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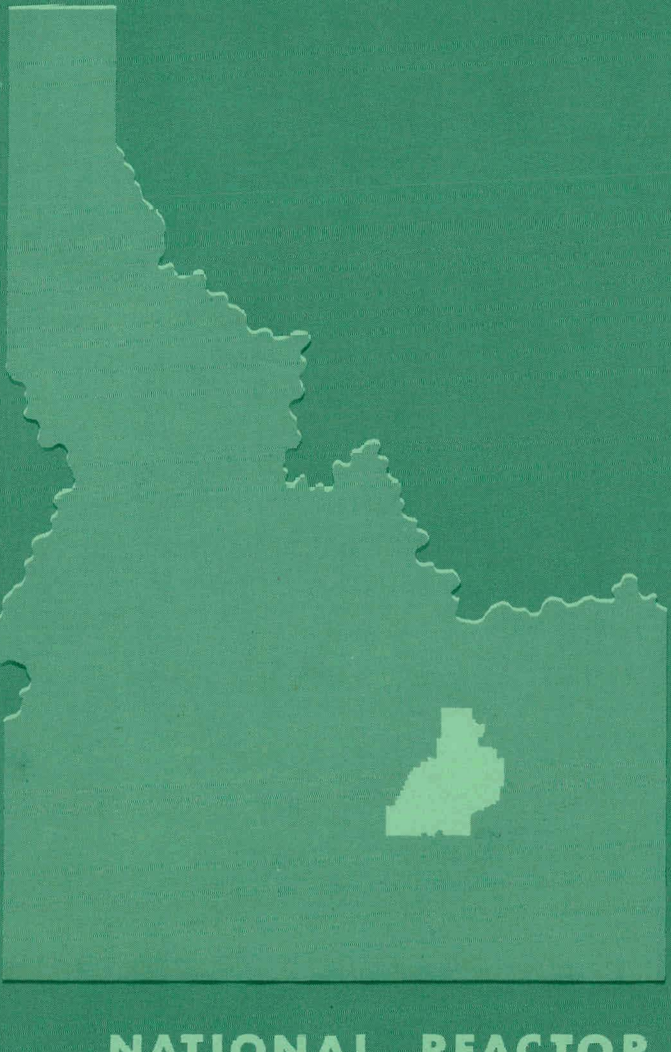
ORGANIC COOLANT REACTOR PROGRAM
QUARTERLY REPORT
September 1 – December 31, 1960



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ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

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Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

Printed in USA

IDO-16675
AEC Research and Development Report
Reactor Technology
TID-4500 (16th Ed.)
Issued: March 28, 1961

ORGANIC COOLANT REACTOR PROGRAM
QUARTERLY REPORT
September 1 - December 31, 1960

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ORGANIC COOLANT REACTOR PROGRAM

1960 QUARTER 4

September 1 - December 31, 1960

SUMMARY

In July 1960 Phillips undertook at the request of the AEC important programs in the development of organic reactor technology. One phase of this work is a broad basic study of the fundamentals of radiolytic breakdown of organic materials leading eventually into the selection of new more resistant coolants, stabilization against radiation damage, and reclamation of deteriorated coolants. This portion of the program is being conducted in the Company's research laboratories at Bartlesville, Oklahoma. The other phase of the work is concerned with the operation and experimental program of the EOCR now being constructed at the National Reactor Testing Station.

In the work on organic coolant technology, equipment has been readied and techniques developed. A 4 kw electron linear accelerator is being used for a source of high radiation dose rates (3×10^{10} r/hr) to screen organic samples. A calorimetric dosimeter and accompanying standard radiation cells have been fabricated. A dynamic loop to provide simulated reactor temperature, pressure and flow conditions in the radiation cell is in operation. A similar loop is provided to study pyrolytic decomposition. Other static radiation cells for use on the accelerator have been built to study the effect of additives on coolant stability. Two continuous flow high pressure catalytic hydrocracking units have been put into operation in a study of reclamation of OMRE high boilers.

In the study of fouling of heat transfer surfaces, irradiation of terphenyl samples containing iron particles gave indications of catalyzed polymer and film formation. Pyrolytic decomposition of Santowax on a hot filament was largely of the ortho- and meta-terphenyls forming high boilers in the quinquephenyl range. A group of typical aromatic heavy oils have been assembled from petroleum refineries to be tested as suitable coolants. Some sixty possible radiation stabilizers against radiation damage have been selected for testing. The synthesis of selected isomers of tetra-, quinque- and hexaphenyls has been started.

In connection with the EOCR, liaison assistance during construction has been provided. A mechanical test facility has been erected to test prototypes of the control rods and their drives which are being designed for the EOCR. It is expected to be in operation in March 1961. This facility will be valuable throughout the operation of the EOCR to proof-test hydraulically and mechanically standard and new fuel elements and control rods before insertion. Pre-operational tests, startup

manuals, and operating procedures are being developed. Material is being assembled and calculations are underway for a final Hazards Summary Report which must be submitted 90 days before startup. Conceptual designs of an Organic Technology Loop and a Fuel Technology Loop for the EOCR have been submitted. Detailed design of the former is underway. Development of in-pile experimental components has been started.

ORGANIC COOLANT REACTOR PROGRAM

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1. INTRODUCTION

J. R. Huffman

The organic cooled reactor is generally conceded to offer one of the more promising avenues to economic nuclear power. This conclusion was reached in the Commission's Civilian Power Reactor Program [1] review conducted last year. The Organic Moderator Reactor Experiment (OMRE) at the National Reactor Testing Station has, within its rather limited experimental capacity, demonstrated that the concept is technically feasible. However, much remains to be done in the area of research and development on the coolant, moderator, and fuel elements before it can be determined with certainty whether the economic potential believed to be inherent in the organic reactor concept can be realized in practice. Following the recommendations in the report [1], the Commission has embarked on an accelerated program in research, development, and engineering to exploit the potential of this power reactor concept. An important part of this program is the provision for the Experimental Organic Cooled Reactor (EOCR). The purpose of this reactor is to provide an experimental tool for the testing of components and coolants for advancing organic reactor technology. At the request of the Commission, a conceptual design was submitted by Phillips on December 1, 1959 [2]. Early in 1960 final design was initiated by The Fluor Corporation Ltd. Construction was started by C F Braun & Co. in May, 1960, and is progressing at this time.

In July, 1960, Phillips was designated as operator of the EOCR and instructed to staff for the job, provide engineering liaison during construction, set up operating procedures, and proceed with the conceptual design and fabrication of experimental loops for insertion in the reactor. Phillips was authorized at this time to design, construct, and operate a test rig to prove the reliability of the prototype control rod drives being designed for the EOCR.

A second major part of the Commission's program is research concerned with organic coolant technology. Efforts regarding this technology are underway at several laboratories. In July, 1960, the Commission requested Phillips to undertake such a program in its Bartlesville laboratories. The basic objectives of this work are the understanding of the mechanism of radiation damage, development of improved coolants, and the solution of some immediate practical problems of fouling, particulate formation, and reclamation of damaged coolants.

These various programs assigned to Phillips got underway in the late summer of 1960.

This is the first quarterly technical progress report. While it normally would cover the period from October 1 through December 31, 1960, information developed prior to this period is included.

2. ORGANIC COOLANT RESEARCH

J. C. Hillyer

To advance the technology of organic fluids as coolants and moderators for nuclear power reactors and so hasten the time when reactors based on this concept become economically competitive, the AEC is sponsoring an extensive research program in this area. Phillips Petroleum Company Research Division in Bartlesville is participating in this program. The purposes in this specific assignment are to bring to bear on the technological problems a team with a wide variety of backgrounds in organic, physical and radiation chemistry, to arrive at tentative solutions to the problems soon enough so that experiments confirming them can be designed and carried out in the EOCR, presently under construction.

The major objectives of the work are twofold. The first is that of developing improved or new coolants primarily through a basic study of the fundamental mechanism of radiolytic degradation of organic materials. This long range objective is supplemented with that of a solution of some of the immediate practical problems related especially to the present terphenyl coolants. This includes fouling of heat transfer surfaces, stabilization against radiation damage, and reclamation of damaged coolants.

The study of the deposition of films and their prevention includes the chemistry of organic precursors of film, the role of particles of inorganic nuclei reported to be found in films on fuel elements, the testing of hypotheses on the film forming process, and the evaluation of practical means for inhibition or prevention of film formation. A linear electron accelerator is available for ionizing radiation for tests.

The search for superior organic moderator-coolants consists of three lines of work: investigation of additives such as stabilizers to enable coolants to perform better; the purification, modification, and testing of commercial organic materials as candidate coolants; and the synthesis and testing of organic compounds with structures intended to confer resistance to radiation and temperature.

Reclamation of coolants from the high boiling polymers is initially being studied by catalytic processes designed to break down the residue into smaller, usable polyphenyl fragments. Separation of usable fractions, either directly from the tar or from catalytic processing, will employ solvent extraction techniques as required.

2.1 Radiolytic Experiments (P. S. Hudson, H. R. Anderson, Jr., H. W. Parker, R. A. Mengelkamp, P. W. Solomon, A. J. Moffat)

Most radiolytic experiments conducted during this quarterly period were directed toward film formation. Incidental, but not subordinate to this work, was the study of compositional changes in the coolant during radiation. Particular attention was devoted to the identification of high boilers which formed. Isolation of the major high boiler components will furnish a key to the mechanism of radiolytic breakdown. Knowledge of the radiolytic mechanism should lead to coolants with improved stability.

One problem encountered in the use of polyphenyl coolants in atomic power reactors is film formation. Film formation on the fuel elements causes lower heat transfer coefficients [3]. Ultimately, poor heat transfer leads to carbonization and possible burn-out. The formation of films appears to involve a complex combination of chemical, radiolytic, hydraulic, and thermal factors. To understand and control film formation, each factor must be evaluated and placed in its proper perspective. Less tangible aspects of the problem may be stated as three specific goals:

(1) Develop experimental techniques which will isolate and study the significant variables in film formation.

(2) Explore various hypotheses of film formation with the above experimental techniques.

(3) Propose and test new means of preventing film formation.

A linear electron accelerator (Linac) is available at Phillips Research Center, Bartlesville, as a source of ionizing radiation. This apparatus was built by Applied Radiation Corporation. In it (Fig. 1) electrons are generated at the top and pulse-accelerated down a traveling-wave, disc-loaded, wave guide. The manufacturers represent the maximum power to be 4 kw at 6 Mev. This corresponds to an average maximum dose rate of 3×10^{10} r/hr.

One of the advantages of this Linac for the present work is that useful dosage can be obtained in a very short time and the effects of pyrolysis can be minimized. The high capacity enables several samples to be treated in a day, and allows results to be quickly obtained. The Linac introduces other problems, however. The beam consists of electrons having a spread of energies. This prevents the use of electric current flowing from a target to measure dose rate. The beam varies in power unless carefully controlled. The beam diverges strongly on leaving the Linac window (Fig. 2) and wanders in a seemingly random manner. Some means is needed to continually monitor the dosage rate received by a sample under the Linac.

Accelerated radiolytic damage to various organic coolants with intense electron irradiation posed a problem in dosimetry early in the study. Many of the established dosimeters were ruled out because the contemplated irradiations required high temperatures and excessive dosages. In addition, the operating characteristics of the Linac are such that it produces a pulsed beam which varies in space and time. An *in situ* calorimeter has been proposed to monitor the Linac and to

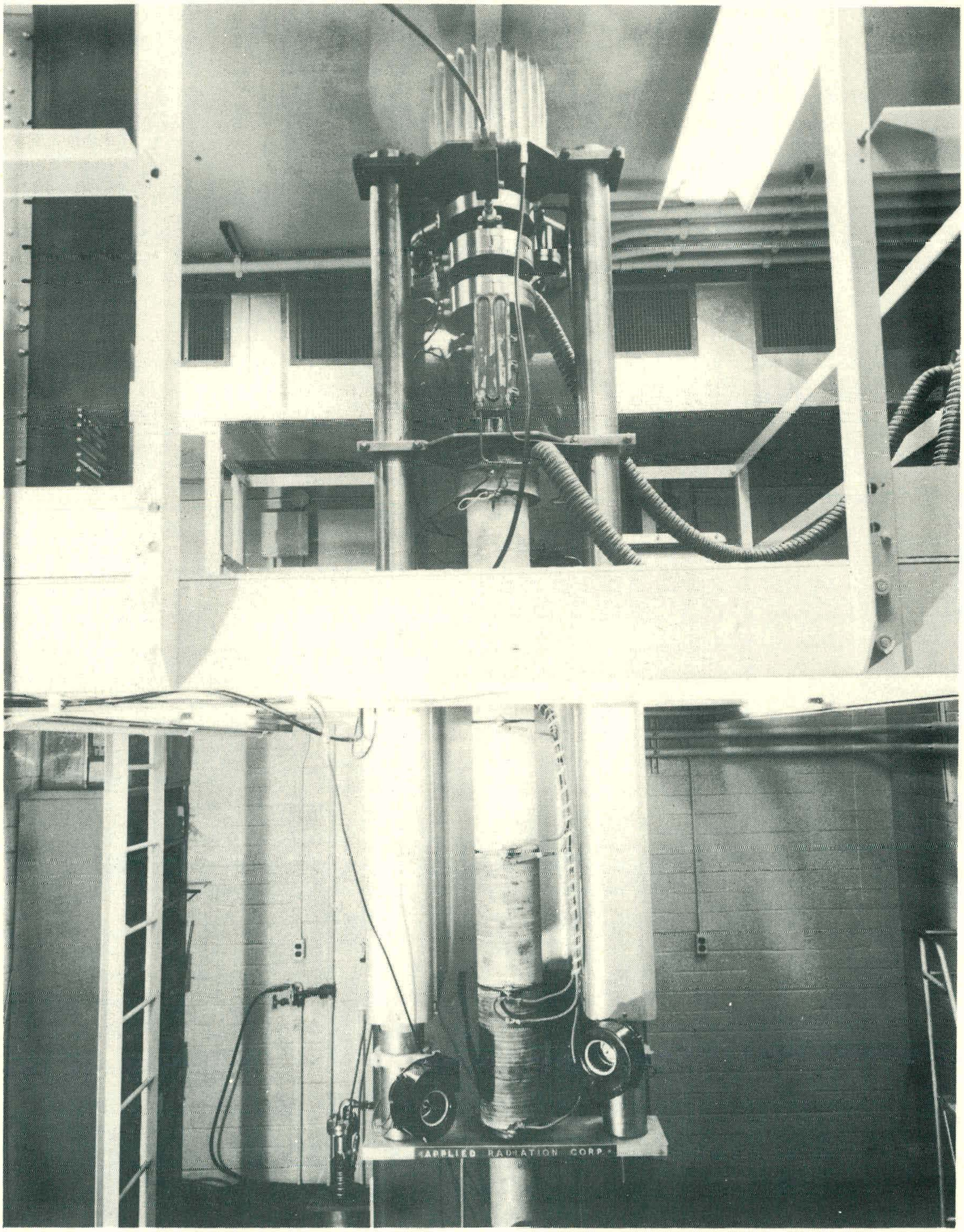


Fig. 1. Linac.

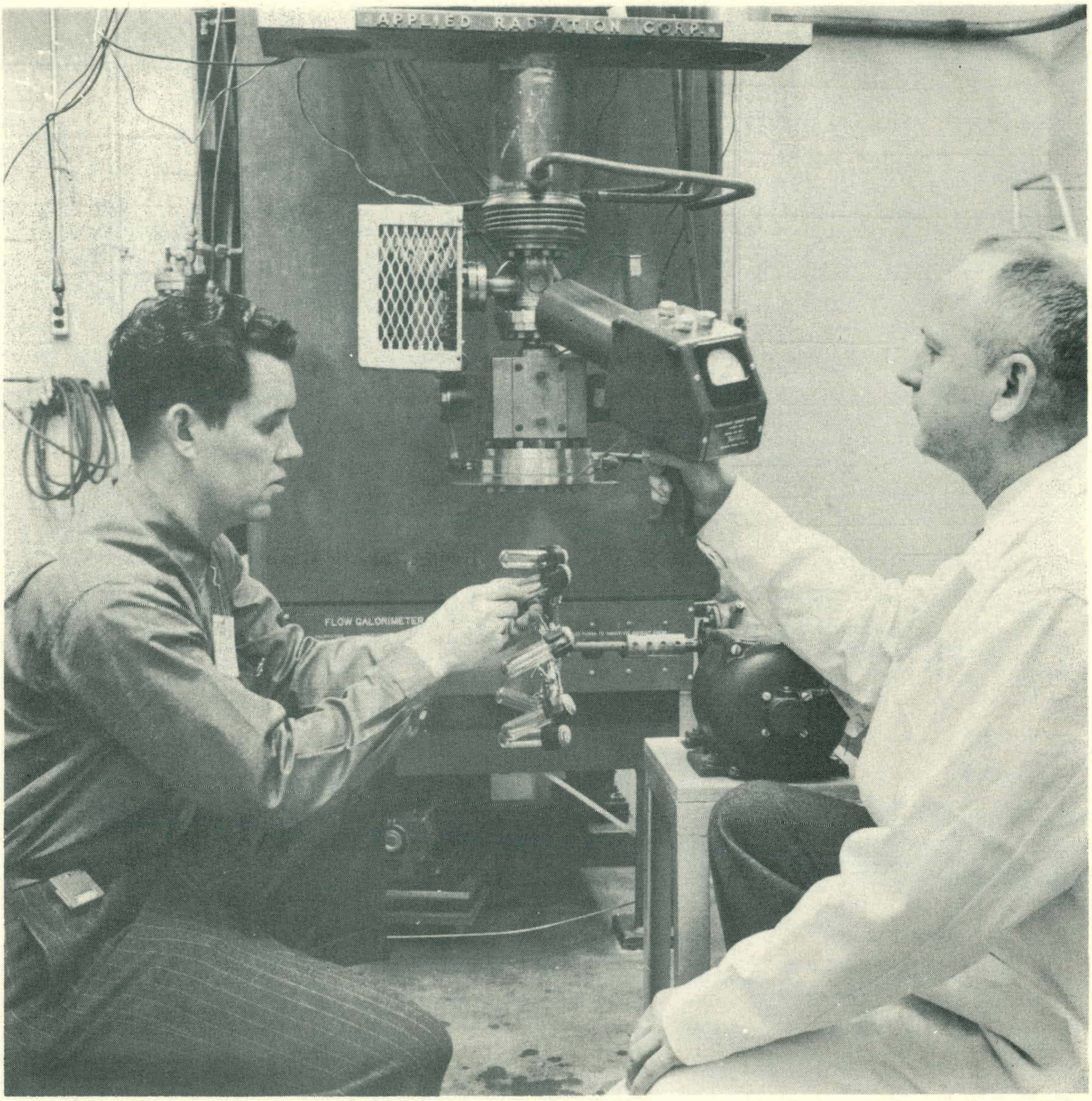


Fig. 2. Linac window.

measure radiation doses received by organic coolants in a special irradiation cell.

Fig. 3 and 4 depict equipment which has been designed and is now being constructed for irradiation of organic coolants under the Linac. The beam has an elliptical shape which diverges very rapidly with distance. Since dosage is the energy absorbed by a system, it is desirable to measure this quantity. A calorimeter is capable of measuring the power, and hence the dose rate delivered by the machine. It is only possible to get reliable dosage values if the beam is collimated, periodically sampled, and completely absorbed.

The calorimeter assembly (Fig. 4) features a collimator beam sampler and calorimeter. The collimator is water cooled to take care of

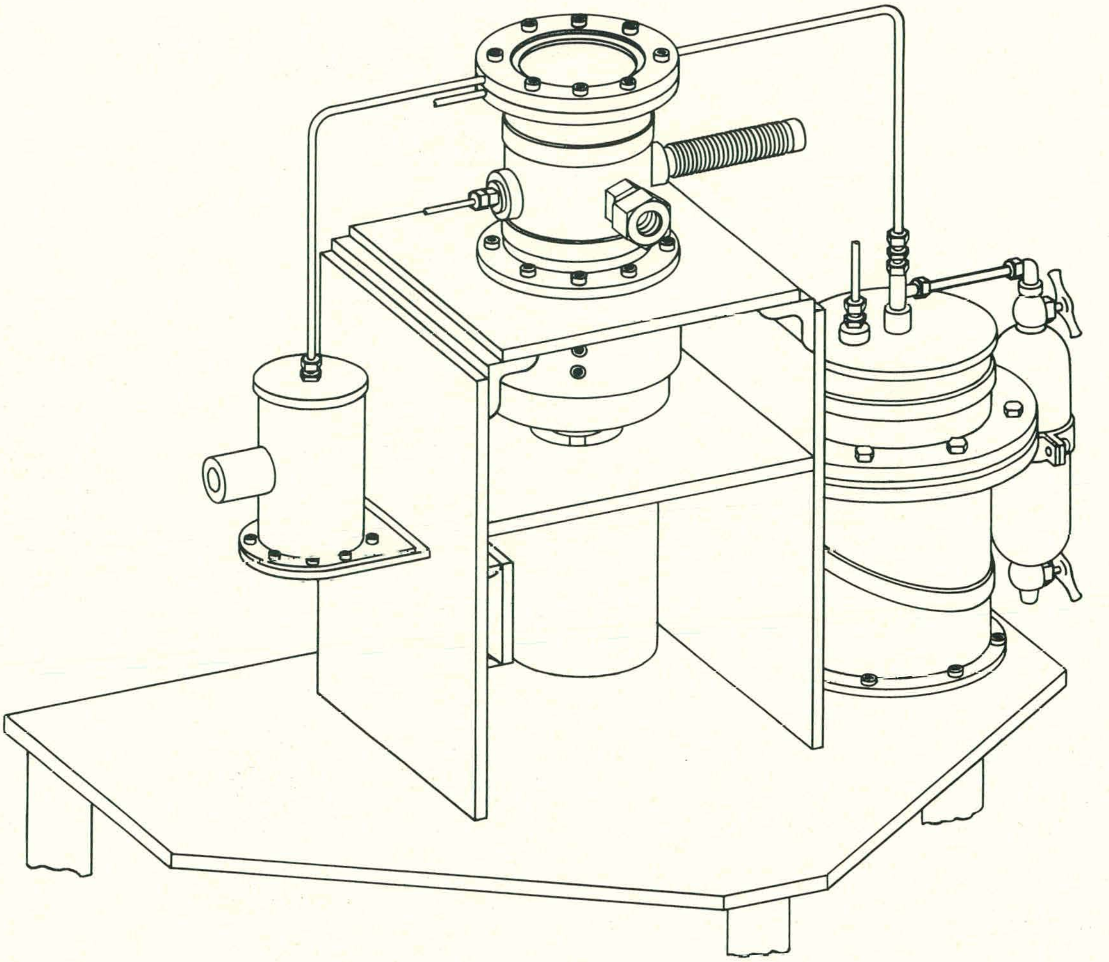


Fig. 3. Irradiation cell for use with calorimeter.

beam spill-over. The beam sampler has been designed to absorb, periodically, most of the electrons which emerge from the collimator (some are lost in the window of the sampler chamber). Heat generated in the beam sampler is then transferred by circulating water to a reservoir in the calorimeter. Heat losses are minimized by having the sampler oscillate in an evacuated chamber. A controlled flow of water is then used to dissipate the heat transferred to the reservoir. Resistance thermometers are used to monitor the inlet and outlet temperatures of the flow calorimeter. Any other form of heat dissipation out of the calorimeter is minimized with an adiabatic shield which is designed to follow the temperature rise of the reservoir.

This _in situ_ calorimeter is designed to sample the beam from 1 to 10% of the time. The fraction of the beam that is not sampled will be absorbed completely by the organic medium. Calibration of this calorimeter will be carried out by replacing the organic medium with a calibrated flow calorimeter. Comparison of concurrent responses of the two calorimeters will provide a basis for obtaining dosage received by an organic medium.

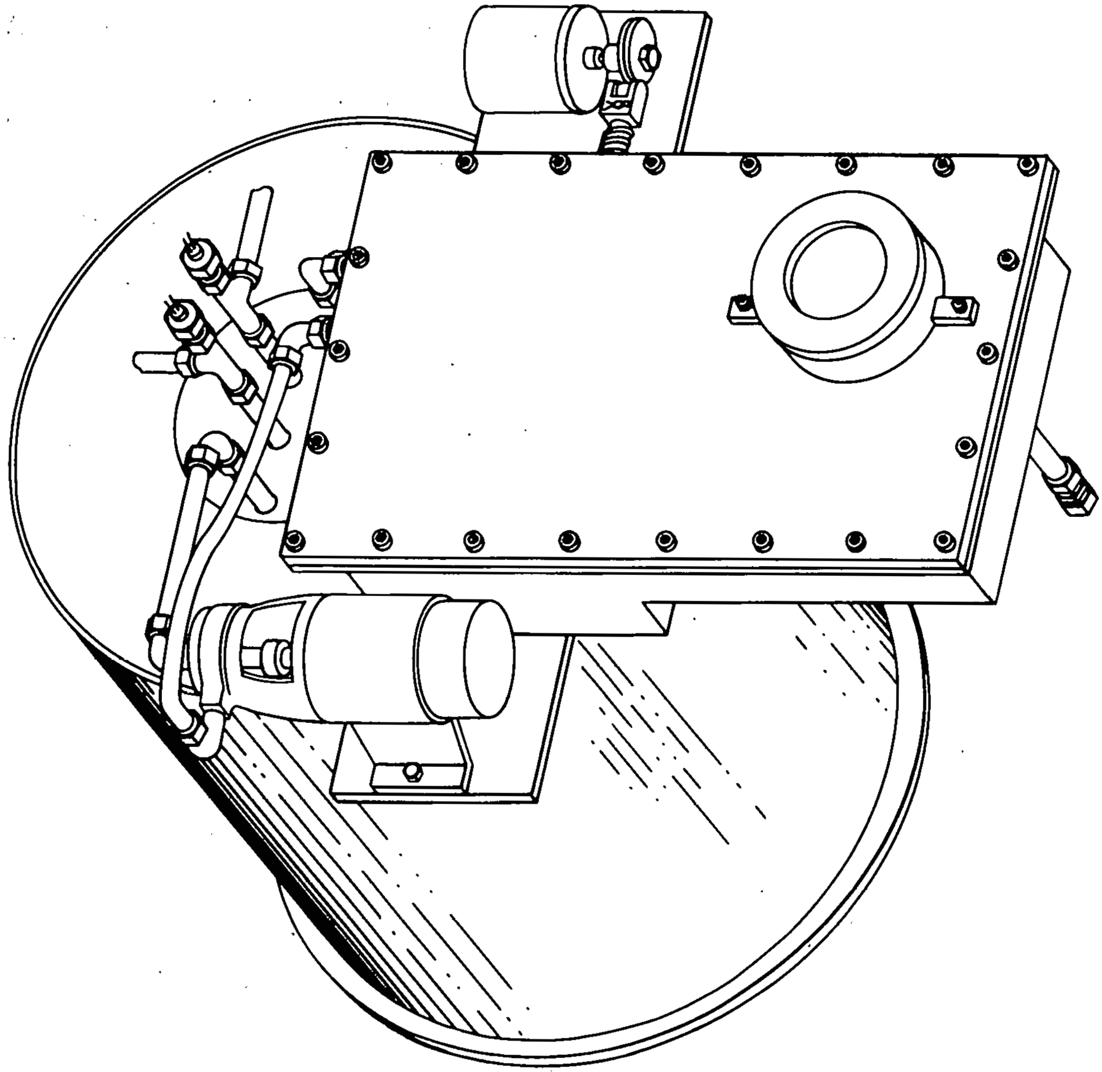


Fig. 4. Calorimeter.

The irradiation cell (Fig. 3) has been designed so that the organic medium absorbs all of the collimated electron beam. The cell features temperature control, internal stirring, and sampling devices. Such cell design will permit refined experiments to follow radiation damage to organic coolants. It will be possible to determine damage as a function of temperature, dosage, and dose rate. Such information will be useful in determining the chemical kinetics of coolant damage.

Circulating Loops In order to evaluate variables affecting the formation of fouling films on fuel elements of organic cooled reactor systems, two circulating loops have been designed. The first circulating loop comprises a system which is designed for electron irradiations, while the second circulating loop is designed for thermal exposures and heat transfer studies (Fig. 5 and 6).

The electron irradiation loop consists of a stainless steel cell which encloses a rectangular channel 8.250 in. long with a cross section

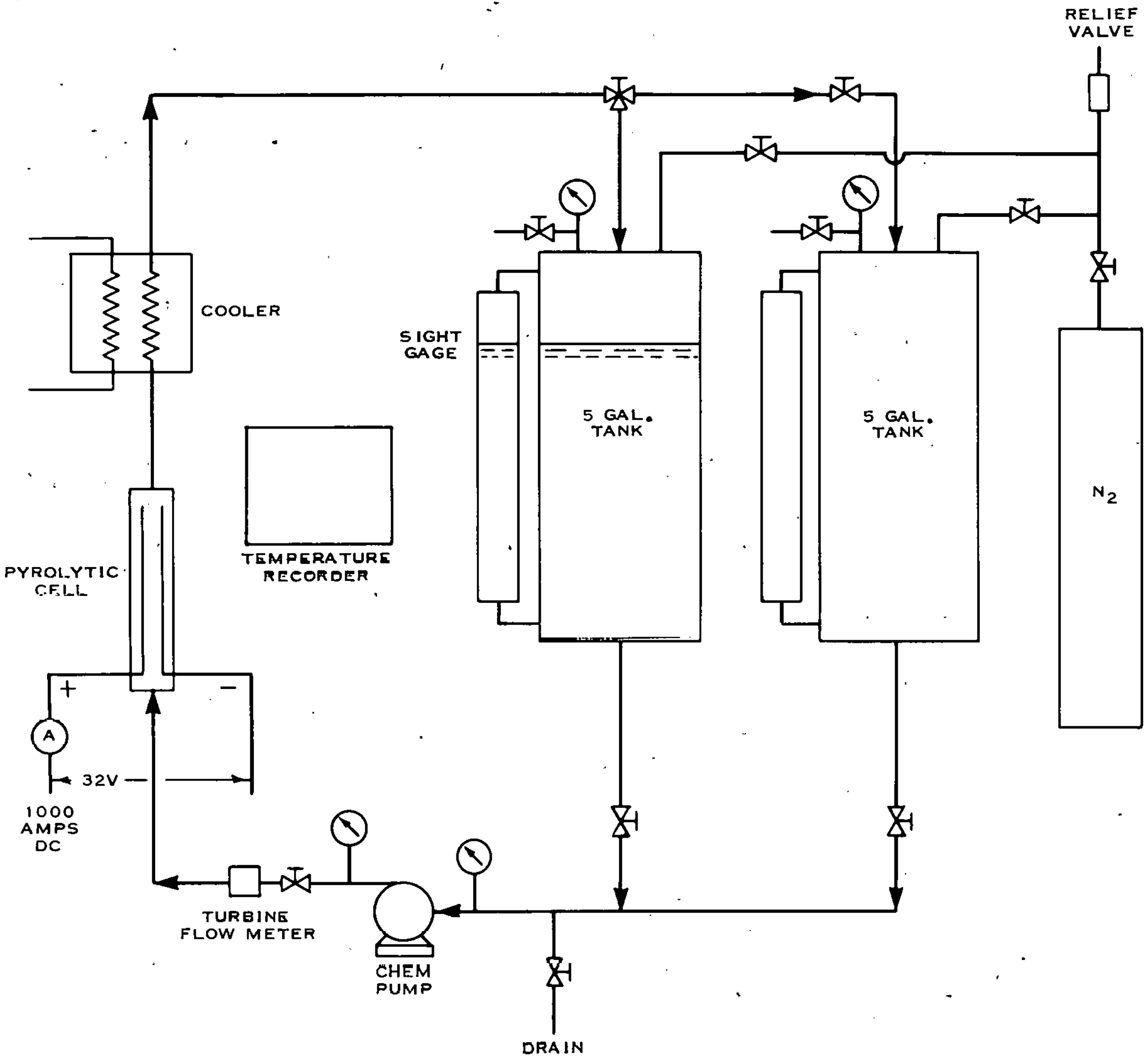


Fig. 5. Pyrolytic flow loop.

of 2.750 x 0.134 in. This simulates the geometry of a single OMRE coolant channel. An electron irradiation stainless steel window 0.780 in. in diam and 0.020 in. thick is located centrally in one of the wide faces of the channel. Opposite this window a stainless steel plate 1.125 in. thick is used to absorb the electrons which are not absorbed in the coolant flowing past the window. Other essential components are a canned rotor centrifugal pump, a turbine flow meter, two 5 gal tanks for calibration and reservoir purposes, a 4.5 kw heater, and valves. Thus, provisions are available to control essential OMRE parameters of coolant bulk temperature and surface temperature, system pressure, linear velocity, and Reynolds number. It is possible to vary these parameters over desired ranges. Electrical resistance heaters are used to trace heat the system (flow diagram in Fig. 6).

Initial shakedown tests have been conducted on the electron irradiation circulation loop with Santowax OM. This included one test under

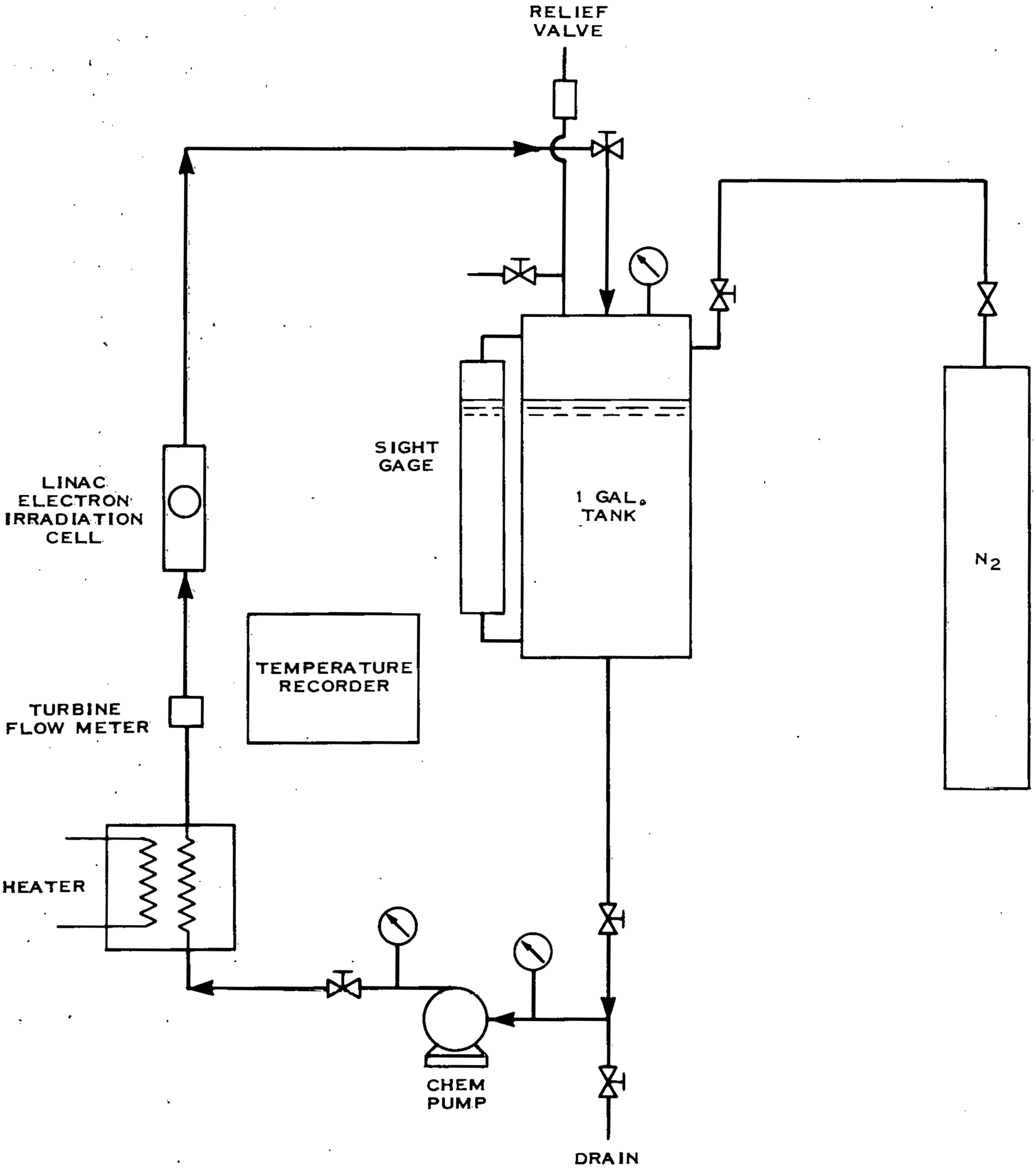


Fig. 6. Electron irradiation flow loop.

the Linac electron linear accelerator under the following conditions: coolant velocities up to 12 ft/sec; system pressure, 81 psia max.; bulk fluid temp, 630°F max.; and test time, 10 hr. Four gallons of coolant were charged to the loop system. Dose rates were not calculated due to temporary erratic Linac operation. Maximum electron beam power at the cell was estimated to be only 700 w max. No significant fouling was observed on the cell window.

Overall, the pumping loop performed satisfactorily with several minor exceptions. First, the threaded pipe joints tended to leak. This is being remedied by welding all threaded joints and using flanges where loop components must be installed and removed from the system. Secondly, the electron window was noted to be too small to accommodate the full electron beam. This was corrected by enlarging the window diameter to 2.0 in. Finally, the system reservoir was changed from a 5 gal. tank to a 1 gal. tank. This will greatly reduce the coolant charge and increase overall irradiation dose rate. It appears that the electron loop design is basically sound and should function satisfactorily.

Formation of Particulate Nuclei (Kernels) Film formed on OMRE fuel elements was reported [4] to be agglomerates of particles consisting of iron carbide nuclei surrounded by organic material (gel). The chemical composition of the film nuclei closely resembles that of the particulate matter suspended in the coolant. The reported analysis of the particulate matter has shown an inorganic kernel of iron carbide, Fe_2C. The nuclei were presumably formed by the conversion of particles of ferric oxide contaminant in the coolant resulting from corrosion of steel piping. The following reaction sequence has been suggested: $Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow Fe_2C$. Several experiments were performed in order to verify this sequence.

One-half gram of ferric oxide (red) was dispersed in 10 g of Santowax R, placed in a 50 ml bomb and heated 22 hr at 500°F. No change in the ferric oxide was observed. The experiment was repeated in the presence of hydrogen (5 psig). In this case, black magnetite, Fe_3O_4, was recovered and identified by x-ray analysis. The reduction of ferric oxide to magnetite also has been observed during electron irradiation of Santowax R with suspended ferric oxide.

Similar experiments in the bomb were performed with 0.5 g magnetite and 20 g of Santowax R at 700°F for 24 hr under an atmosphere of hydrogen (50 psig) and methane (15 psig). X-ray analysis showed ~ 10% alpha-iron had formed. Again, during the irradiation of Santowax R with magnetite, iron was formed. The reduction of magnetite to free iron may occur prior to iron carbide (Hägg). Iron carbide has been prepared from iron metal and butane at 500°F [5].

Heating Santowax R with alpha-iron and methane (50 psig) for 18 hr at 650°F did not produce the carbide. However, methane is quite stable thermally. A run with 0.02 g of iron powder suspended in 10 g of Santowax R with butane (30 psig) for 48 hr at 500°F did not yield iron carbide. Evidently, under these conditions, iron carbide has not had sufficient time to form.

Conclusions drawn from these experiments support the hypothesis that inorganic nuclei in the particulate matter arise from ferric oxide. The reduction of ferric oxide to magnetite occurs quite easily. However, complete reduction to free iron requires either a longer time or more drastic conditions. Failure to detect iron carbide may indicate that free iron may be a precursor. Thus, the sequence of reactions may be: $Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow Fe \longrightarrow Fe_2C$.

Future work will be directed toward the formation of iron carbide. The carbide may form after a film has been deposited on an inorganic precursor.

Particulate Deposition by Beta Current The role of beta current in film formation is important from two aspects. Atomics International has ascribed a role in the fouling of OMRE fuel elements to beta current [4]. Direct experimental evaluation of this concept would be of considerable value. Even if beta current were demonstrated not to be a major cause of film formation in the OMRE, beta current problems must again be considered in regard to the intense electron beam from the Linac, which is being employed for radiation tests.

To examine the role of beta current in particulate deposition, a series of "U" tubes (Fig. 7) have been irradiated under the Linac. Identical electrodes were placed in each leg of the "U" except that one electrode was insulated and the other grounded. The Pyrex "U" was 12 cm high, 21 cm wide and 18 mm i.d. The electrodes were 10 mil 304 stainless steel, 1.8 cm wide and 5 cm long. The liquid used in the "U" tube was the liquid phase drawn from Santowax OM at room temperature. In two experiments this liquid was contaminated with particulate iron by intensely contacting it with water, air, and iron filings for 44 hr at room temperature. This procedure had suspended ~ 200 ppm of iron so well that it settled only very slowly in 24 hr.

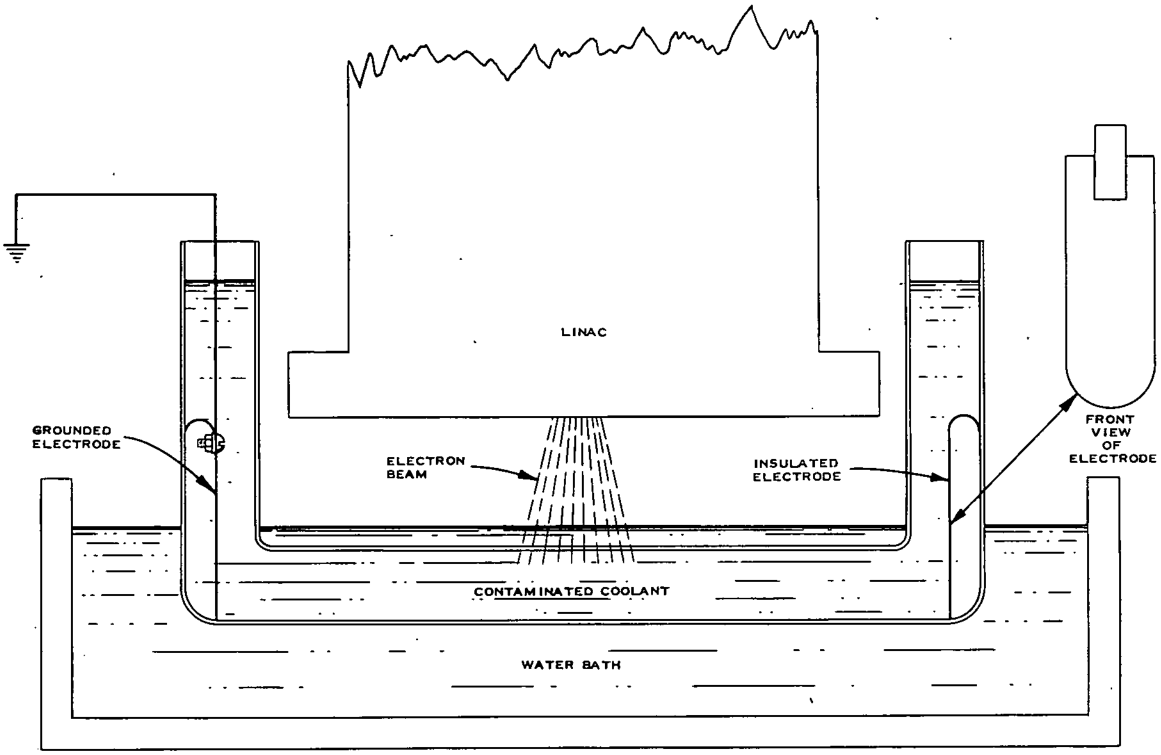


Fig. 7. "U" tube irradiation apparatus.

If beta current aided in the deposition of particulate matter from organic liquids, it would be expected that more particulates would be found attached to the grounded electrode than the insulated one after irradiation. Table 1 gives the results of three experiments.

Table 1

MATERIAL DEPOSITED ON GROUNDED AND INSULATED ELECTRODES DURING ELECTRON IRRADIATION

Experiment No.	Liquid Material	Wt Increase, mg Grounded Electrode	Wt Increase, mg Insulated Electrode	Irradiation Time, hr	Distance Below Linac Flange, in.
1	**	8.4	2.7	2	2
2	**	6.4	5.5	2	4.5
3	*	0.5	0.2	2	2

* The liquid employed in this test was the liquid phase drawn from a sample of Santowax OM at room temp.

** Same as above plus ~ 200 ppm iron containing particulate matter.

Experiment 1 gives a clear demonstration of preferential deposition of particulate matter on the grounded electrode, 8.4 mg vs 2.7 mg on the insulated one. Much of the particulate deposit was near the bottom of the grounded electrode facing the base of the "U" tube. In contrast the deposit on the insulated electrode was spread over a larger portion of the electrode including the back side. Also, the deposit on the grounded electrode appeared more adherent. X-ray diffraction analysis of the deposit reported the presence of magnetite (Fe_3O_4).

Experiment 2 was much less conclusive due to two factors: it was impossible to be as near to the Linac due to mechanical difficulties, and the Linac was frequently stopped to observe the rate of particulate deposition on the electrodes. It was noted that the particulate matter began clearing from the liquid after only 20 sec at 1/2 power from the Linac, and the liquid was completely clear after 19 min.

The third experiment was a control with no intentional iron contamination. Due to the small weight of film deposited, the results from this experiment may not be significant. No reasonable estimate could be made of the electron dose received by the organic liquid due to the complex geometry of the system. Temperatures measured back of the grounded electrode varied from 200-300°F. However, high temperature gradients existed due to the intense local heating by the electron beam.

In addition to the quantities of material deposited on the electrodes several qualitative observations were made. It was noted that the glass "U" tube adjacent to the grounded electrode had very little particulate matter on it. In contrast, the glass adjacent to the insulated electrode received a deposit of film. This indicates that the grounded electrode was acting to protect adjacent surfaces from particulate deposition. Preferential deposition of particulate material on the portion of the glass tube not cooled by the water was also noted.

In summary, a series of qualitative experiments has demonstrated that beta current appears to aid deposition of particulates on a grounded surface. Drafting is now being done on more sophisticated equipment to study beta current effects. This will be a flowing system in which electrodes may be placed either under the electron beam or just downstream from the electron beam. It will be capable of operating at up to 600°F and 200 psig. Further beta current tests on simple static systems are also planned.

Formation of Particulate Matter During Irradiation In order to induce the formation of particulate matter and deposit a film, Santowax R was irradiated under the Linac electron beam. Two test conditions were used: (1) Santowax R was irradiated with stainless steel strips; and (2) with stainless steel strips contaminated with 200 ppm ferric oxide.

Twenty-milliliter glass tubes sealed with a crown cap were filled with 12.5 g of Santowax R. Each tube contained a stainless steel strip 3 x 0.5 x 0.005 in. Some tubes contained 200 ppm ferric oxide. The tubes were irradiated for various times under the electron beam. Temperature was 600°F due to radiation heating at 80% power. After the run, all samples were dissolved in benzene and filtered through a millipore filter (0.45 μ). Table 2 lists the irradiation conditions.

Examination of the steel strips showed no deposits occurred until irradiation time reached 100 min. Electron micrographs of all films

Table 2

IRRADIATION CONDITIONS

Test No.	Particulate Matter	Dose Time, min	Estimated Dose, 10^8r
1	200 ppm Fe_2O_3	20	1
2	200 ppm Fe_2O_3	100	7
3	200 ppm Fe_2O_3	200	13
4	200 ppm Fe_2O_3	240	15
5	None	20	1
6	None	100	7
7	None	200	13
8	None	240	15

formed on the steel strips in contact with uncontaminated liquid showed a black, non-characterizable material. However, when ferric oxide was present in the Santowax R, electron micrographs of the film from the strips showed a filament structure. This may be polymer according to the microscopist.

X-ray diffraction showed no iron species in the film samples formed from uncontaminated liquid. However, the liquid samples which contained ferric oxide originally formed film that contained metallic iron. No magnetite or iron carbides were detected. X-ray analysis also showed the presence of zinc oxide and sulfide. These materials came from the rubber gasket in the bottle caps. Aluminum foil was used in later experiments to avoid these contaminants. The reduction of the ferric oxide to free iron substantiates results obtained in a non-irradiated control run with Santowax R, ferric oxide, and hydrogen. The formation of iron carbide reported by Atomics International [3] was not found in the irradiation products.

After the particulates were removed from the irradiated Santowax R, it was analyzed by gas chromatography. The (approx.) quantitative results are shown in Table 3.

Table 3

GAS CHROMATOGRAPHIC ANALYSIS OF IRRADIATED SANTOWAX R

Run Time, min	Estimated Dose, 10^8r	wt% ϕ_2	o-ϕ_3	m-ϕ_3	p-ϕ_3	U-1[b]	Triphenylene	U-2	U-3	m,m-ϕ_4	m,p-ϕ_4	p,p-ϕ_4	HB[c]
Original Santowax R													
-	-	0.1	10	50	28	- 3	1	2	0.3	2	3	0.6	-
Irradiated Santowax R													
20	1	[a]	10	50	29	2	1	2	0.5	3	3	0.6	-
100	7	[a]	10	50	30	2	1	2	0.4	3	2	0.3	Trace
200	13	[a]	9	51	27	2	1	2	0.5	3	3	0.6	0.6
Irradiated Santowax R + 200 ppm Ferric Oxide													
20	1	[a]	10	52	28	2	1	2	0.4	3	2	0.3	-
200	13	[a]	9	48	30	2	1	2	0.6	3	3	0.6	0.7
240	15	[a]	6	49	33	2	1	2	0.5	3	2	0.4	0.9

[a] Not determined.

[b] Unknown peaks.

[c] High boiler > quaterphenyls.

Some trends are evident in the samples containing ferric oxide:

(1) As the dosage increased, the relative stability of the terphenyls was: para > meta > ortho. The same trend was noted in a pyrolytic run.

(2) As the dosage increased, high boilers above the quaterphenyl range increased. Again, these results are similar to those in a pyrolytic run.

2.2 Pyrolytic Experiments (P. S. Hudson, R. A. Mengelkamp, P. W. Solomon, H. W. Parker, H. R. Anderson, Jr., A. J. Moffat)

In addition to radiolytic damage, the pyrolysis of organic coolants should also be studied because of exposure to high temperatures in a nuclear power reactor. Several areas in which pyrolytic experiments will be conducted include:

(1) The role of pyrolysis in film formation.

(2) Thermal stability of previously irradiated coolant.

(3) Comparison of radiolytic damage and pyrolytic damage.

(4) Tests in a full-scale pyrolytic loop which closely approximates flow and heat transfer conditions in the reactor.

(5) Evaluation of new coolants which have better thermal stability so higher operating temperatures can be obtained.

With these objectives in mind, equipment has been designed and several exploratory pyrolyses have been made.

Pyrolysis of Santowax R Santowax R was pyrolyzed in order to compare thermal damage with radiolytic damage. Conditions were made severe to accelerate the damage. Also, it was hoped severe conditions would generate particulate matters.

A spiral wire heating element was inserted in a one-liter stainless steel bomb which was equipped with a thermocouple, pressure gauge, relief valve, and nitrogen purge line. The Santowax R was heated under a nitrogen atmosphere and vented occasionally to relieve the pressure build-up. The following tabulation gives the conditions of the run:

Wt of Santowax R	329 g
Bulk temp	730°F
Heating wire temp	2000°F (calc)
Wire specifications	24 gauge Chromel A
Wire resistance	1.6 ohm/ft
Reaction time	26 hr
Heat input	42 w-hr/g
Pressure	7.0 psig

A hard, black solid was deposited on the heating wire. It was scraped off and washed with benzene to remove the Santowax R. Electron micrographs of these particles showed no evidence of a metallic nucleus surrounded by polymeric film. Evidently, particulate matter had not formed. Elemental analysis of this material showed 96.6% carbon and 0.6% hydrogen. This material from the wire appears to be graphitic. The analyst reported a graphitic residue remained in the combustion boat.

The bulk portion of the pyrolyzed Santowax R was analyzed by infrared spectrometry, gas chromatography, and fractional distillation. Table 4 shows the chromatographic analysis of pyrolyzed and original Santowax R.

Table 4

CHROMATOGRAPHIC ANALYSIS OF SANTOWAX R

Component	Wt% Original	Wt% Pyrolyzed
Biphenyl*	0.1	0.8
o-Terphenyl*	10	7
m-Terphenyl*	50	46
p-Terphenyl*	28	28
Unknown peak 1	3	2
Triphenylene*	1	1
Unknown peak 2	2	2
Unknown peak 3	0.3	0.7
m-Quaterphenyl*	2	3
3,4'-Bisphenyl-biphenyl*	3	3
p,p-Quaterphenyl*	1	1
Quinquephenyls + Hexaphenyls	-	5

* Species identified by authentic samples, melting point, mol wt and fractional distillation.

Distillation of the pyrolyzed Santowax R was compared with the original material. "High boilers" are arbitrarily designated as that fraction boiling above 270°C at 30 mm. This cut-point eliminated all terphenyls. Table 5 shows the compositional change in the pyrolyzed Santowax R. It should be noted the original Santowax R contained 9.4% high boiler.

Table 5

COMPOSITIONAL CHANGE IN PYROLYZED SANTOWAX R

	Still Head Conditions		Wt%, Cumulative			
Fraction	Temp, °C	Press., mm	Original	Mol Wt	Pyrolyzed	Mol Wt
1	157-226	30	-		0.9	
2	226-236	30	11.0		12.3	
3	236-248	30	39.0		46.6	
4	248-255	30	77.4		73.3	
5	255-270	30	90.6	237	79.5	233
6	270-330	30	100.0	294	79.5	
7	330-350	30			88.0	279
8	240-260	0.5			93.6	314
9	260-350	0.5			93.6	
10	350-380	0.5			96.3	362
11	Residue				100.0	

Mol wt determined by benzene boiling point elevation.

Molecular weight determinations showed the Santowax R increased from 239 (terphenyl 230) to 246 during pyrolysis. The high boiler fraction of the pyrolyzed Santowax R had a calculated mol wt near 400 (quinquephenyl 382).

From the various data presented, the following generalizations can be made about the pyrolysis of Santowax R:

(1) About 1% biphenyl is formed.

(2) Degradation occurred mainly at the expense of the ortho and meta terphenyls.

(3) Most of the high boiler (distillable) was in the quinquephenyl range.

(4) About 6% was non-distillable. This fraction contained hexaphenyls and higher polyphenyls.

(5) The insoluble products which formed on the heating wire were mainly carbonaceous deposits.

Thermal Test Apparatus Fig. 8 is a sketch of an apparatus in which films have formed on a heated 1/8 in. o.d. stainless steel tube. This apparatus in under development as a means of testing small quantities

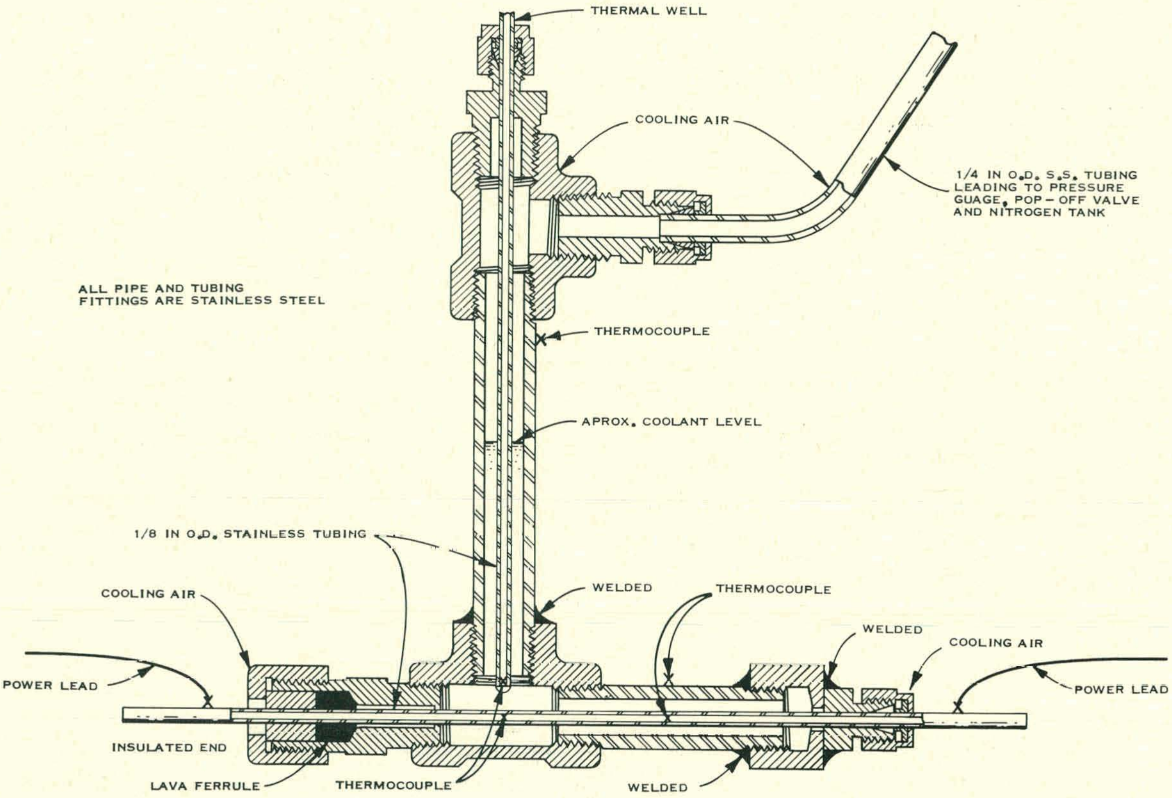


Fig. 8. Thermal film apparatus.

of coolant. It may be operated as shown in the figure to test particular coolants, or water and iron wire can be placed in the vertical pipe to continuously corrode and supply particulate matter to the coolant. The apparatus can be operated up to 1000°F and 400 psia pressure.

Another type of pyrolytic equipment is a modified thermal test bomb (Fig. 9). Originally, it was designed for jet fuel testing [6]. The bomb has an i.d. of $1\frac{1}{2}$ in. and the o.d. of the heater is 3/4 in. The heating element is only in the lower 7 in. of the bomb. This bomb will be used to evaluate various terphenyl mixtures. Also, it may be useful for some thermal film studies.

<u>Pyrolytic Circulating Loop</u> The electron irradiation loop has been described previously. A pyrolytic circulating loop has been designed (Fig. 5) and is very similar to the electron irradiation loop. One major difference is that a heat sink has been installed in the pyrolytic loop instead of an auxiliary heater. Also, the design features of the pyrolytic cell are obviously different. In the pyrolytic cell or test section, the coolant flows through a thin rectangular channel similar to the OMRE channels. Electrical heat is supplied by the wide faces of the channel. These faces are 2.750 in. wide, 7.0 in. long and 0.005 in. thick and constructed of AISI 304 stainless steel. The plates are insulated from a 1.125 in. thick cell housing with a zirconia coating 0.006 in. thick. Current up to 1000 amp at 32 v is available to provide heat fluxes of about 400,000 Btu/hr-sq ft (flow diagram in Fig. 5).

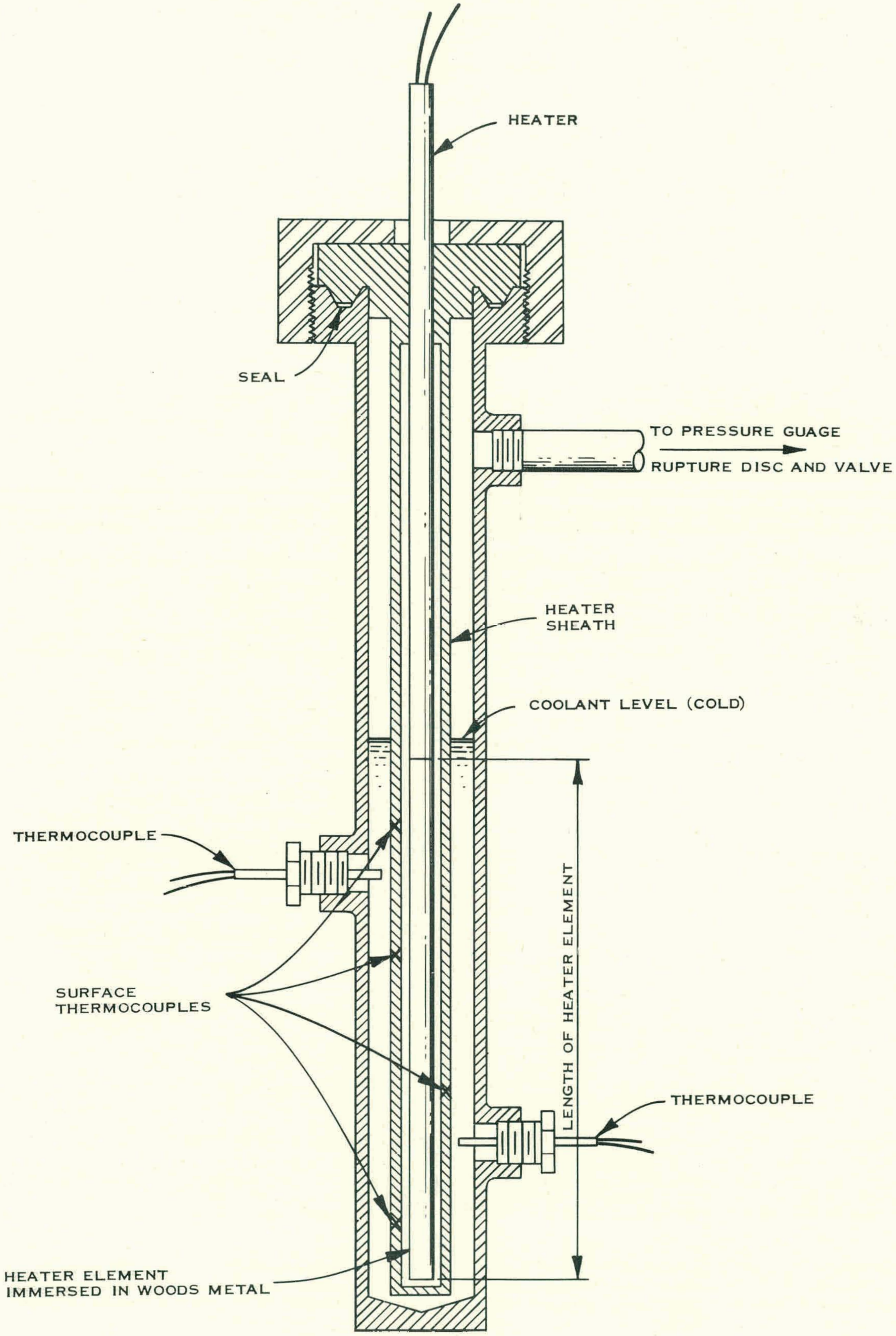


Fig. 9. Thermal test bomb.

Most components of the pyrolytic loop are on order or are on hand at the present time. With the exception of the pyrolytic cell all components are essentially similar to the proven electron irradiation loop and no serious technical difficulties are anticipated.

Because the pyrolytic loop will closely simulate the conditions found in the reactor, accurate data should be obtained concerning the pyrolytic stability of coolants. The effects of particulate matter, irradiated coolant, detergents, stabilizers, flow rates, and temperature will be studied in film formation.

2.3 Gas Chromatographic Separation of Polyphenyls (P. S. Hudson, A. J. Moffat)

The radiolysis of polyphenyls produces a large variety of high boiling compounds (commonly called "high boiler" or polymer). It has been reported that the high boiler may contain as many as 22 different compounds in the terphenyl, quaterphenyl, and quinquephenyl range [7]. One of the major problems encountered in doing a complete study of the effects of radiation upon polyphenyls is, therefore, the separation and identification of at least the principal polyphenyl products. Gas chromatography appears to be the most feasible means of separating this variety of polyphenyl products obtained from the radiolysis of any single polyphenyl. Identification of the more important chromatographic fractions is to be made.

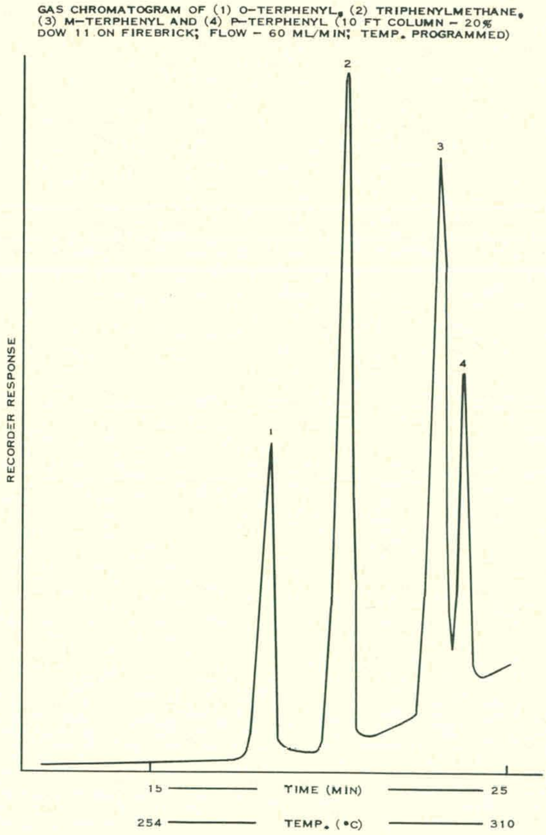


Fig. 10. Gas chromatogram.

An F and M Model 500 Programmed Temperature Gas Chromatograph is being used with various types of column packings. Stationary liquid phase and firebrick-salt mixtures have been used to separate polyphenyls ranging from biphenyl to m-octaphenyl.

A 10 ft column (Dow 11 silicone grease on firebrick) was found to be successful in the separation of a mixture of o-terphenyl, triphenylene, m-terphenyl, and p-terphenyl (Fig. 10). However, the thermal stability of this liquid phase column limits its use to temperatures below ~ 300°C.

Silicone rubber (20% on firebrick) was used to pack two columns (2 ft and 15 ft) which have an upper temperature limit of ~ 375°C. The 2 ft column was found to be effective in separating a mixture of biphenyl, o- and m-terphenyl, triphenylene, m-quaterphenyl, m-quinquephenyl, and m-hexaphenyl. However, the 2 ft column was not successful in resolving m- and p-terphenyl or m,m- and m,p-quaterphenyl (Fig. 11). The 15 ft silicone rubber column achieved adequate separation of m- and p-terphenyl in isothermal runs at 225°C (Fig. 12), but poor separation was obtained on programmed temperature runs.

A 20 ft fused salt column (lithium, sodium, and potassium nitrate) [8] was found to be reasonably successful in separating mixtures of o-, m-, and p-terphenyls. However, for high temperature runs (greater than 350-400°C) the nitrate column decomposed. The performance of the fused salt column at temperatures below the 150°C eutectic melting point indicated that it was not necessary for the salt mixture to be molten in order to obtain reasonable separations of low boiling mixtures near 100°C. It was decided to use a column packing of firebrick which had been impregnated with lithium chloride. This salt is stable at temperatures well above 500°C which is the limit of the F and M Model 500 Chromatograph. Lithium chloride is not molten in the temperature range to be used.

To prepare the packing material, a slurry of aqueous lithium chloride solution and firebrick was dried and then heated to ~ 740°C for 1 hr to fuse the salt on the support. The performance of the resultant 20% lithium chloride-firebrick mixture as a column packing material can be seen by comparing Fig. 11 with Fig. 13 and 14. Fig. 11 shows that the 2 ft silicone rubber column does not adequately separate meta- and para-terphenyl, unknowns (4) and (5), and m,m- and m,p-quaterphenyl. Even though the 5 ft, 20% lithium chloride column is operated ~ 100°C higher than the silicone rubber column, complete separations of m- and p-terphenyls, and m,m- and m,p-quaterphenyls were obtained in programmed temperature runs (Fig. 13).

GAS CHROMATOGRAM OF SANTOWAX R HIGH BOILING FRACTION: (1) M-TERPHENYL, (2) P-TERPHENYL, (3) TRIPHENYLENE, (4) AND (5) UNKNOWN, (6) M,M-QUATERPHENYL, AND (7) M,P-QUATERPHENYL (2FT COLUMN - 20% SILICONE RUBBER ON FIREBRICK; FLOW - 60 ML/MIN; TEMPERATURE PROGRAMMED)

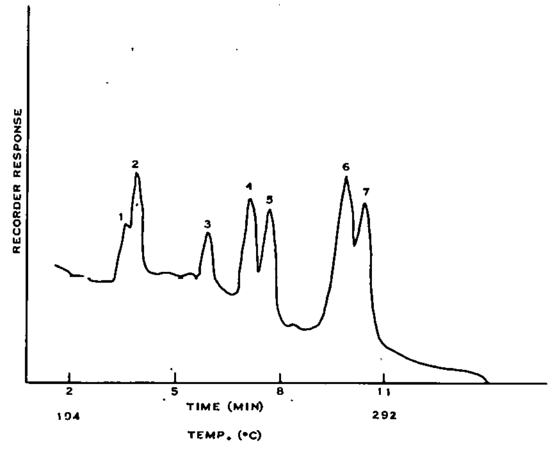


Fig. 11. Gas chromatogram.

GAS CHROMATOGRAM OF (1) O-TERPHENYL, (2) TRIPHENYLMETHANE, (3) M-TERPHENYL, (4) P-TERPHENYL (15 FT COLUMN - 20% SILICONE RUBBER ON FIREBRICK; FLOW RATE - 60 ML/MIN; TEMPERATURE - 225°C)

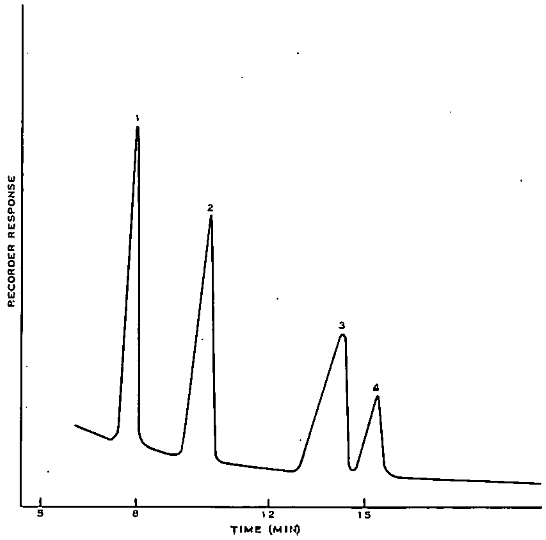


Fig. 12. Gas chromatogram.

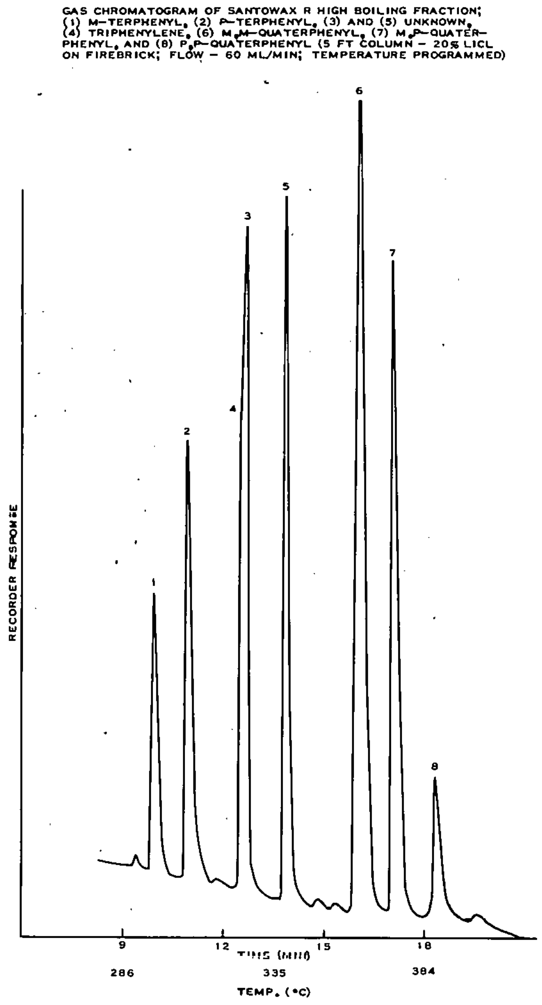

GAS CHROMATOGRAM OF SANTOWAX R HIGH BOILING FRACTION; (1) M-TERPHENYL, (2) P-TERPHENYL, (3) AND (5) UNKNOWN, (4) TRIPHENYLENE, (6) M,M-QUATERPHENYL, (7) M,P-QUATERPHENYL, AND (8) P,P-QUATERPHENYL (5 FT COLUMN – 20% LICL ON FIREBRICK; FLOW – 60 ML/MIN; TEMPERATURE PROGRAMMED)

Fig. 13. Gas chromatogram.

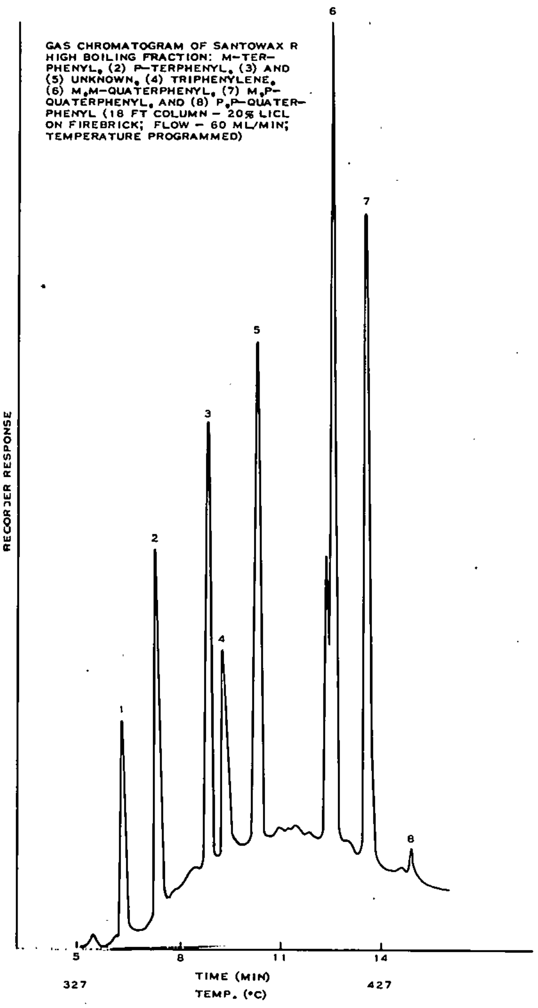

GAS CHROMATOGRAM OF SANTOWAX R HIGH BOILING FRACTION: M-TERPHENYL, (2) P-TERPHENYL, (3) AND (5) UNKNOWN, (4) TRIPHENYLENE, (6) M,M-QUATERPHENYL, (7) M,P-QUATERPHENYL, AND (8) P,P-QUATERPHENYL (18 FT COLUMN – 20% LICL ON FIREBRICK; FLOW – 60 ML/MIN; TEMPERATURE PROGRAMMED)

Fig. 14. Gas chromatogram.

An 18 ft lithium chloride-firebrick column was more effective than the 5 ft column in separating the various components of the Santowax R high boiling fraction (compare Fig. 13 and 14). However, the 5 ft lithium chloride column appeared to be more desirable because it can be operated at lower temperatures; the polyphenyls up to and including m-hexaphenyl and a few of the higher polyphenyls can be separated at temperatures below 425°C (Fig. 15).

Operating from 450 to 500°C (18 ft column) has resulted in the decomposition of m-hexaphenyl. This was evidenced by reduced peak area with increasing temperature. Even the differences noted in the peak tentatively identified as p,p-quaterphenyl (compare Fig. 13 and 14) may be due to thermal decomposition at the higher temperature (Fig. 14).

m-Octaphenyl has been successfully detected in isothermal runs at 450°C using a 5 ft lithium chloride column. The retention time was ~ 8 min (helium flow at 60 ml/min). However, it was noted that injection port temperatures greater than the 450 to 500°C were necessary to completely vaporize the m-octaphenyl sample. Also, very little is

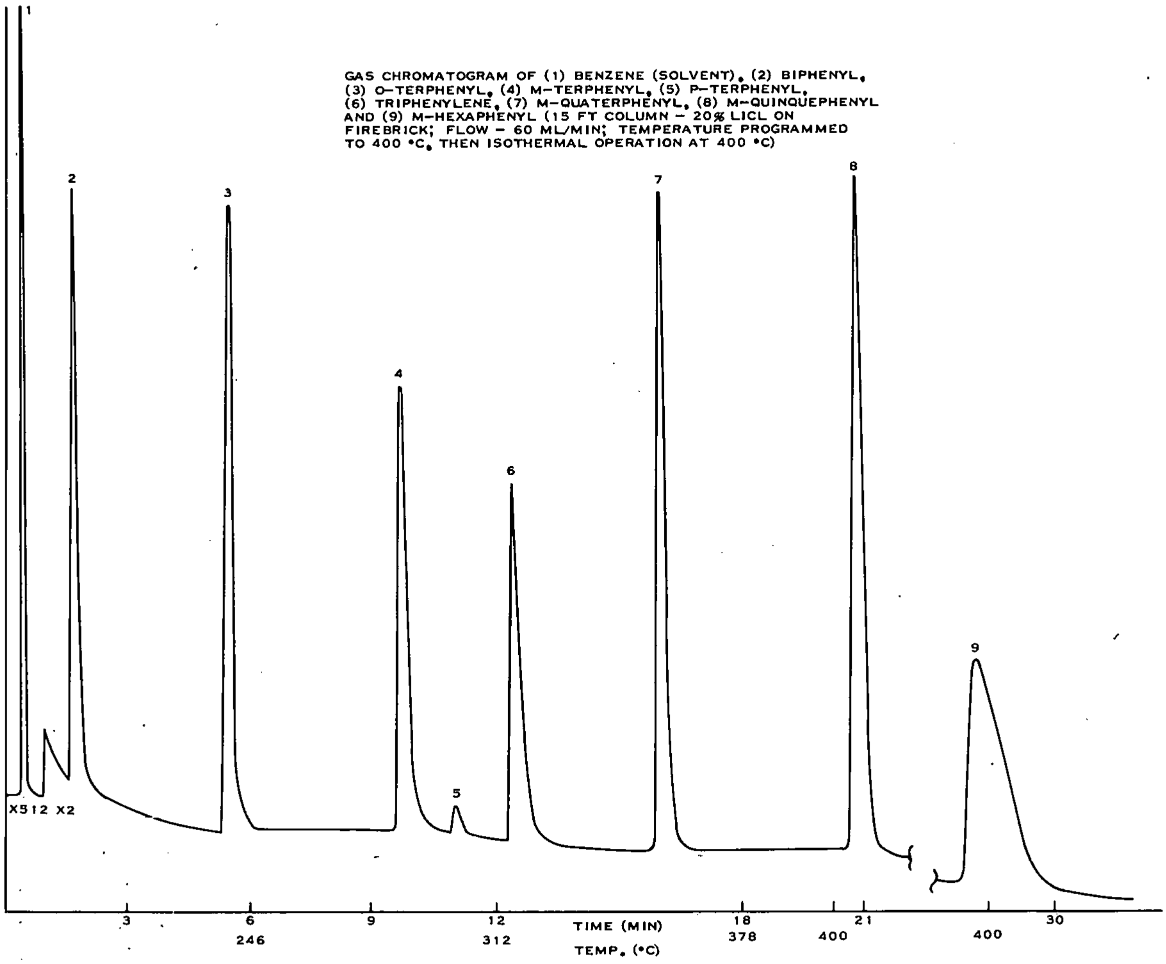


Fig. 15. Gas chromatogram.

known about the thermal stability of m-octaphenyl on the lithium chloride-firebrick column.

Isothermal runs on the lithium chloride column were successful in the complete separation of m,m-quaterphenyl and the unknown compound which appears as a shoulder on the m,m-quaterphenyl peak (Fig. 14).

A 15 ft lithium chloride-firebrick preparative column has been developed which will handle samples up to 500 µl. Good separations in programmed temperature runs with this column were comparable to those in the analytical column (Fig. 13).

Of all the columns examined to date for the gas chromatographic separation of polyphenyls and related compounds, the lithium chloride-firebrick column is superior. Some of the advantages of lithium chloride as the stationary phase are:

(1) Excellent resolution at high temperatures.

(2) Absence of bleeding which resulted in baseline stability. (Organic stationary phases normally bleed at high temperatures.)

(3) Longer column life due to the stability of the impregnating material.

(4) No upper temperature limit need be considered except that set by the thermal stability of the polyphenyls themselves.

(5) It has the capability of separating a wide variety of polyphenyl components up to and including m-octaphenyl.

2.4 Radiation Stabilizer Studies (R. B. Regier, H. A. Hartzfeld)

During the period covered by this first quarterly report, an experimental program on radiation stabilizers has been devised and all apparatus and materials needed for it have been prepared for use.

Before planning an experimental program, it was necessary to make a comprehensive survey of the literature pertinent to this subject. This survey showed that while considerable work has been done to determine the effect of ionizing radiation on organic moderator-coolants, comparatively little has been done in the way of attempting to improve the radiation stability of the best organic materials, the polyphenyls. West has reported results of work done by the California Research Corporation [9] in which the effect of seven different additives upon the stability of various polyphenyls was studied in in-pile irradiations at BNL. Five of the additives tested were found beneficial. These were dibenzyl selenide, and thianthrene, and to a lesser extent phenazine, phthalocyanine, and naphthalene. Gercke [10] of Atomics International has reported that in screening tests made on 94 individual organic additives by irradiations at elevated temperatures in the MTR Gamma Facility, four of the additives provided significant reduction in radiolytic damage. These were α-truxene, 1,6-diphenylhexatriene, thianthrene, and triphenylamine. Aromatic compounds have been shown to provide significant radiolytic protection to more easily damaged hydrocarbons, but studies of the protection of aromatic compounds themselves have been less fruitful. The problem of radiolytic protection has been discussed by Burton and Lipsky [11].

For the current work, Santowax OMP (Manufactured by Monsanto Chemical Company. Composition: lighter than o-terphenyl, 0.8%; o-terphenyl, 11.9%; m-terphenyl, 55.9%; p-terphenyl, 21.4%.) has been selected as the base material in which potential stabilizers will be tested. A 460 lb drum has been obtained, to insure an adequate supply of uniform composition. Apparatus for making irradiations under the Linac has been built and used successfully (Fig. 16). It consists of an assembly of four aluminum cells clamped to an aluminum block that is attached to a 10 rpm motor. Each cell, $7\frac{1}{2}$ in. long x 7/8 in. o.d. x 1/16 in. wall thickness, is closed by a Swagelok fitting and a needle valve. The

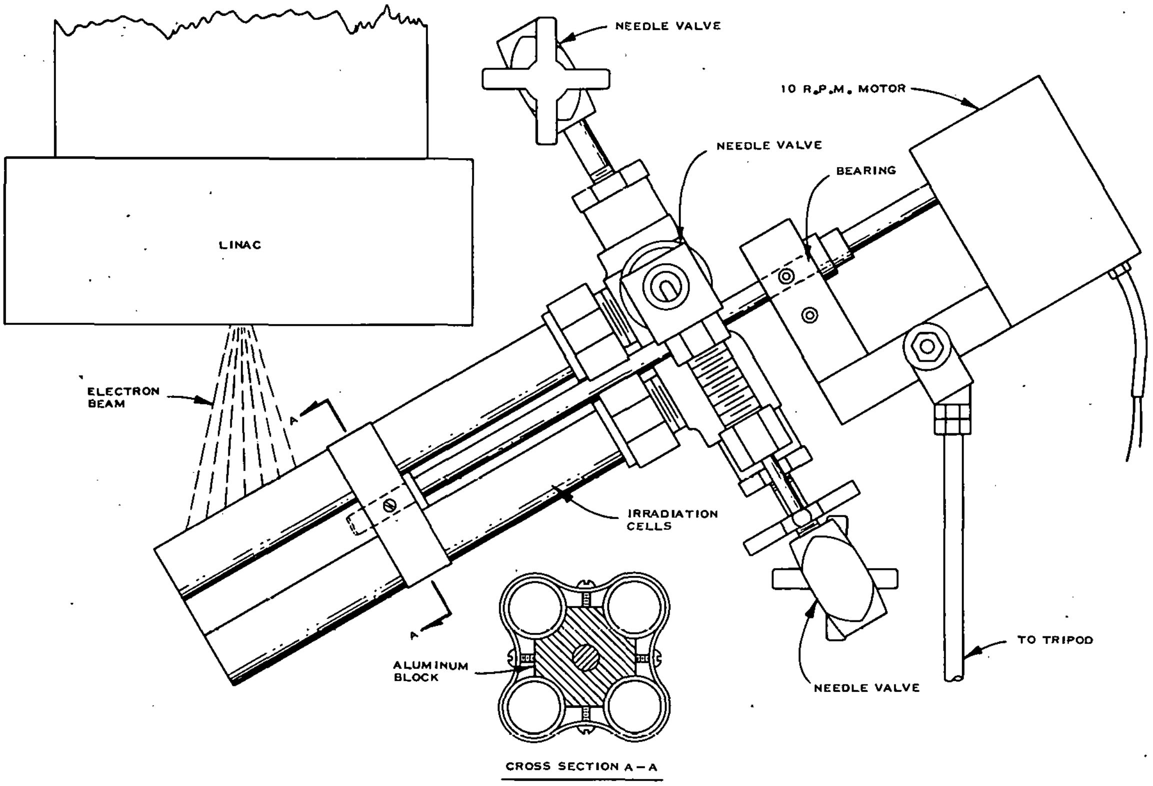


Fig. 16. Apparatus for radiation of stabilizers.

aluminum block promotes thermal equilibrium between the four samples that are irradiated simultaneously. In use, each cell is filled approximately one-third full, the sample is deaerated, and the cell is filled with argon. A stream of air directed against the upper ends of the rotating cells helps remove heat from the system during irradiation. Because of instability of the electron beam, both in space and in energy, this method of irradiation was selected rather than attempting to make absolute charge input measurements on single samples. One control sample of untreated Santowax OMP will be irradiated with three samples being tested; all will receive essentially identical radiation doses at nearly the same temperature. Estimates of absolute doses received will be made by referring the measured radiolytic damage to curves that have been prepared by workers at Atomics International and at the A.E.R.E. in Harwell.

The criteria that have been selected for measuring radiolytic damage are gas and polymer production and viscosity increase. The quantity of gas produced will be determined in a calibrated vacuum line, and its composition by mass spectrometry. Polymer will be measured using the procedure described by Bates et al [12], which consists of subliming the terphenyls and any more volatile material from the polymer at 0.1 mm Hg pressure at temperatures of 180-240°C. Viscosity will be measured in Cannon-Fenske viscometer pipets in a controlled temperature bath operated at 200°C. This temperature was selected in preference to temperatures that approximate reactor operating conditions because the rate of change of viscosity with polymer concentration is greater at lower temperatures, thus making the measurement more sensitive to changes in polymer production.

Approximately 60 compounds have been acquired for testing as radiation stabilizers. The selection of many of them was based on previous experimental work that had indicated their efficacy as radiolysis stabilizers, oxidation inhibitors, or free radical scavengers. Others were selected because of structural similarity to effective compounds or because of their high thermal stability. In the choice of candidate additives, consideration was given to their vapor pressures at the radiation temperature, high volatility being undesirable. Types of additives which will be investigated include (1) fused aromatic hydrocarbons such as fluorene, naphthacene, and pyrene; (2) heterocyclic compounds such as quinoxaline, dibenzofuran, and phenothiazine; (3) ultraviolet stabilizers such as 2-hydroxy-4-methoxybenzophenone; (4) miscellaneous organic compounds including phenyl selenide, azobenzene, and tetracyanoethylene; (5) selected inorganic substances including sulfur, graphite, and carbon black; and (6) metal-containing organic compounds such as ferrocene and metal acetylacetonates.

For initial screening tests, these materials will be irradiated singly at a concentration of 3 mole per cent.

It is anticipated that these compounds will be tested at the rate of about 12-15 per month.

2.5 Ideal Organic Moderator-Coolants (W. M. Hutchinson, R. C. Doss)

Synthesis of Reference Polyphenyls One of the objectives of the organic coolant program is to determine mechanisms by which terphenyls react under ionizing radiation. In the study of reaction mechanism, it is often necessary to determine the products formed by the reaction. The products from irradiation of a terphenyl are many. Numerous peaks have been observed in the quater-, quinque-, and hexaphenyl ranges of gas chromatograms of electron-irradiated m-terphenyl. Two types of reference compounds are needed for analysis by chromatography and identification by melting point and spectrometry:

(1) Those to show where in a chromatogram a molecular weight class begins and ends.

(2) Those to identify products by elution rate, physical properties, and cracking pattern in a mass spectrometer.

The first set of references is needed to determine to what degree overlapping between molecular weight classes occur in the best chromatographic separations. For first determinations only one or two low-boiling and high-boiling isomers in each molecular weight class (ϕ_4, ϕ_5, ϕ_6) should be sufficient. The following isomers were selected because of their known or expected low or high boiling point. All of these are known.

Class	Low-Boiling	High-Boiling
ϕ_4	1,2,4-triphenylbenzene o,o-quaterphenyl	p,p-quaterphenyl
ϕ_5	1,2,3,4-tetraphenylbenzene o,o,o-quinquephenyl	p,p,p-quinquephenyl
ϕ_6	1,2,3,4,5-pentaphenylbenzene	p,p,p,p-hexaphenyl

Some of the polyphenyls synthesized for reference compounds will also be tested for radiation stability. Their varied structures should lead to valuable clues to ideal moderator-coolants.

The p-polyphenyls have been ordered but if not received within a reasonable length of time they will be synthesized. These compounds are well characterized in the literature.

The triphenylbenzene has been requested from Atomics International. More of this may have to be made. The 2',4'-dibromoacetanilide has been prepared as an intermediate of this and other reference polyphenyls. The tetraphenylbenzene is being prepared and the pentaphenylbenzene is planned. These two compounds have an available intermediate, tetraphenylcyclopentadienone, that is on hand.

The synthesis of o,o-quaterphenyl by the Ullman reaction of 2-iodobiphenyl was unsuccessful. Coupling of 2-biphenylyl lithium with oxygen is to be tried soon. If this fails it will be more laboriously made from 2-biphenylyl lithium and 2-phenylcyclohexanone (from 2-chlorocyclohexanone and phenyl lithium). This synthesis will be used for o,o,o-quinquephenyl.

The other set of reference compounds is needed to identify irradiation products and must be identical with them. To be effective these reference compounds must be those formed in considerable yield relative to other products. The chief products from irradiation of a terphenyl are expected to be hexaphenyls formed by reaction of a terphenyl radical with a terphenyl molecule. No analysis of hexaphenyl isomers formed from irradiation has apparently been made. Forty-five linear hexaphenyls and many more branched hexaphenyls are possible. The number N of linear hexaphenyls is given by

$$N = \frac{(3^{n-2} - 3^p)}{2} + 3^p$$

where

$$p = \frac{n + 1}{2} - 1$$

when n is odd, and

$$p = \frac{n}{2} - 1$$

when n is even.

Clearly some means of predicting the isomeric hexaphenyls produced by irradiation of a pure terphenyl is needed. Yields have been predicted for irradiations of m-terphenyl near 80°C and at ~ 700°F. Eight hexaphenyls with yields (relative to other hexaphenyls) of 5% or greater have been predicted to be formed at 700°F. Two of these are known: m,p,m,m-ϕ_6 (3,4'-di-[3-xenyl]-biphenyl), and m,m,m,m-ϕ_6 (m-hexaphenyl). A sample of the latter is on hand. The others are to be prepared. The reactions to be used in making these hexaphenyls are similar and involve similar and sometimes identical intermediates.

These reactions are expected to yield the specific isomers. The reactions have been tested with similar compounds [13]. All envisioned intermediates are known with the exception of 2,3'-dibromobiphenyl and 3,5-diphenyl cyclohexenone, but their immediate precursors are known. Aryllithiums do not isomerize under the conditions of these reactions and are conveniently prepared by mixing the aryl bromide with butyllithium. Of the dibromobenzenes, only the 1,2-isomer behaved abnormally and is a convenient source of 2,2'-dibromobiphenyl. It will be desirable to check some of the preparations by synthesis with alternate routes because all but one of these hexaphenyls are unknown. No satisfactory proof of structure of the higher polyphenyls is known [13]. Progress in the synthesis and preparation of intermediates is given in the following paragraphs.

<u>2-Bromobiphenyl</u> This compound was prepared by diazotization of 2-aminobiphenyl in hydrobromic acid followed by the decomposition of the diazonium bromide with cuprous bromide [14]. The material, which distilled at 144-156°C/10 mm as a pale yellow oil, was obtained in a 44% yield.

<u>2-Iodobiphenyl</u> The diazonium chloride salt of 2-aminobiphenyl was converted by treatment with aqueous potassium iodide to 2-iodobiphenyl in a 58% yield [15]. The yellow oil distilled at 128°C/2.5 mm and had an index of refraction of 1.6562 at 20°C. S. J. Bowden [15] reports the material obtained in a 45% yield and distilling at 189-192°C/36 mm. This corresponds to ~ 125°C at 2.5 mm. D. R. Augood et al [14], reports the material as possessing an index of refraction of 1.6620 at 20°C.

<u>3-Bromobiphenyl</u> This compound was prepared by the method described by W. F. Heber et al [16]. Briefly the method consists of acetylating 2-aminobiphenyl to 2-acetaminobiphenyl followed by bromination to 2-acetamino-5-bromobiphenyl. The product was then deacetylated and deaminated to give 3-bromobiphenyl distilling at 160°C/10 mm. Each step was carried out in yields > 75% with the exception of the acetylating step which resulted in a 57% yield.

<u>4-Nitrobiphenyl</u> Biphenyl was nitrated with fuming nitric acid at 70-80°C, according to the procedure of G. T. Morgan and L. P. Walls [17] to yield 4-nitrobiphenyl, melting point at 110-112°C, in a 47% yield. No attempt was made to isolate the 2-nitrobiphenyl which forms in about equal amounts.

<u>4-Aminobiphenyl</u> This compound was prepared by reducing 4-nitrobiphenyl with water and iron filings in the presence of a catalytic amount of hydrochloric acid, according to the procedure of G. T. Morgan

and L. P. Walls [17]. A 79% yield of the 4-aminobiphenyl was obtained which distilled at 172-175°C/5.6 mm, and melted when heated to 50-52°C. Morgan and Walls [17] reported the material distilling at 166°C/5 mm and possessing a mp of 50-52°C.

4-Acetaminobiphenyl 4-Aminobiphenyl (136 g, 0.8 mole) was dissolved in 300 ml of pyridine and the mixture stirred and cooled to ~ 10°C. Acetyl chloride (90 ml, 96 g, 1.2 moles) was slowly added. After the addition, the mixture was stirred for 1 hr and then poured into 400 ml of ice cold concentrated hydrochloric acid. The crystalline product formed was filtered, washed with cold water and air dried. An 83% yield of the desired product was obtained which melted at 168-172°C after being recrystallized from 50% aqueous acetic acid.

3.4'-Dibromo-4-Acetaminobiphenyl This compound was prepared by brominating 4-acetaminobiphenyl in glacial acetic acid and in the presence of anhydrous fused sodium acetate. The method was the same as that described by F. H. Case and H. A. Sloviter [18]. Case et al obtained the desired material in ~ 44% yield which melted at 194-195°C after recrystallization. The material described in the present report was obtained in a 27% yield and melted at 184°C before recrystallization. This compound is to be deaminated to produce 3,4'-dibromobiphenyl.

4'-Bromo-m-Terphenyl This compound was prepared by brominating m-terphenyl in ethylene dichloride solvent. The material was obtained in an 80% yield and distilled at 183-195°C/2 mm. The preparation of this material has been described by J. J. E. Schmidt et al [19]. They obtained a 46% yield and reported a bp of 183°C/1.5 mm.

4'-Carboxy-m-Terphenyl Anhydrous ether (200 ml) was charged to a 200 ml 3-necked flask equipped with a magnetic stirrer, dropping funnel, condenser, thermometer, drying tube, and rubber diaphragm inlet. The system was then placed under a continuous nitrogen atmosphere. A 1 molar solution (30 ml) of butyllithium (2.0 g, 0.031 mole) in n-heptane was added and the mixture cooled at 3°C. A solution of 4'-bromo-m-terphenyl (9.3 g, 0.03 mole) in anhydrous ether (30 ml) was slowly added over a period of 30 min. After the addition, the mixture was stirred for 1 hr at 5°C and then gently warmed to 32°C for a few minutes and cooled. The milky looking mixture was poured portionwise onto a large excess of powdered dry-ice while a rapid stream of nitrogen was passed over the system. After the excess carbon dioxide had sublimed, the ethereal solution was mixed with a 10% aqueous sodium hydroxide solution (75 ml). The basic aqueous layer was separated, diluted with water (~ 100 ml), filtered to remove some foreign matter, and acidified with 5N hydrochloric acid. The white flocculant material which separated was filtered and washed with water. The compound was recrystallized from a water-methanol mixture. Approximately 5 g of material was obtained which melted at 167.5-169.5°C. C. K. Bradsher and I. Severlick [20] have described the preparation of this compound by a similar method and have reported its mp at 168-169°C.

o,o-Quaterphenyl The literature [15] has described the preparation of o,o-quaterphenyl whereby 2-iodobiphenyl is coupled with copper bronze at 255°C. Attempts to duplicate this work have not met with any success.

Several types of copper metal were used to carry out this Ullmann reaction. Besides using the readily available copper metal and copper bronze, the reaction was carried out by activating the copper bronze with iodine in acetone, washing with dilute hydrochloric acid and acetone, and drying in a desiccator. Another form of copper used was that of precipitated copper metal made by reacting zinc dust with an aqueous solution of copper sulfate followed by washing with alcohol, ether and drying.

Another method of coupling is that of N. Kornblum and D. L. Kendall [21] whereby a relatively reactive aryl halide is refluxed in the presence of copper powder in dimethylformamide solvent.

Consequently, 2-bromobiphenyl (15 g, 0.21 mole) was dissolved in 30 ml of dimethylformamide and the mixture stirred and heated to 158°C. While the temp was held at 158°C, one portion of copper powder (4 g) was added and the mixture continued to be stirred and heated at 158°C. After 4 hr another 4 g of copper powder was added and the mixture again stirred for 4 hr at 158°C. The mixture was cooled and poured into 200 ml cold water. The residue was filtered and washed with acetone. The acetone filtrate was evaporated to dryness yielding only the starting material, 2-bromobiphenyl. The insoluble residue was dried and weighed. This material, 7.8 g, was assumed to be copper.

2',4'-Dibromoacetanilide Bromine (66 g) was added in about 10 g increments to a solution of acetanilide (27 g) in glacial acetic acid (600 ml)-anhydrous sodium acetate (51 g) at room temperature. The reaction was very slow after half of the bromine had been added ($\emptyset$-NHAc + $\mathrm{Br_2} \longrightarrow \emptyset$NBrAc + HBr). Aluminum chloride (anhydrous, about 0.1 g) was added and the deep red solution bleached to light red immediately. One and one-half vol of warm water was added, the resulting crystals were filtered off, and washed with warm water. On recrystallization from 50-50 methanol-water, 15 g of 2',4'-dibromoacetanilide was obtained that melted at 144.0-144.5°C (corr.). The literature [22] value is 145-146°C. Hydrolysis of the acetanilide yielded 2,4-dibromoaniline which, when recrystallized from 50-50 methanol-water, melted at 79.0-79.5°C (corr.). The literature [23] value is 79°C. The bromination is cleaner than indicated by the yield of recrystallized product. The mother liquor yielded good crystals about equal in amount to the first crystals.

2-Chlorocyclohexanone This compound was prepared at room temp from cyclohexanone by chlorination with sulfuryl chloride in carbon tetrachloride [13]. A crude product was obtained by repeatedly washing the reaction product with water and bicarbonate solution, and vacuum distilling the residue. The distillate was cooled to 0°F to crystallize it and the impure liquid was filtered off. Redistillation of the purified material at 83-85°C/12 mm Hg gave a product boiling near the literature [13] value, 82-85°/15 mm Hg.

Heterocyclic Compounds as Ideal Moderator-Coolants Aromatic heterocyclic compounds may possess advantages over aromatic hydrocarbons as organic moderators. Some heterocycles may have ability to absorb energy in ground states pictured as partially ionic in form. This may result in lower G values. Some may be more resistant to forming condensed ring systems than polyphenyls. Thus, they may have less tendency to form carbon. An untested hypothesis to explain film formation from polyphenyls is that conjugated double bond systems (such as a cyclohexadiene ring) that readily polymerize are formed by partial hydrogenation of polyphenyls. Some heterocycles would not behave in this way and thus may not form this type of film.

Some heteroatoms are not tolerable in a moderator and others are undesirable for reasons of induced radioactivity. A decision must be made on levels of the heteroatoms nitrogen, oxygen, and sulfur that are tolerable. Until this is done heterocycles containing these atoms will not be excluded from consideration as ideal coolants.

A literature survey of heterocyclic compounds that are likely candidate moderator-coolants is under way. The following indications have been obtained to date.

(1) Nitrogen Heterocycles Polypyridyls may be insufficiently stable thermally for use as moderators.

Benzimidazole is reported to distill unchanged above 300°C [25]. Its melting point is rather high (170°C), but substitution on the 1-(N-) position strongly reduces the melting point.

2,4,6-Triphenyl-s-triazine (kyaphenine) should be stable but melts too high (232°C) to be used alone [26]. Substitution of o-tolyl for phenyl lowers the mp to 110°C. 2,4,5-Triphenylimidizole (lophine) melts too high (273°C).

(2) Oxygen Heterocycles 2,5-Diphenyloxazole is reported to be very stable thermally and should have considerable resonance stabilization energy. Its mp is low (72°C). The report [27] that it is a good scintillation counter may indicate conjugation between rings.

(3) Sulfur Heterocycles The polythienyls linked at the 2-position are reported to be thermally stable. Bithienyl melts at 33°C, terthienyl melts at 95°C but quaterthienyl melts at 215°C [28].

2,3:4,5-Dibenzothiophene is reported to have thermal stability superior to biphenyl (the best of the polyphenyls). Dibenzothiophene melts at 99°C and is readily available from biphenyl and sulfur (yield about 70% of theoretical).

Single ring heterocycles boil too low to be used as coolants. Substitution with phenyl groups or

linking of two or more heterocycle nuclei
together are available methods of raising
their boiling points.

2.6 Industrial Sources for Organic Coolants (W. M. Hutchinson, L. V. Wilson)

One of the prime areas of interest in the organic moderator field is finding the most economical coolant. At the present price of terphenyls, a promising low cost stock could undergo several processing and purification steps and still be more economical than the terphenyls. A lower starting cost may also allow higher coolant losses to gas and high boiler to be tolerated. A decrease in reactor fouling would also be an economic advantage.

Previous work has indicated that the condensed aromatic structure is the best prospect for a good coolant from industrial stocks. Work in this field is being directed towards isolating, modifying, and testing fractions which contain condensed aromatics and alkyl condensed aromatics.

A large variety of samples of industrial oils have been obtained which are high in condensed aromatics. These are described in Tables 6, 7, and 8. For the petroleum fractions, Tables 6 and 7, samples have been obtained from various areas of the country so as to vary the crude source. Because refractory compounds in the desired boiling range are concentrated in catalytic cracker cycle oils and decant oils, a number of these are being studied. Two heavy phenol extracts and a sulfur dioxide extract of lube oil are included because phenol and SO_2 extractions concentrate aromatics. In Table 8 the sample of resins from highly aromatic Wafra crude was prepared from the vacuum reduced crude by removing asphaltenes with pentane and removing oils with propane extraction. The coal tar sample has been filtered and vacuum flashed for removal of heavy ends.

These various stocks are being tested for thermal stability. Three aluminum blocks have been set up so that thermal stability of many samples can be determined simultaneously at different temperatures. Each aluminum block is 20 in. sq and 5.5 in. thick and is surrounded by 4 in. of insulation (Fig. 17). Each block contains 45 holes in staggered rows, with the center of each hole equidistant to the centers of the surrounding holes. Each block contains eight 400 w Watlow cartridge heaters. Four heaters are controlled by a Micromax controller, and four heaters are manually controlled. Temperatures now being used are 700°F, 780°F, and 820°F. The temperature differential across the block is 2°F, and the controllers have a dead space that allow temperatures to vary by 5°F.

The body of the sample holder was made by welding a 1 in. piece of schedule 80 mild steel pipe to a 0.5 in. extra strong steel weld cap. The top of the sample holder is a 3000 lb mild steel pipe cap drilled and tapped for 1/8 in. pipe. A 6 in. piece of steel tubing extends from the sample holder to a high pressure valve. The sample holder capacity is ~ 7 cc. The pipe dope now being used for the pipe fittings subjected to high temperature is "Silver Goop" distributed by Crawford Fitting Company, 884 East 140th Street, Cleveland 10, Ohio.

Table 6

INDUSTRIAL OILS - PHILLIPS REFINERIES

	Grav. API	BMCI*
Kansas City		
Heavy Cycle Oil	26.4	
Decant Oil	11.9	83.4
SAE 50 Phenol Extract		
SAE 250 Phenol Extract		
Lube Asphalt	85 penetration	
Borger, Texas		
Light Cycle Oil		
Heavy Cycle Oil	33.5	34.7
Decant Oil	23.4	49.1
SO_2 Extract from Cycle and Decant Oils	11.3	91.1
Refinery Pitch	2.0	106.7
Sweeny, Texas		
Heavy Cycle Oil		
Decant Oil		
Woods Cross, Utah		
Heavy Cycle Oil	22.7	
Synthetic Tower Bottoms	7.7	
Great Falls, Montana		
Cycle Oil		
Decant Oil		
Okmulgee, Oklahoma		
Decant Oil	9.3	93.5

* Bureau of Mines Correlation Index =

$$\frac{67030}{131.5+{}^\circ\text{API}} - 456.8 + \frac{87553}{\text{avg bp}({}^\circ\text{R})}$$

is measure of aromatic content.

Table 7

INDUSTRIAL OILS - OUTSIDE REFINERIES

	Gulf Oil Co. Port Arthur	Colorado City Oil Co.	Esso Arom. Concentrate, Baton Rouge	D-X Sunray	Cities Service, Lake Charles
Gravity, °API	0.6	3.9	3.0	3.0	3.4
BMCI	121.7	107.6	109.9	111.2	113.6
Carbon, wt%	89.94	87.27	89.46	90.2	90.4
Hydrogen, wt%	8.47	9.63	9.03	8.9	8.6
Sulfur, wt%	1.84	3.10	1.11	0.96	0.97
Pour Point, °F	30	-	70	75	25
Residue, wt%	19.4	13.6	3.45	9.13	8.30
Viscosity					
SUS @ 100°F	653.8	876.9	117.3 @ 175	-	375.5
SUS @ 210°F	52.9	57.9	-	71.5	46.8
Distillation, °F @ 760 mm					
IBP	455	527	637	718	496
5	580	571	675	759	566
10	644	640	694	773	601
20	688	684	725	796	657
30	716	725	754	811	689
40	743	762	788	830	713
50	773	802	821	848	738
60	808	841	880	869	762
70	849	882	926	900	793
80		930		965	826
90		1007			864
95					883
EP					

A sample is placed in the holder and the holder is carefully evacuated at about 150°F. Nitrogen is bled into the holder several times before final evacuation. After a set length of time in the thermal block, the volume of gas given off is measured and the change in oil viscosity is determined.

Various unit operations are being performed on these stocks, such as distillation, dewaxing, and extraction in order to determine the effect on thermal stability. Determination of the effect of desulfurizing and dealkylating these better stocks is also planned. The stocks which look good during thermal testing will then be subjected to irradiation to determine the combined effect of temperature and radiation.

Table 8

INDUSTRIAL OILS - MISCELLANEOUS

	Resins from Wafra Crude	Dimethylsulfoxide Extract of Borger SO_2 Extract	Coal Tar from Pittsburg Chemical
Gravity, °API	7.0	2.7	3.2
Viscosity, SFS @ 210°F	537		
Softening Point, °F	95		
Analyses, wt%			
Carbon	83.7	87.83	
Hydrogen	10.4	9.15	
Oxygen	0.34	0.89	
Nitrogen	0.31	0.14	
Sulfur	5.70	1.99	
Mol wt	805	220	
Metals, ppm	125		
RI_{20}		1.6293	
BMCI			101.3
Dist. Range, °F			500-950

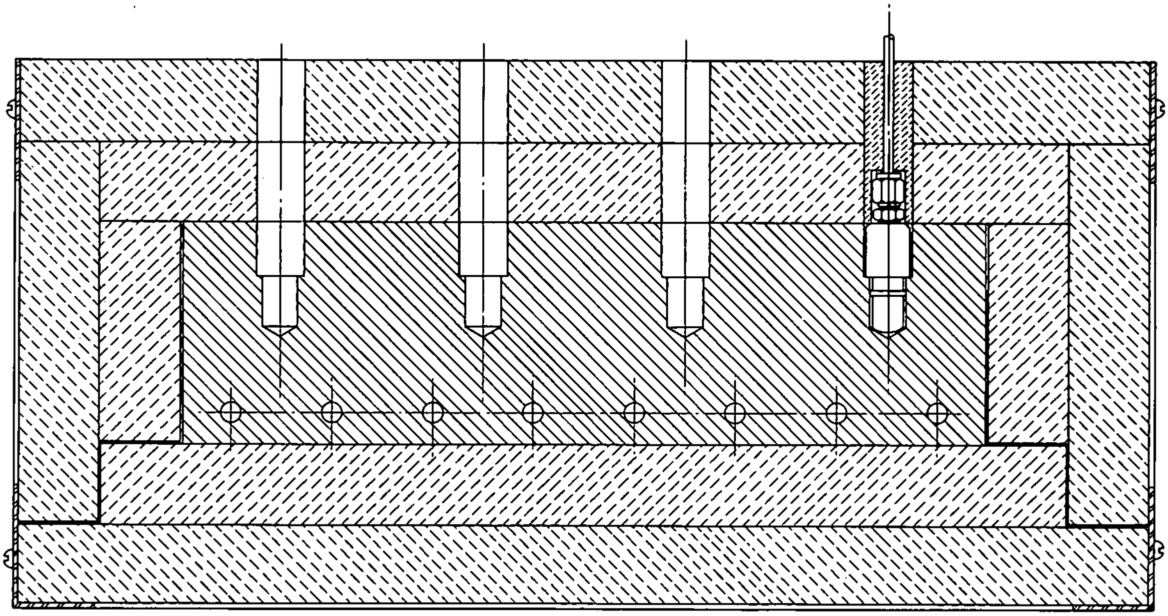


Fig. 17. Thermal block.

2.7 Organic Coolant Reclamation (W. M. Hutchinson, L. E. Gardner)

There are several possible methods of conversion of high boiler to usable coolant. At the present time a program is in progress to study the feasibility of catalytic hydrocracking in a continuous flow, pressurized, fixed bed system. The desirable reactions in this type of conversion may be summarized as follows:

(1) Cracking of the carbon-carbon bond between polyphenyls and phenyltriphenylenes with subsequent saturation of the fragments to prevent side reactions.

(2) Hydrogenation of a central ring in a long-chained polyphenyl followed by cracking of this ring to two alkyl polyphenyl molecules of lower molecular weight.

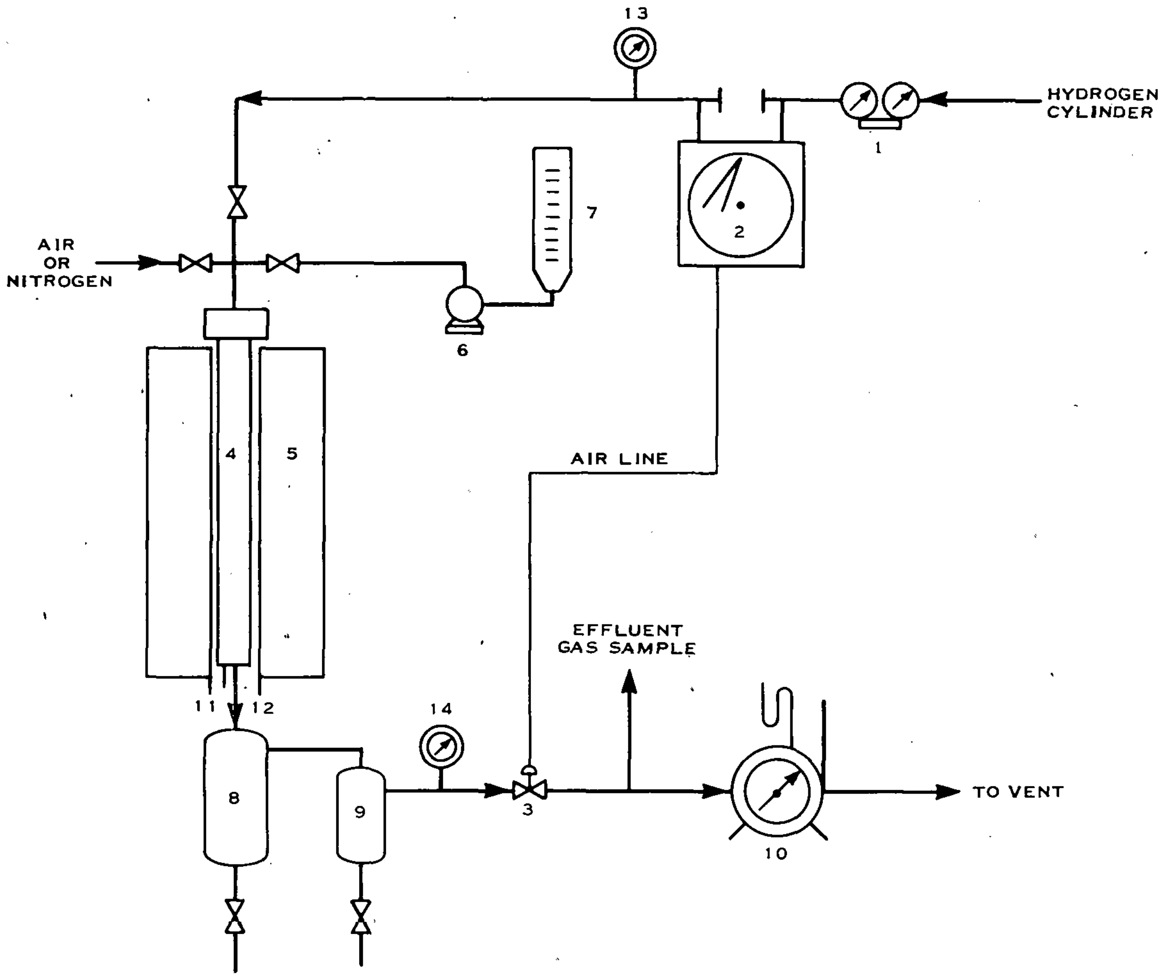
(3) Selective hydrocracking to terphenyls and quaterphenyls with minimum production of biphenyl, benzene, or lower molecular weight materials.

(4) Hydrogenation of high molecular weight condensed aromatics followed by cracking to lower boiling aromatics (preferably three ring structures).

The above reactions indicate that two types of hydrocracking are required for conversion of high boiler. One of these is splitting of the carbon-carbon linkage between phenylene groups, and the other is ring saturation of high boiling aromatics. The first reaction type may occur thermally in a temperature range of 1000-1200°F. However, at these temperatures, condensed aromatics would tend to polymerize and condense to more coke-like material. Also, these temperatures are in the range of the decomposition points of the terphenyls. Thus, a catalyst with good cracking activity must be substituted for this high reaction temperature. The catalyst should also have sufficient hydrogenation activity to suppress coke formation. This suggests the use of an acidic catalyst such as silica-alumina, boria-alumina, or HF-treated alumina promoted with hydrogen-active metal or metal oxide. Another complicating factor is that although ring hydrogenation is desirable for the condensed aromatics, it is not desirable for saturation of three- or four- membered polyphenyl rings.

The ultimate solution to the above reaction requirements might include a two-stage process in which the first step is selective saturation (or partial selective saturation) of the condensed aromatics under thermodynamically favorable conditions for hydrogenation. The second step would be the cracking stage at higher temperatures (but probably the same pressure) which would be selective for carbon-carbon bond cracking without further ring hydrogenation. Much of this quarter has been spent in designing and fabrication of high pressure, continuous flow equipment for catalyst evaluation, and in working out techniques for conducting experiments and analytical procedures. Two nearly identical units have been constructed and tested for operation under conditions up to 1100°F and 1000 psig. In general, catalyst evaluation is carried out in one unit using pure compounds such as biphenyl or a terphenyl isomer. The other unit is used for treatment of high boiler and studying process variables. Up to the present time four catalysts have been evaluated for activity in hydrocracking the carbon-carbon linkage, and some preliminary runs have been made on OMRE high boiler.

Fig. 18 shows the bench scale hydrocracking unit in the flow diagram. System pressure is controlled by a Victor pressure regulator (1).



1. PRESSURE REGULATOR
2. TAYLOR FLOW CONTROLLER
3. AIR OPERATED MOTOR VALVE
4. REACTOR
5. 3-ELEMENT FURNACE CONTROLLED BY CELECTRAY
6. LAPP PULSAFEEDER WITH REMOTE HEAD
7. CHARGE COLUMN
8. HIGH PRESSURE SEPARATOR (USUALLY HOT)
9. HIGH PRESSURE SEPARATOR (USUALLY COLD)
10. WET TEST METER
11. THERMOWELL IN REACTOR, 3/16 OD, FOR CATALYST TEMPERATURES
12. THERMOWELL IN SLEEVE OF FURNACE FOR CONTROL THERMOCOUPLES
13. UPSTREAM PRESSURE GAUGE
14. DOWNSTREAM PRESSURE GAUGE

Fig. 18. Flow diagram for hydrocracking

Flow rates are controlled by a Taylor Flow Controller (2) which activates the downstream motor valve (3), and the quantity of hydrogen and pressure level entering the system is recorded by this instrument. The charge stock is pumped with either a Lapp Pulsafeeder or an American Bosch Pump (6). The Lapp pump is equipped with a remote mounting pump head-reagent head which can be heated to 400°F at 1000 psig. The reactor furnace (5) contains three equally spaced heating elements which are controlled electronically by a Tagliabue Celectray. The reactor (4) has a 5/8 in. i.d. and a 1 in. o.d. and is constructed of 347 stainless steel. A 3/16 in. thermowell (11) is mounted concentric to the reactor. The catalyst bed is made up of 80 cc of 10-20 mesh particles (17 in. depth) with a preheat section in the top part of the reactor. Liquid products are separated out in two high pressure separators which can be either heated or cooled. The air-operated motor valve reduces system pressure to atmospheric, and the effluent gases are passed through a sampling system and through a wet test meter.

Catalyst evaluation tests have been run using biphenyl or a terphenyl isomer in either benzene or toluene solution (20-30 wt%). Thirteen runs have been made at 500 psig and temperatures in the range of 800-950°F. Hydrogen flow rates were equivalent to a 10 to 1 mole ratio of hydrogen to hydrocarbon. Charge rates were 1.0 vol of liquid per vol of catalyst per hr (v_L/v_C/hr). For these runs on pure compounds analytical techniques have included distillation, gas chromatography, and mass spectrometry. Chromatographic analyses were made using an F and M 202 programmed instrument with a 20 ft silicone grease on firebrick column. A brief summary of tests on four catalysts for hydrocracking biphenyl is shown in the following tabulation:

Catalyst	% Conversion of Biphenyl
$CoMoO_4$ on Al_2O_3	16
Pt-$CoMoO_4$ on Al_2O_3	13
Pt on SiO_2-Al_2O_3	14
$CoMoO_4$ on B_2O_3-Al_2O_3	25

Run conditions for the above runs were 500 psig, 900°F, 1.0 v_L/v_C/hr, 10 to 1 hydrogen to hydrocarbon mole ratio, and charge stock of 20 wt% biphenyl in benzene. Products from these runs contained small amounts of toluene and ethyl, propyl, and amyl benzenes which indicated that some of the biphenyl was converted by ring hydrogenation with subsequent cracking to alkyl benzenes. Variation of temperature from 850-950°F increased conversion very slightly for all four catalysts.

Runs using o-terphenyl indicates that as the polyphenyl chain length increases the carbon-carbon bond between rings becomes less refractory towards hydrocracking. It was of interest to compare the relative reactivities of benzene, biphenyl, and the terphenyls to hydrocracking at the same conditions. This was done using $CoMoO_4$ on B_2O_3-Al_2O_3 catalyst at 500 psig, 850-900°F, 1.0 v_L/v_C/hr, and 10 to 1 hydrogen to hydrocarbon mole ratio. The following tabulation compares the runs.

Compound	% Conversion 850°F	% Conversion 900°F
Benzene	9	15
Biphenyl	20	25
o-Terphenyl	80	65

In runs using benzene as solvent it was observed that 5-15 wt% was lost. However, only trace amounts of cyclohexane were found in the liquid product. High methane content of the effluent gas indicated that benzene disappearance was due to hydrogenation followed immediately by cracking to light gas (C_1-C_4's). Blank runs on benzene at all temperatures confirmed this. At 900°F isomerization of o-terphenyl was observed and both meta and para isomers were found in the residue. Thus the 65% conversion figure represents conversion to material lighter than the terphenyls. The above data indicate that catalytic hydrocracking of the longer chain polyphenyls may occur at moderately low temperatures.

Other catalysts which are to be tested include the following:

- Pt-$CoMoO_4$ on B_2O_3-Al_2O_3
- Cr_2O_3 on Al_2O_3
- Cr_2O_3 on SiO_2-Al_2O_3
- Pt-Cr_2O_3 on SiO_2-Al_2O_3
- NiO on Al_2O_3
- NiO on SiO_2-Al_2O_3
- CoO-V_2O_5 on Al_2O_3
- NiO-$CoMoO_4$ on Al_2O_3
- Rh on SiO_2-Al_2O_3
- HF-treated catalysts

OMRE high boiler has been subjected to three hydrocracking tests in the continuous flow unit using $CoMoO_4$ on B_2O_3-Al_2O_3 catalyst. In the first run conditions were 900°F, 500 psig, 1.0 v_L/v_C/hr and 22.5 std ℓ/hr hydrogen flow. The charge consisted of 39.2 wt% high boiler in benzene solution. Liquid products from the first 2 hr were clear, yellow fluorescent materials and became darker in the 3rd hr. Chromatographic analysis of the 2nd hr product gave the following composition:

Compound	Wt%
Methylcyclopentane 2,4-Dimethylpentane	3.4
Cyclohexane	
Benzene	78.2
Toluene	1.0
Ethylbenzene	3.5
Biphenyl	9.2
Quaterphenyl	4.7

During this run there was a large amount of degradation of the high boiler to gas and coke. Also benzene in excess of that in the charge was found in the product. Using a combination of chromatography, distillation, catalyst burn-off, and mass spectrometer analysis of effluent gas, the following product distribution was calculated for the 3 hr run:

Product Fraction	Wt% of High Boiler Charged
Gas (C_1-C_4's)	20.7
Benzene	16.7
Biphenyl	
Terphenyls	24.8
Quaterphenyls	
Coke	26.4
Unconverted High Boiler	11.4 (By Difference)

The above data indicate that reaction conditions were much too severe for efficient conversion of high boiler. Two additional runs have been made at 800°F and 850°F holding the other conditions constant. Toluene was used as solvent for the high boiler to improve mechanical and analytical techniques. Complete analyses of the products are not available at the present time.

Experiments are in progress to find optimum process conditions which will minimize undesirable coke and gas formation. The $CoMoO_4$ on B_2O_3-Al_2O_3 catalyst will be used for this work until a more active catalyst is found in the catalyst evaluation program.

Product samples from runs on high boilers are being run by chromatography using the F and M 500 programmed instrument. However, at the present time data are not quantitative.

3. ORGANIC COOLED REACTOR DEVELOPMENT

W. B. Lewis

3.1 General Plans

When the EOCR becomes operable, enlarged programs in development and basic technology will be undertaken. Major problems in fuel and coolant technology, and in new fuel-coolant-moderator combinations, will be investigated. The emphasis at the EOCR will be on engineering tests in the areas of fuel element development, new coolants, radiation damage, and reactor technology.

Until the in-pile programs begin, the EOCR experimental staff will continue to expend its efforts on conceptual designs of in-pile loops, liaison during detail design and construction, and in designing, building, and bench-testing prototype experimental equipment and devices for insertion into the loops. This experimental equipment includes such items as special cells to measure specific physical parameters of the coolant, and specially instrumented fuel plates and fuel assemblies for detailed engineering studies.

3.2 Loop Design

During the last quarter of 1960 the objectives and conceptual designs for two loops were developed: the Fuel Technology Loop (FTL) and the Coolant Technology Loop (CTL). Detailed design of the latter is now underway by The Fluor Corporation Ltd.

The experimental objectives for the CTL are to advance coolant technology by studying coolant behavior under core conditions of radiation, and controlled conditions of coolant temperature, pressure, and flow. Surface effects will be studied by inserting electrically heated metal surfaces at controlled temperatures into the coolant stream. Simultaneous measurements can be made on many parameters, such as electrical conductivity, film coefficient of heat conductivity, and rate of film buildup.

Similarly, the experimental objectives for the FTL are to advance fuel technology by studying fuel plates and fuel assemblies under core conditions of neutron flux and controlled conditions of coolant temperature, pressure, and flow. The loop conditions can be made more severe than those existing in the EOCR, or in any operating reactor. Such tests are essential before a reactor can be designed to operate under such conditions.

The conceptual designs for both loops are similar in most of the essential components. There are an in-pile tube, circulating pumps, a surge tank, a heat exchanger to reject power absorbed during passage through the in-pile section, a topping heater to maintain specified temperature of the coolant, by-pass valving to a degasser to remove gaseous and low-boiling components of radiolytic and thermolytic reactions, and by-pass valving from the degasser-return to a distillation column to remove the high-boiling components of the damaged coolant. Both purification processes operate continuously and maintain the coolant composition within specified composition limits. Particulate content is maintained within specified limits by continuous filtration of another shunt stream. Both loops can be decontaminated independently of any other reactor facility. Makeup facilities for the loops operate independently. Design specifications for in-pile and out-of-pile components are based on 1000°F maximum temperature and 300 psig maximum pressure. Means for removing samples and reinserting irradiated samples are provided. Adequate shielding is provided to handle the expected coolant activity.

The CTL has an H-type in-pile section and a large in-flux to out-of-flux ratio for the primary circulation. The FTL has a re-entrant type in-pile section.

The proposed FTL in-pile tube is single-walled in the core region and is designed to take as large a sample as possible while remaining consistent with space limitations. There is an adapter located below the core into which the sample is fitted. In this region coolant flow is directed up through an inner tube, and passed through the adapter to the sample. After passing through the sample, the flow reverses, flows down around the outer walls of the sample, and leaves through the annulus between the outer tube and the inner tube.

External shielding is heavier in the FTL than in the CTL as the presence of fission products, from accidentally or deliberately defected fuel plates, must be considered. Fuel element testing will proceed to burnout conditions, and high activity in the circulating coolant is expected.

As mentioned previously, the decision has been made to proceed with the design and construction of the CTL. Work on the FTL has been deferred until comparisons can be made with other laboratories' objectives.

The experimental group has been given the assignment of preparing the final Hazards Summary Report for submission to the Commission 90 days before the planned startup of the EOCR. Current work on this assignment includes preparing definitive tabulations of dimensions and physical parameters of the EOCR prior to making reactor physics calculations for initial loadings of the reactor. All aspects of the reactor operations and interrelations with the experimental program will be considered.

4. EXPERIMENTAL ORGANIC COOLED REACTOR OPERATIONS

T. R. Wilson

4.1 General Planning

The operating staff is being planned and assembled as needed. Initial efforts of this staff have been in a liaison capacity with the Architect Engineer. This has been a major job during this quarter and will continue until late 1961 when the reactor and its plant are completed. In addition, planning of pre-operational tests, startup tests, and operating manuals and procedures is in progress.

The behavior of the EOCR itself will provide valuable information in the field of organic reactor technology. During startup, many physics measurements will provide data on static and dynamic behavior. Examination of fuel elements and study of the organic coolant during operation will provide information on fouling and damage. Operation of the organic clean-up system will provide decomposition rates and information on the performance of various clean-up equipment.

Active planning on the part of both the experimental group and the operating staff is underway to evaluate the behavior of the EOCR in its normal operation as a tool for research in loops and capsules.

4.2 EOCR Test Facility

On April 28, 1960, the Idaho Operations Office of the AEC directed Phillips to proceed with the design, procurement, fabrication, erection, and operation of an organic flow test facility in which pre-operational tests on an EOCR control rod drive prototype would be conducted. During the conceptual design phase, it became evident that this facility should also be designed for environmental testing of the EOCR driver fuel elements and prototype power fuel elements. Conceptual design drawings and preliminary cost estimates covering this facility were transmitted to the Idaho Operations Office on June 22, 1960, and this project was approved on July 22, 1960.

The EOCR Test Facility will permit testing, calibration, etc., of the EOCR control rod drives, EOCR driver fuel elements, and prototype power fuel elements under reactor environmental conditions of flow, pressure, and temperature. This facility is being erected in Building CF-656, previously used for testing the Spert III control rod drive.

Basic units of EOCR Test Facility are the test vessel proper, a surge tank, a bulk organic heater, a bulk organic cooler, a steam generator, an organic circulating pump, piping, rod drive control console for the drive units, and instrumentation for process control. Basic environmental conditions provided by this facility are a maximum flow of 1200 gpm of Santowax R at temperatures ranging from 300-850°F and pressures up to 400 psia. Direction of flow will be from the bottom of the test vessel to the top, the same as in the EOCR reactor vessel.

The most important component of the facility is the test vessel. This is designed to reproduce conditions surrounding the control rod as they will exist in the EOCR. The vessel is 12 in. in diameter, 32 ft high, and closed by flanges. The lower head will carry the "seat switch tail rod seal". The upper flanges include an intermediate flange for hanging a prototype reactor structure (spiders, grid, and control rod orifice boot) inside the test vessel. The upper head mates with this hanger flange and receives the control rod drive mounting flange as designed for the EOCR. Eight-inch nozzles are provided for inlet and outlet coolant and are located to simulate the actual EOCR reactor vessel.

Because of the urgent nature of this project, and because of scheduling problems in Phillips shops, almost all fabrication work on the basic units for this facility was accomplished through outside fabricators. Installation work is now being accomplished by Phillips forces, and is ~ 90% complete. All major components have been received and installed. Remaining work includes steam tracing, pipe insulation, loop instrumentation installation, and other minor items. Initial operation of the EOCR Test Facility is expected to begin the first week in March, 1961.

A prototype control rod and rod drive were delivered early in December, 1960. The rod drive has been operationally checked in a dry environment at ambient temperatures and appears to function satisfactorily. The Test Facility operating staff are presently familiarizing themselves with the facility, the control rod drive, and other operational features.

Tests on the prototype control rod drive to be conducted in this unit include verification of the hydraulic data used as a design basis for the control rod drives; static and dynamic seal tests; mechanical adequacy of the control rod drive unit; determination of control drop times under different conditions of pressure, temperature, and flow; stall characteristics, and repeatability, etc. of the control drive.

Future use of this facility will be to calibrate and flow test EOCR control rods, to determine hydraulic characteristics of EOCR fuel elements, and to make similar tests on improved fuel elements and experimental components prepared for loops in the reactor. Experience with the MTR and ETR indicates clearly that this facility will be of immeasurable value in the operation of the EOCR.

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