 2.91 |
| 3 | 1.70 | 0.71 | 0.065 | 2.93 |
| 4 | 3.00 | 0.70 | 0.125 | 2.90 |
| 5 | 8.12 | 0.69 | 0.285 | 2.93 |
| 6 | 12.78 | 0.65 | 0.47 | 2.91 |
| 7 | 16.49 | 0.64 | 0.55 | 2.89 |
| 8 | 18.52 | 0.62 | 0.64 | 2.98 |
| 9 | 38.88 | 0.51 | 1.70 | 2.95 |
| 10 | 55.6 | 0.44 | 3.33 | 3.04 |
| 11 | 71.2 | 0.34 | 5.93 | 3.12 |
| 12 | 96.5 | 0.15 | 16.56 | 2.94 |
| 13 | 113.7 | 0.10 | 39.00 | 2.92 |
| 14 | 123.5 | 0.054 | 79.4 | 2.97 |
| 15 | 127.8 | 0.030 | 129.6 | 2.93 |
| 16 | 132.1 | 0.090 | 256.8 | 3.05 |

## TABLE XIIb Uranium Distribution Between $3\underline{N}$ $HNO_3$ and 32.2 Per Cent TBP-67.8 Per Cent Degraded Suntide Odorless Mineral Spirits (Extraction)

Aqueous: UNH Solutions $\geq 3\underline{N}$ $HNO_3$
Organic: 32.2% TBP-67.8% Degraded Suntide Odorless Mineral Spirits
Room Temperature

| UNH Solution No. | Organic Phase | | Aqueous Phase | |
|---|---|---|---|---|
| | U (g/l) | $HNO_3$ ($\underline{N}$) | U (g/l) | $HNO_3$ ($\underline{N}$) |
| 1 | 0.27 | 0.67 | 0.013 | 2.9 |
| 2 | 2.1 | 0.66 | 0.075 | 3.0 |
| 3 | 3.8 | 0.65 | 0.15 | 2.9 |
| 4 | 8.1 | 0.67 | 0.31 | 3.0 |
| 5 | 12 | 0.61 | 0.55 | 2.9 |
| 6 | 18 | 0.59 | 0.73 | 2.9 |
| 7 | 38 | 0.50 | 2.0 | 3.0 |
| 8 | 73 | 0.33 | 7.4 | 3.0 |
| 9 | 94 | 0.27 | 20.5 | 2.9 |
| 10 | 108 | 0.21 | 47.8 | 2.9 |
| 11 | 120 | 0.15 | 143 | 2.9 |
| 12 | 126 | 0.10 | 273 | 3.1 |

### TABLE XIIc Uranium Distribution Between $3\underline{N}$ $HNO_3$ and 32.2 Per Cent TBP-67.8 Per Cent Degraded Shell 140 Solvent (Extraction)

Aqueous: UNH Solutions, $\geq 3\underline{N}$ $HNO_3$.
Organic: 32.2% TBP-67.8% Degraded Shell 140 Solvent
Room Temperature

| UNH Solution | Organic Phase | | Aqueous Phase | |
|---|---|---|---|---|
| No. | U (g/l) | $HNO_3(\underline{N})$ | U (g/l) | $HNO_3(\underline{N})$ |
| 1 | 0.28 | 0.67 | 0.011 | 3.0 |
| 2 | 2.1 | 0.67 | 0.076 | 3.0 |
| 3 | 3.8 | 0.65 | 0.14 | 2.9 |
| 4 | 8.6 | 0.65 | 0.30 | 2.95 |
| 5 | 13.1 | 0.62 | 0.45 | 2.95 |
| 6 | 19.4 | 0.59 | 0.75 | 3.0 |
| 7 | 38.1 | 0.50 | 2.20 | 3.0 |
| 8 | 71.0 | 0.36 | 8 | 3.0 |
| 9 | 94.0 | 0.25 | 21 | 2.9 |
| 10 | 108 | 0.20 | 46 | 3.0 |
| 11 | 121 | 0.13 | 139 | 3.0 |
| 12 | 125 | 0.10 | 258 | 3.1 |

### TABLE XIId Uranium Distribution Between $3\underline{N}$ $HNO_3$ and 33 Per Cent TBP-67 Per Cent Degraded Apco 140 (Extraction)

Aqueous: UNH Solutions, $\geq 3\underline{N}$ $HNO_3$
Organic: 33% TBP-67% degraded Apco 140
Room Temperature

| UNH Solution | Organic Phase | | Aqueous Phase | |
|---|---|---|---|---|
| No. | U (g/l) | $HNO_3(\underline{N})$ | U (g/l) | $HNO_3(\underline{N})$ |
| 1 | 0.29 | 0.66 | 0.024 | 2.9 |
| 2 | 2.1 | 0.66 | 0.077 | 2.9 |
| 3 | 3.9 | 0.57 | 0.17 | 2.95 |
| 4 | 8.4 | 0.65 | 0.29 | 3.0 |
| 5 | 13.0 | 0.62 | 0.48 | 2.95 |
| 6 | 19.0 | 0.60 | 0.77 | 3.0 |
| 7 | 39.2 | 0.49 | 1.95 | 3.0 |
| 8 | 72 | 0.37 | 8 | 3.0 |
| 9 | 95 | 0.27 | 22 | 2.9 |
| 10 | 109 | 0.21 | 48 | 2.9 |
| 11 | 119 | 0.15 | 139 | 3.0 |
| 12 | 126 | 0.11 | 256 | 3.1 |

### TABLE XIIe Uranium Distribution Between 33 Per Cent - 67 Per Cent Fresh Bronoco 140 Solvent and Distilled Water (Re-extraction)

Organic: 33% TBP-67% Fresh Bronoco 140 Solvent, 92.8 g/l U, $0.2\underline{N}$ $HNO_3$
Aqueous: Distilled water
Room Temperature

| Stage | Organic Phase U (g/l) | Aqueous Phase U (g/l) |
|---|---|---|
| 1 | 68.1 | 52.3 |
| 2 | 45.0 | 46.1 |
| 3 | 27.7 | 34.6 |
| 4 | 15.0 | 25.3 |
| 5 | 6.6 | 17.3 |
| 6 | 1.4 | 9.53 |
| 7 | 0.078 | 2.78 |
| 8 | 0.002 | 0.19 |
| 9 | <0.0005 | 0.014 |
| 10 | <0.0005 | 0.006 |
| 11 | <0.0005 | 0.0007 |
| 12 | <0.0005 | 0.0008 |

### TABLE XIIf Uranium Distribution Between 32.2 Per Cent TBP-67.8 Per Cent Degraded Suntide Odorless Mineral Spirits and Distilled Water (Re-extraction)

Organic: 32.2% TBP-67.8% Degraded Suntide Odorless Mineral Spirits, 98.5 g/l U, $0.2\underline{N}$ $HNO_3$.
Aqueous: Distilled water
Room Temperature

| Stage | Organic Phase U (g/l) | Aqueous Phase U (g/l) |
|---|---|---|
| 1 | 53.7 | 45.7 |
| 2 | 29.3 | 31.1 |
| 3 | 7.4 | 17.2 |
| 4 | 0.58 | 6.1 |
| 5 | 0.12 | 0.91 |
| 6 | — | 0.055 |
| 7 | 0.076 | 0.012 |
| 8 | — | 0.011 |
| 9 | 0.073 | 0.012 |

(—) indicates not sampled.

## TABLE XIIg Uranium Distribution Between 32.2 Per Cent TBP-67.8 Per Cent Degraded Shell 140 Solvent and Distilled Water (Re-extraction)

Organic: 32.2% TBP-67.8% Degraded Shell 140 Solvent, 97.1 g/l U, 0.2N $HNO_3$
Aqueous: Distilled water
Room Temperature

| Stage | Organic Phase U (g/l) | Aqueous Phase U (g/l) |
|---|---|---|
| 1 | 54.2 | 44.9 |
| 2 | 24.9 | 31.8 |
| 3 | 7.67 | 18.0 |
| 4 | 0.72 | 6.4 |
| 5 | 0.16 | 1.1 |
| 6 | — | 0.081 |
| 7 | 0.092 | 0.037 |
| 8 | — | 0.029 |
| 9 | 0.063 | 0.020 |

(—) indicates not sampled

## TABLE XIIh Uranium Distribution Between 33 Per Cent TBP-67 Per Cent Degraded Bronoco 140 Solvent and Distilled Water (Re-extraction)

Organic: 33% TBP-67% Degraded Bronoco 140 Solvent, 95.3 g/l U, 0.2N $HNO_3$
Aqueous: Distilled water
Room Temperature

| Stage | Organic Phase U (g/l) | Aqueous Phase U (g/l) |
|---|---|---|
| 1 | 67.4 | 53.8 |
| 2 | 44.1 | 47.0 |
| 3 | 26.4 | 35.5 |
| 4 | 14.3 | 25.3 |
| 5 | 5.7 | 16.7 |
| 6 | 1.2 | 9.17 |
| 7 | 0.86 | 2.59 |
| 8 | 0.73 | 0.28 |
| 9 | 0.58 | 0.062 |
| 10 | 0.61 | 0.038 |
| 11 | 0.58 | 0.030 |
| 12 | 0.65 | 0.026 |

# APPENDIX D – ACCURACY OF ANALYTICAL PROCEDURES FOR URANIUM AND NITRIC ACID

All analyses were conducted by the Analytical Department.

In the organic phase, uranium was determined colorimetrically when >1.0 g/l and fluorometrically when <1.0 g/l. In the aqueous phase, uranium was determined colorimetrically when >2.0 g/l and fluorometrically when <2.0 g/l.

Acidities were determined by titration with NaOH. The analytical errors are as follows:

| Analysis | Phase | Error* (%) |
|---|---|---|
| $HNO_3$ | Organic | ±13 |
| | Aqueous | ±7 |
| Colorimetric U | Aqueous | ±4 |
| | Organic | ±7 |
| Fluorometric U | Aqueous | ±40 |
| | Organic | ±40 |

* Error represents the 95% confidence limit.