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ORGANIC COOLANT RESEARCH SUMMARY REPORT

July 1, 1960 - March 31, 1963

MASTER

J. C. Hillyer

**PHILLIPS
PETROLEUM
COMPANY**

ATOMIC ENERGY DIVISION

**NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION**

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ORGANIC COOLANT RESEARCH SUMMARY REPORT
JULY 1, 1960 - MARCH 31, 1963

by

J. C. Hillyer
Manager, OCR Project,
Bartlesville

PHILLIPS
PETROLEUM
COMPANY

Research and Development Department
Bartlesville, Oklahoma
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Idaho Operations Office
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ORGANIC COOLANT RESEARCH
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SUMMARY

Under Contract AT(10-1)-1080 with the Idaho Operations Office, U. S. Atomic Energy Commission, Phillips Petroleum Co. initiated a project in the Bartlesville laboratories of the Research Division in July 1960 to study certain problems in the technology of the use of organic liquids as moderator-coolants for nuclear reactors. Work on this contract was terminated January 31, 1963. This report constitutes the final summary of the work done.

A major part of the study was devoted to a study of the mechanism of radiolytic damage to coolant. A mathematical treatment for handling information on the relative reactivity of different positions on an aromatic ring was developed in some detail. Determinations on products from the radiolysis of terphenyls, biphenyl, and mixtures of these with benzene indicate that free radicals may be the main reactive species generated but that others are present. Comparison of the data with reactions of chemically or photochemically generated free radicals shows that the radiolysis is not random, especially at 300°C, but that meta radicals are more frequently formed. Attack by the active species on another molecule is favored in the para position and repressed at the ortho position compared to the meta. The distribution of isomers found indicates that hydrogen abstraction by the free radicals and isomerization reactions do not occur to an appreciable extent.

New analytical methods had to be developed to carry out this study. Chromatography on a solid salt column using LiCl proved to be a very satisfactory method for quaterphenyls and most hexaphenyls. Elution peak shifts between LiCl, CsCl, and CaCl₂ columns were correlated with structure, and made possible separation and identification of certain isomers not possible on a single column. For the calibration of the columns and position identification, authentic samples of all the quaterphenyls, several quinquephenyls, and 13 hexaphenyls were obtained or synthesized by unequivocal methods. Several of these were obtained in fairly large quantity and five were new compounds. Using these known materials, important correlations were developed in the fine structure of the infrared spectra which, together with the elution peak shifting between salt columns, made possible identification of many additional isomers for which calibration samples were not available.

9,10-Dihydrophenanthrene was found to give only 17 percent as much polymer as terphenyl under irradiation. It appeared to function as a hydrogen donor and was the most promising of this type of new coolant. A concept of "self-healing" coolants was developed, which offers an attractive field for further research.

A survey of candidate stabilizers revealed that radiolysis of terphenyl could be reduced 15 to 25 percent by addition of 3 mol percent of compounds either containing divalent sulfur or compounds having the anthracene ring system but with the central ring containing N, S, O, or Se atoms at one or both positions.

An even more effective and much cheaper stabilizer was elemental sulfur, which was most effective at 0.7 mol percent.

Apparatus was devised in which the deposition of film from contaminated coolant under electron irradiation and pyrolytic conditions could be studied, including circulating loops in which cells simulating fuel element coolant channel geometry and other types could be used. In these tests with spent reactor coolant containing high-boiling polymer and inorganic particulate matter it was found as the iron concentration increased the amount of film increased linearly if sufficient organic polymer was present for a binder. The relationship of binder concentration to film deposited varied with the device used. Film thickness increased exponentially with surface temperature and was inversely proportional to coolant velocity in a non-corroding (stainless steel) system. There was evidence of a positive effect of beta current on film deposition. A hydrogen blanket did not reduce the amount of film deposited, but there was less reduction in heat transfer due to reduction of the oxide in the film to metal.

In corrodible mild steel systems, film deposition appears to be proceeding also by another mechanism in which mass transport of iron in solution from the external system and deposition accompanied by a phase change is the route followed. Characteristic films were deposited from coolant containing iron chelated with oxygenated organic compounds similar to those which might result from oxidation of irradiated coolant. Irradiated coolant, when exposed to air, developed the ability to corrode iron, and films could be deposited from the resultant contaminated coolant. Carbon monoxide was found to result from irradiated coolant oxidation and to carburize iron oxide deposits on heat transfer surfaces. The new phase, iron percarbide, formed a tightly adhering film. Iron oxide precipitated in the bulk coolant did not reach a sufficient temperature to undergo this change. Some evidence for corrosion and transport by chlorine compounds also was seen.

Inexpensive, highly aromatic oils available as residues from fluid cracking and other operations in petroleum refineries have shown some promise as candidate coolants. After desulfurizing and hydrodealkylating, some fractions were produced which had lower rates of degradation to polymer than terphenyls and were thermally stable up to 700 to 725°F. A fruitful field for further research was indicated.

A process for reclamation of degraded coolant by catalytic hydrocracking was developed. A catalyst-screening program showed that the desired small degree of cracking ability together with little ring hydrogenation, promotion of the hydrogenation of the cracked fragments, and low coke formation could be obtained in cobalt molybdate, nickel oxide, or platinum preparations on low-surface-area, basic, alumina support. Applied to high boiler in a low-conversion recycle process, radiolytically and thermally stable coolant-range product was produced in 80 percent yield. A more desirable operation was application of the process to total spent coolant. Regenerated coolant was recovered in 95 percent or better yield, and with utilization of the hydrogen liberated in reactor operation, the goal of closed system operation was approached.

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I. INTRODUCTION

In July 1960, arrangements were completed between Idaho Operations Office, U. S. Atomic Energy Commission, and Phillips Petroleum Co. whereby Phillips was to undertake in the Bartlesville laboratories of the Research Division a rather comprehensive investigation into the technology of organic liquids used as coolant-moderators in nuclear reactors. A fundamental study of the behavior of stable organic fluids under high-temperature irradiation was to be made, to obtain a more complete understanding of the chemical and physical mechanisms involved. Building on the knowledge expected to be obtained in this study and in concurrent research programs of others, the possibilities of stabilizing coolants against radiolysis, and of synthesizing, or finding amongst available industrial materials, new coolants more stable or cheaper than present terphenyl coolants, were to be considered in a systematic, scientific manner.

The 4-kw, 6-Mev electron linear accelerator (Linac) of the Research Division was to constitute a primary tool to provide irradiations around which the experimental program would be centered. Broad experience in organic chemistry, petrochemistry, petroleum technology, catalysis, etc, as well as radiation chemistry would be brought to the problem in the backgrounds of the experienced staff to be assigned to this project. The staff was assembled and experimental investigations were begun in September 1960. They continued through January 1963, when work was discontinued in view of the imminent termination of all AEC contract work in the organic-moderated reactor field.

During the period when arrangements for the program were being negotiated, problems associated with fouling of heat transfer surfaces by the present terphenyl coolant became critical, and Phillips was asked to add to its fundamental, long-range program certain problems of current coolant technology. Accordingly, studies on the causes, mechanisms, and prevention of surface fouling, and on reclamation of waste products of coolant radiolysis, were included in the program.

This report presents a summary of the work accomplished during the life of the contract in the various areas in which experimental work has been done. The experiments and apparatus have been described, and the data reported in detail in the series of quarterly progress reports which have been issued, and in various topical reports which have been prepared from time to time. For this reason, few details of experimental work or tables of data are included here. Instead, an effort has been made to show the objectives of each sub-project described, the relation of each to the overall effort, and in brief, the significant results and the conclusions which can be drawn from them. Very complete cross referencing to the appropriate quarterly and topical reports has been attempted. The organization follows that used in the program plans presented to AEC in budget requests, and program reviews. It includes the five headings of fundamental radiolysis, fouling film deposition, new coolants, reclamation, and stabilizers. It differs therefore somewhat from the organization which has been used in the quarterly reports.

II. FUNDAMENTAL STUDIES OF RADIOLYSIS

(P. S. Hudson, W. M. Hutchinson, A. J. Moffat, P. W. Solomon, R. C. Doss)

1. GENERAL PROGRAM AND ORGANIZATION

The objective of this part of the program was to make a thorough, basic scientific study of the radiolysis of terphenyls and, more broadly, of all organic molecules at elevated temperatures. The aim was to learn in detail the nature of the products of irradiation of various polyphenyl molecules, and to try to deduce from them the mechanism of the radiolysis and the process by which radiation damage is initiated in these coolants. The ultimate objective was to develop at least a working hypothesis of radiolysis which could be applied to the prediction of molecular structures more stable than terphenyls or to additives which could serve as stabilizers so that a test program in these areas could be intelligently and efficiently prosecuted. Application of such a hypothesis to the prevention of the type of radiolysis leading to deposition of film on heat transfer surfaces became an objective of the program soon after its start.

Research proceeded in several distinct areas. Radiolysis of the pure terphenyl isomers, of biphenyl, and of other pure organic compounds as well as mixtures is obviously one area of investigation. It also was known at the start that methods of analysis for the coolants and their more simple polymers and fragments would have to be developed, and this was a second area of work initiated at the start. An important requirement of the analytical developments was for calibration samples of the terphenyl dimers, of known structure, and of the dimers and codimers with biphenyl. Consequently, one major part of the work in this area comprised a synthetic program in which authentic samples of all the quaterphenyls, some quinquephenyls, and many of the hexaphenyls were prepared. A third area comprised the study of the composition of high boiler and methods for its analysis.

In these general areas, a number of individual projects, some of considerable scope in themselves, were initiated from time to time. In the following sections each of these is described, with its objective, relation to the overall effort, and significance of results.

2. REACTIVITIES IN RADIOLYSIS

2.1 Reactivity of Individual Positions on an Aromatic Ring

2.11 Basis and Objective. Mechanisms of radiolysis of aromatic compounds could be understood better if two questions could be answered:

- (1) Is the radiolysis of an aromatic ring so very rapid as to be random; or, is there sufficient redistribution of energy to enable selectivity by such effects as resonance and electron density?
- (2) What kinds of reactive species are formed by radiolysis? Free radicals? Ions? Ion-molecules? Excited molecules?

It usually has been assumed that radiolysis is random because the energy required is much smaller than the energy of common ionizing radiations. The evidence for this conclusion is tenuous, however, because it is known that aromatic molecules are able to convert a large fraction of incident energy into heat. If such internal conversion could occur before radiolysis, then it seemed reasonable that incident energy could be redistributed in an aromatic molecule prior to radiolysis so that this process might become selective. No method was available for detecting such selectivity or randomness. The object of this study has been to develop such methods and so to provide answers to the two questions posed. It had commonly been thought that free radicals were the reactive species generated in organic molecules by radiolysis. This was reasonable since the dissociation energy of homolytic scission is usually considerably smaller than that of heterolytic scission. However, photons or ionizing particles often have far more than sufficient energy to perform either scission. Better evidence for free radicals was from ESR spectra of irradiated materials and the nature of products resulting from radiation. Granted that some of the reactive species generated by irradiation of organic molecules are free radicals, are there any other species formed? These questions could be answered in principle by a mathematical model that was developed in this program for the radiolysis of aromatic compounds.

The details of this model are given in a topical report [1]. Results obtained with the model and their significance to radiolytic mechanism are given in the following sections.

2.2 Reactivity of Biphenyl to Radiolysis and to Free Radicals Attack

When biphenyl is radiolyzed six isomeric quaterphenyls are produced. The model relates the relative yield or distribution of these isomers to the individual reactivities of the different positions of the biphenyl molecule in two independent reactions involved:

- (1) Generation of the reactive species (radicals, ions, etc) by radiolysis
- (2) Reaction of the reactive species with biphenyl molecules (scavenging or substitution reaction)

The individual reactivities in the first, or radiolytic, reaction are designated by r_o , r_m , and r_p with the subscripts relating to the ortho, meta, and para positions on the biphenyl molecules. The individual reactivities in the second reaction are designated by k_o , k_m , and k_p and correspond to the partial rate factors commonly obtained by competitive reactions of aromatic compounds with free radicals, ions (such as NO_2^+ in nitration), etc. However, the latter are usually related to benzene as the standard competing reactant while the reactivities given here relate to the meta position of biphenyl as the standard ($k_m = \text{unity}$, $r_m = \text{unity}$).

Table I gives the individual reactivities (partial rate factors) of the three positions of biphenyl in the generation of reactive species (r_o , r_p) and in scavenging or substitution reaction (k_o , k_p) obtained from radiolysis of biphenyl at 80° and 300°C. Table II gives the reactivities of the same positions of biphenyl in the substitution reaction with free biphenylyl radicals generated by ultraviolet irradiation at 80°C of the three individual iodobiphenyls dissolved in biphenyl.

TABLE I
PARTIAL RATE FACTORS OF BIPHENYL UNDER ELECTRON IRRADIATION

<u>Irradiation Temperature (°C)</u>	<u>r_o</u>	<u>r_p</u>	<u>k_o</u>	<u>k_p</u>
80	0.85	0.90	1.5	2.9
300	0.55	0.80	0.45	2.5

TABLE II
PARTIAL RATE FACTORS OF BIPHENYL IN
SUBSTITUTION BY BIPHENYL FREE RADICALS AT 80°C

<u>Radical Isomer</u>	<u>k_o</u>	<u>k_p</u>
o-biphenylyl	1.7	2.9
m-biphenylyl	1.7	2.2
p-biphenylyl	2.0	2.2
Weighted average:	1.76	2.46

To compare the k values obtained by radiolysis of biphenyl with k values obtained with the three biphenyl free radicals, the latter must be weighted according to their probabilities of being formed by radiolysis.

This weighted average is given at the bottom of Table II. It will be noted that the k_o obtained from radiolysis of biphenyl at 80°C is smaller than the average k_o obtained with free radicals but that the radiolytic k_p is larger.

The similarity between the radiolytic and free radical k values indicates that free radicals may be the main reactive species generated by radiolysis at 80°C. However, the differences indicate that some reactive species less ortho-selective and more para-selective than free radicals also are formed. The prevalence of such species should be inversely proportional to their differences in selectivity from free radicals.

The low r_o and r_p values obtained by radiolysis of biphenyl at 300°C definitely indicate that radiolysis is not random. However, it is apparently less selective at 80° than at 300°C. An explanation for this selectivity should explain not only why meta-radicals are formed more frequently than ortho and para radicals but also why r_o is smaller than r_p and why the radiolytic process is more random at the lower temperature. The idea of selectivity because of resonance stabilization of the radical does not apply here because it is the ortho and para radicals that would be stabilized and hence favored in formation. Weaker C-H bonds at the meta position could explain the selectivity for this position and also the rise in selectivity with temperature. It does not explain why r_o is less than r_p.

When o-iodobiphenyl in biphenyl was irradiated with ultraviolet light at 80°C only o,o-, o,m-, and o,p-quaterphenyl were found. Similarly m-iodobiphenyl yielded only o,m-, m,m-, and p,p-quaterphenyl, and p-iodobiphenyl yielded only o,p-, m,p-, and p,p-quaterphenyl. Had any of the free radicals derived from the iodobiphenyls abstracted hydrogen from biphenyl, then other quaterphenyls would have been formed. Similarly, isomerization of the free radicals or the final products would have resulted in other isomers being formed. Therefore, it is concluded that under ultraviolet irradiation at 80°C no hydrogen abstraction nor isomerization occurred. Hydrogen abstraction and isomerization are believed to be also unlikely under radiolysis conditions.

3. RADIOLYSIS OF POLYPHENYL MIXTURES

3.1 Objectives and Basis

The radiolysis of the isomeric terphenyl coolant in an organic-moderated reactor gives mainly higher-molecular-weight polyphenyls. Complete product analysis is extremely difficult due to the great number of isomers present. However, some insight into the electron irradiation behavior of polyphenyls can be obtained by studying the radiolysis of various polyphenyls mixed with benzene. Individual polyphenyl isomers can be compared with one another by first comparing them with benzene.

The following scheme illustrates the general approach:

Product analysis requires only the yield of each class of polyphenyl, not all the individual isomers in each class. The yields were assumed to result from two acts: (a) the generation of a reactive species and (b) the attack of that species upon a neutral molecule.

3.2 Experiments and Discussion

Mathematical expressions were developed for the generation of benzene excited species n , the polyphenyl excited species $(1-n)$, the scavenging probability for benzene N , and the scavenging probability for the polyphenyl molecule $(1-N)$. This mathematical treatment has been described in detail [1 - 6].

Table III gives the mole ratios of excited species and scavenging ability for several individual polyphenyls compared to benzene.

TABLE III
FORMATION AND SCAVENGING PROBABILITIES
FOR SEVERAL POLYPHENYLS WITH RESPECT TO BENZENE

<u>Mixtures (Equal Molar)</u>	<u>Formation of Reactive Species, Mole Ratio</u>	<u>Scavenging, Mole Ratio</u>
Biphenyl/benzene	1.04	2.45
m-Terphenyl/benzene	1.27	6.70
Perdeuterobenzene/benzene	0.38	0.87

The tabulation shows higher-molecular-weight polyphenyls scavenge radicals or reactive species much more effectively than lower members. The formation of reactive species was near unity which means all polyphenyls generate reactive species equally on a molar basis. Thus, the composition of the radiolytic high boiler is governed largely by scavenging ability. Since the higher members scavenge better, the molecular weight distribution of the high boiler would be higher than expected from purely statistical considerations.

Generating chemical free radicals (from iodobiphenyl and ultraviolet light) in polyphenyl mixtures gave a comparison between radical and irradiation data for the probability of benzene reacting with an activated species β (Table IV).

TABLE IV
FREE RADICAL AND ELECTRON RADIATION DATA
FOR THE PROBABILITY OF BENZENE REACTING (β)

	<u>Mixtures</u>	
	<u>$\phi_1 + \phi_2$</u>	<u>$\phi_1 + m-\phi_3$</u>
Electron	0.29	0.13
Free Radical	0.25	0.15

The good agreement between the radical and electron data may indicate a free radical process occurs during irradiation. In addition, a linear relationship was found between mixture concentrations and the scavenging or forming ratios.

A detailed analysis was made on a benzene-biphenyl electron radiolysis mixture. The yields of all the isomeric terphenyls and quaterphenyls was determined and partial rate factors calculated. In a previous section the partial factors were reported for the radiolysis of pure biphenyl. There was good agreement between the two experiments, although the mixtures gave lower r_0 values. No simple explanation for this behavior is apparent.

A detailed study of m-terphenyl in benzene and perdeuterobenzene gave information concerning the partial rate factors for each position in m-terphenyl [5]. The rigorous mathematical treatment [4] is omitted here. The

two reactants were used so that all 21 possible isomeric hexaphenyls need not be determined individually. From the yield of biphenyl, the individual quaterphenyl isomers and the total hexaphenyl isomers, the partial rate factors were calculated:

Partial rate factors were calculated for m-terphenyl using data from the biphenyl experiment (Table V). In the calculations, an additivity principle was assumed. The reactivity of a given position of terphenyl is a product of the corresponding factor from biphenyl. For example, k_d above is a product of k_o^2 from biphenyl. Good agreement was obtained between the experimental values for m-terphenyl and those calculated from biphenyl.

TABLE V
PARTIAL RATE FACTORS FOR m-TERPHENYL AT 80°C

Formation of Radicals		Scavenging by Molecules	
r_a	0.71	k_a	1.17
r_b	1.00	k_b	1.00
r_c	1.34	k_c	2.62
r_d	0.96	k_d	1.31
r_e	0.88	k_e	2.68
r_f	0.72	k_f	0.88

A parallel was noted between the mechanism (radiolytic gas production) proposed by Dyne and Jenkinson [7] and the general polyphenyl mechanism proposed above.

Second Order Mechanism (Dyne)

Dyne explained the hydrogen yields on the basis of a second-order process and a first-order process:

This laboratory's radical and scavenging probabilities based on the initial polyphenyl products can be used to describe the hydrogen yields obtained by Dyne from the radiolysis of benzene-perdeuterobenzene mixtures.

The above experiments have contributed to understanding the radiolysis mechanism of polyphenyl. The following conclusions can be drawn:

- (1) The radiolysis process is not random; certain reactions are favored.
- (2) The scavenging reactions largely determine the distribution of the products.
- (3) The additivity principle appears to operate for higher polyphenyls so calculations can be used.
- (4) The hydrogen gas production can be related to polymer formation.
- (5) A free radical process appears to explain the products fairly well.

4. CHLOROBENZENE RADIOLYSIS

There were two objectives in studying the radiolysis of chlorobenzene: (a) to learn whether products from beta radiation resembled those from gamma radiation, (b) to learn whether products from radiolysis resembled those from a free radical process. The experimental details are given in previous reports [8, 9]. The following tabulation gives the results from radiolysis at 80°C:

Treatment	ϕ_H	Dichlorobenzenes			ϕ_2	Monochlorobiphenyl		
		o-	m-	p		2-	3-	4-
Beta	60.1	5.0	2.2	4.3	6.7	8.2	7.4	6.1
Gamma	49.8	4.8	2.0	4.3	5.1	14.4	10.7	8.9

The analytical data were poor but results indicate the same type of products in about the same yield were obtained for both forms of radiation. This result would be expected if one assumes gamma irradiation ejects electrons from the molecules and most of the damage is due to the subsequent events.

The products from chlorobenzene radiolysis and free radical were normalized to biphenyl and the isomeric chlorobiphenyls (Table VI).

TABLE VI
CHLOROBENZENE IRRADIATIONS

Treatment	Monochlorobiphenyls			
	ϕ_2	2-	3-	4-
Beta radiation	23.2	28.6	26.2	22.0
Gamma radiation	13.3	37.0	27.2	22.5
Gamma m- $\phi_3/\phi Cl$ (50 mole %)	9.4	46.7	28.0	15.9
$\phi Cl + (\phi-COO)_2$ } Free Radical	6.0	54.1	26.6	13.3
$\phi Cl + \phi I$ (U.V.)	-	52.3	32.3	15.4

The analytical data were poor but if the biphenyl yield is combined with the 2-chlorobiphenyl yield, the product yields from radiolysis resemble those from free radical reactions. Biphenyl appeared to be formed at the expense of 2-chlorobiphenyl in systems where acids were present. The conversion could arise from the following sequence:

The elimination of HCl from the cyclohexadiene may be favored by acid conditions which were present under radiolysis and the benzoylperoxide experiment. The iodide experiment generated free iodine rather than HI during the reaction.

These results indicate the radiolysis products resembled those from free radical reactions. In the radiolysis, all products found could be rationalized on the basis that the principal act was the formation of a chlorine atom and a phenyl radical.

5. ELECTRON IRRADIATION KINETICS OF POLYPHENYLS

In order to understand the mechanism of electron radiolysis, experiments were made to determine the kinetic order of the reaction. Biphenyl, the three isomeric terphenyls, and Santowax OMP were irradiated with 6-Mev electrons at 600°F. About 40 percent conversion was reached in 40 hours. Experimental details were reported previously [10].

The data were rough but appeared to fit second-order kinetics somewhat better than first-order. The ratio of the rate constants was about the same as gas values reported by Colichman and Gercke [11].

<u>Terphenyl</u>	<u>$k \times 10^{12}$ (liter/mole-rads)</u>	<u>Ratio</u>	<u>G (gas) $\times 10^3$</u>	<u>Ratio</u>
Ortho	14.9	1.50	8.5	1.47
Meta	12.1	1.22	7.1	1.22
Para	9.9	1.00	5.8	1.00

In the electron radiolysis of Santowax OMP, a linear relationship was observed between dosage and molecular weight of the sample [12]. As stated previously, the second-order kinetics generated a high-boiler curve which increased at decreasing rate with dose.

In the biphenyl radiolysis the quaterphenyl, hexaphenyl, and octaphenyl products were determined and the rate constants for the various reaction steps were determined:

As the data show, the rate constants for subsequent reactions increase. This tendency was observed with the scavenging order of polyphenyls. The sum of the rates for the individual reactions steps was equal to the rate of disappearance for the biphenyl at low conversions. At higher conversions, the sum of the individual rates became increasingly larger than the rate of disappearance. This discrepancy probably arose from the assumption that all the higher products were polyphenyls. NMR analysis showed successively greater amounts of alkyl hydrogens in the higher fractions. Also, polyphenyls above octaphenyl were not considered.

Fractional sublimation of Santowax R radiolysis products (16 hours at 600°F, 23 percent HB generated) gave the following distribution: 61 percent hexaphenyls,

27 percent nonaphenyls, 10 percent dodecaphenyls, 2 percent pentadecaphenyls [13]. Again, the data show the products are primarily multiples of the starting polyphenyl. Also, the higher polyphenyls build up rather quickly.

The following conclusions can be made from studying the kinetic behavior of polyphenyls under electrons at 600°F:

- (1) Second-order kinetics best described the radiolysis
- (2) The stability of the terphenyl isomers were: para > meta > ortho. This is the same sequence as noted with the gaseous products.
- (3) Rate constants for each subsequent step in the biphenyl radiolysis increased. This reflects the increased scavenging ability of higher polyphenyls.
- (4) Product analysis from biphenyl and m-terphenyl electron radiolysis showed a rapid rise in higher polyphenyls which were molecular weight multiples of the starting material.
- (5) A linear relationship was found between dose and molecular weight.

6. REACTIONS OF POLYPHENYLS WITH HYDROGEN ATOMS

In the radiolysis of polyphenyls, the G values for hydrogen formation are about an order of magnitude less than the G polymer values assuming radiolysis proceeds largely by a free radical process. The fate of most of the hydrogen atoms formed is therefore unknown. To study this, hydrogen atoms were generated and passed through o-terphenyl and m-terphenyl at 80°C and the products then subjected to analytical sublimation (Table VII) [14].

NMR and infrared analysis indicated the aliphatic structure was of the ring type. No methyl groups were indicated. The above data suggest the hydrogen

TABLE VII
PRODUCTS FROM HYDROGEN ATOM REACTIONS

Property	Total	o-Terphenyl		Total	m-Terphenyl	
		Sublimate	Residue		Sublimate	Residue
Weight percent	100	93	7	100	92	8
Molecular weight	246	237	469	248	235	502
Melting point (°C)	-	-	60-75	68-80	60-80	70-80
NMR:						
% Aromatic protons	93	94	57	89	90	49
% Olefinic protons	2	2	9	2	1	8
% Aliphatic protons	5	4	34	9	9	43

atoms cause dimerization and partial hydrogenation in the higher fractions. Since phenyl radicals were found to prefer to add to higher polyphenyls, it can perhaps be assumed that hydrogen atoms behave similarly.

The data do not point to any definite conclusion but an obvious explanation would be that the hydrogen atoms added to double bonds in the aromatic rings. Subsequent steps may be disproportionation, dimerization, and polymerization. The latter two reactions would favor higher-molecular-weight products and these products may add hydrogen more effectively than the starting material.

7. PURE POLYPHENYL REFERENCE SAMPLES

7.1 Objective

The purpose of this work was to make available pure samples of polyphenyls to aid in the full understanding of the radiation chemistry of these materials. Very pure biphenyl and the terphenyl isomers were needed for radiolytic experiments. The quaterphenyl and hexaphenyl dimers of these were necessary for calibration of analytical instruments and positive identification of the radiolysis products.

The program comprised several aspects: (a) purification of large samples of biphenyl and the terphenyl isomers, (b) a synthetic program to produce small samples for identification and calibration purposes of all the quaterphenyls and of the hexaphenyl isomers expected in greatest amount from dimerization of each of the terphenyls, and (c) preparation and purification of larger amounts of certain polyphenyls.

It was part of the objective of this work to make the synthesized polyphenyls available to the other U. S. contractors, the AECL, and Euratom wherever possible and in turn to obtain such isomers as they synthesized. The Euratom program in quinquephenyls was particularly helpful.

7.2 Experimental Procedures

7.21 Purification of Biphenyl and Terphenyls. Most of the commercial biphenyl obtained was found by analysis on the chromatograph to be free of contaminants. Some samples required vacuum distillation. Purification of p-terphenyl was easily done by simple recrystallization [15]. Ortho-terphenyl in most cases was recrystallizable to a very pure material [15]. In some impure samples encountered by others a minor quantity of a bright yellow substance difficult to separate was encountered. Studies in the identification of this material, which was found only in Santowax, are described elsewhere in this report.

The purification of m-terphenyl proved difficult, since the best commercial samples yielded the eutectic mixture with p-terphenyl containing 4.3 percent of the latter. Ordinary recrystallization produced no change of course. A two-stage process was developed, depending upon the slower growth of the p-terphenyl crystals at low concentration [16]. The sample was first dissolved in hot cyclohexane, cooled to 30°C, and filtered to remove substantially pure para isomer. Further cooling to 10°C gave the bulk of the material as 98 percent meta

isomer. It was then recrystallized by dissolving in hot methanol-ethanol solvent, and separating the pure meta isomer that separated above 40 to 45°C. Below this temperature the characteristic platelets of the para isomer appear. Prepared in this manner meta-terphenyl of 99.8 percent purity was obtained. Recrystallization gave a product in which no impurity could be detected on the chromatograph [16].

7.22 Synthetic Program. In this program, it was decided that all the possible quaterphenyls would be obtained. Calculations were made earlier [17] whereby relative yields of hexaphenyls formed from the electron irradiation of m-terphenyl and p-terphenyl at 500 to 600°F were predicted. The 9 most plentiful predicted from the meta isomer and 10 from the para isomer were to be prepared. Quinquephenyls would be included only as convenient incidental to other preparations. Some substituted polyphenyls were later of interest.

Four meta-linked polyphenyls were supplied by the U. S. Bureau of Standards and two quaterphenyls were found to be commercially available. In addition, the present synthesis program afforded 6 quaterphenyls, 2 quinquephenyls, and 11 hexaphenyls, 5 of which were heretofore unknown compounds (Table VIII). The balance of the program has been directed towards the preparation of intermediates necessary in the syntheses of these selected hexaphenyls.

A brief review of the literature quickly revealed a number of potential routes to the synthesis of polyphenyls. It would be superfluous to list all of these numerous methods, many of which are considered "classical text book" reactions. Most appeared to have certain disadvantages. The Wurtz reaction ($R-X + 2Na \rightarrow R-R$) invariably gives mixtures; the Ullmann reaction ($2RI \xrightarrow{Cu} R-R$) is not satisfactory for unsymmetrical polyphenyls; and the Gomberg-Bachmann reaction ($RN_2Cl + NaOH + R' \rightarrow R-R'$) generally gives both low yields and mixtures.

The addition of Grignards or aryllithiums to polyaryl cyclic ketones followed by dehydration and aromatization proved to be the most successful method both from the standpoint of ease of synthesis of the organo-metallic and from the availability of the aryl bromides and cyclic ketones. This general method is given as follows:

TABLE VIII
COMPOUNDS PREPARED UNDER CONTRACT

<u>A. QUATERPHENYLS</u>				
No.	Compound	a. M.P.C.	Reference	
		b. B.P.C.	IDO No.	Page
1	2,2'-Diphenyl-biphenyl	a. 117-118	16705	37
2	2,3'-Diphenyl-biphenyl	a. 90-90.5	16705	38
3	2,4'-Diphenyl-biphenyl	a. 117-118	16705	38
4	3,4'-Diphenyl-biphenyl	a. 166-168	16734	34
5	1,2,3-Triphenylbenzene	a. 156	16734	32
6	1,2,4-Triphenylbenzene	a. 96-97	16705	38
<u>B. QUINQUEPHENYLS</u>				
7	1,2,3,4-Tetraphenylbenzene	a. 193	16705	38
8	1,4-Bis(3-xenyl)-benzene	a. 232	16705	39
<u>C. HEXAPHENYLS</u>				
9	1,2,3,4,5-Pentaphenyl-benzene	a. 250	16705	39
10	4,4'-Di-(3-xenyl)-biphenyl	a. 280	16705	40
11	2,4-Di-phenyl-3'-(3-xenyl)-biphenyl	a. 145-146	16705	40
12	3,4'-Di-(3-xenyl)-biphenyl	a. 192-195	16734	34, 35
13	2,4'-Di-(3-xenyl)-biphenyl	a. 128-130	16734	35
14	3,5-Diphenyl-4'-(3-xenyl)-biphenyl	a. 154-155	16734	35
15	4,4'-Di-(2-xenyl)-biphenyl	a. 228-231	16761	34
16	2,3'-Di-(3-xenyl)-biphenyl	a. 58-60	16787	40, 41
17	3,4'-Di-(4-xenyl)-biphenyl	a. 321-323	16787	41
18	2,4'-Di-(4-xenyl)-biphenyl	a. 231-232	16787	41
19	2,4-Diphenyl-2'-(3-xenyl)-biphenyl	a. 67-70	16869	39
<u>D. SUBSTITUTED BIPHENYLS</u>				
20	2-Bromo-biphenyl	b. 144-156/10 mm	16675	28
21	2-Iodo-biphenyl	b. 190/36 mm	16675	28
22	3-Bromo-biphenyl	b. 160/10 mm	16675	28
23	3-Chloro-biphenyl	b. 120/3.7 mm	16869	38, 39
24	4-Nitro-biphenyl	a. 110-112	16675	28
25	4-Amino-biphenyl	a. 50-52	16675	28, 29
26	4-Acetamino-biphenyl	a. 168-172	16675	29
27	3,4'-Dibromo-4-acetamino-biphenyl	a. 194	16675	29
28	2',4'-Dibromacetanilide	a. 79	16675	30
29	4-Acetamino-4'-nitro-biphenyl	a. 248	16830	42

TABLE VIII (Cont'd)

D. SUBSTITUTED BIPHENYLS (Cont'd)				
No.	Compound	a. M.P.C.	Reference	
		b. B.P.C.	IDO No.	Page
30	3-Bromo-4-acetamion-4'-nitro-biphenyl	a. 233	16830	42
31	3-Bromo-4-amino-4'-nitro-biphenyl	a. 116	16830	42; 43
32	3-Bromo-4'-nitro-biphenyl	a. 90	16830	43
33	3-Bromo-4'-amino-biphenyl·HCl	-	16830	43
E. SUBSTITUTED TERPHENYLS				
34	4'-Bromo-m-terphenyl	b. 189/2 mm	16675	29
35	4'-Carboxy-m-terphenyl	a. 168	16675	29
36	4-Bromo-m-terphenyl	a. 86	16734	33
37	4-Bromo-p-terphenyl	a. 232	16734	33
38	3-Bromo-m-terphenyl	b. 200/1.5 mm	16761	53
39	3-Bromo-p-terphenyl	a. 147	16830	43
40	4-Nitro-p-terphenyl	a. 208	16869	39, 40
41	4-Amino-p-terphenyl	a. 200	16869	40
42	2-Amino-p-terphenyl	a. 159	16869	41
43	4,4''-Dinitro-p-terphenyl	a. 269	16869	41
F. SUBSTITUTED CYCLIC KETONES				
44	3-Ethoxy-cyclohex-2-ene-1-one	b. 80/1 mm	16705	36
45	2-Phenylcyclohexanone	a. 57	16705	36
46	2-Chlorocyclohexanone	b. 83/12 mm	16675	30
47	2-(2-xenyl)-cyclohexanone	b. 145-160/ 0.45 mm	16705	36
48	3-Phenyl-cyclohex-2-enone	a. 61	16705	37
49	3-(3-xenyl)-cyclohex-2-enone	a. 62	16705	37
50	3-Ethoxy-5-phenyl-cyclohex-2-enone	b. 76-8/8 mm	16705	37
51	3-(4-Bromophenyl)-cyclohex-2-enone	a. 79	16734	33
52	3,5-Diphenyl-cyclohex-2-enone	a. 77	16734	33
53	2-(3-Bromophenyl)-cyclohexanone	b. 135/0.5 mm	16734	33, 34
54	2-(3-xenyl)-cyclohexanone	b. 178/0.3 mm	16734	34
55	3-(3-Bromophenyl)-cyclohex-2-enone	b. 170/2 mm	16761	52
56	3-(4-xenyl)-cyclohex-2-enone	a. 159	16787	40
57	2-(4-xenyl)-cyclohexanone	a. 95	16787	40
58	1,4-Diphenyl-but-1-ene-3-one	a. 70	16807	30
59	Ethyl-2,4-dioxo-3,6-diphenyl-cyclohexane carboxylate	a. 173	16807	30
60	2,6-Diphenyl-cyclohexane-1,3-dione	a. 245	16807	31
61	3-Methoxy-2,5-diphenyl-cyclohex-2-enone	a. 137	16830	43, 44
62	2,5-Diphenyl-3-(4-terphenyl)-2-cyclohexenone	a. 180	16830	44

The introduction of various type linkages was brought about by several select compounds. The method developed by G. F. Woods and modified in this laboratory [18] constituted the only procedure for the synthesis of internal meta linkages:

The Grignard addition to 2-chlorocyclohexanone followed by rearrangement reported by Bartlett [19] was the method used for introducing ortho linkages, as represented by the equation below:

Para linkages were introduced into the molecules by para-substituted phenyllithiums according to the general method given in the first equation. It must be noted yields of the desired materials were extremely low when impurities were present and therefore considerable time and effort was spent in purification techniques. The compounds involved in the introduction of various type linkages were as follows:

Position	Linkage		
	ortho	meta	para
internal			
external (ring)			

When a 2-substituted cyclohexanone was used in the coupling reaction, the intermediate alcohol was generally isolated whereas with a 3-substituted cyclohex-2-ene-1-one dehydration occurred spontaneously to produce the intermediate diene which was isolated. Aromatization was completed by heating the

precursor with 10 percent palladium/charcoal, with red phosphorous at 300°C, or if necessary with boiling bromine/chloroform.

Purification of the polyphenyls was for the most part by recrystallization; however, some were purified by passing through an activated alumina column or by sublimation.

Details of the synthesis of the various polyphenyls and intermediates have been given in quarterly reports. Table VIII lists those compounds which have been prepared under this contract. The melting or boiling points are given as well as the report and page number where the details of the preparation of these compounds can be found.

7.23 Polyphenyl Synthesis by Free Radicals. 1,2,3-Triphenylbenzene was needed for a chromatographic reference compound. Classical synthesis of this compound [20] was extremely long and gave poor yields. The compound was prepared by a method involving attack of phenyl free radicals on an aromatic hydrocarbon molecule and separation of the products:

Both routes depend upon the attack of phenyl radicals upon a terphenyl isomer. Orthoterphenyl was chosen because higher yields of the desired product would be expected from statistical and steric consideration.

A pilot run was made by irradiating phenyl iodide in *o*-terphenyl [21]. 1,2,3-Triphenylbenzene was separated on a gas chromatographic prep column and identified by melting point and infrared spectrum. A larger run was made at 90°C with *o*-terphenyl (500 g) and benzoyl peroxide (50 g). The products were partially separated by vacuum distillation. The distillation fractions were analyzed by GSC to determine what isomers were present. Certain fractions were redistilled and products purified by recrystallization from solvents [21]. The following compounds were obtained in pure form: *o, o*-quaterphenyl (2.2 g); 1,2,3-triphenylbenzene (1.4 g) and *o, p*-quaterphenyl (3.5 g). The 1,2,4-triphenylbenzene and *o, m*-quaterphenyl products could not be separated.

Different product distributions were obtained by the ultraviolet and peroxide methods (Table IX).

TABLE IX
RELATIVE YIELDS OF QUATERPHENYLS

Product	Relative Yield		
	UV*	Peroxide	Statistical
o,o- ϕ_4	1.6	1.3	2
1,2,3- Ph_3Bz	1.0	1.0	1
o,m- ϕ_4	1.3	1.8	2
o,p- ϕ_4 and 1,2,4- Ph_3Bz	3.3	3.5	2

* Triphenylene free basis.

Triphenylene was a major product in the ultraviolet method but none was found when peroxide was used. The iodine or light may cause the cyclization reaction. The tabulation indicates a different product ratio between methods. In addition the radical attack upon o-terphenyl did not occur in a statistical fashion. Ortho linkages were less favored and para linkages were more favored. Steric and resonance effects may be operating. The method may have application for the preparation of other polyphenyls. Good means of separating the products are needed for success.

8. ANALYTICAL METHODS FOR POLYPHENYLS

For the study of polyphenyl products from radiolysis and the chemical analysis of fouling film, analytical methods suitable for these materials for a wide variety of determinations were requested. Instrumental analysis such as infrared, nuclear magnetic resonance, molecular weight, neutron activation, X-ray diffraction, X-ray fluorescence, electron microscopy, as well as chemical methods were useful in characterizing these products. A topical report [22] gives all the experimental details and results of high-boiler analysis. Additional details, particularly on chromatography, are included in another topical report [23]. Some methods gave new data or offered new interpretation concerning high-boiler structure.

8.1 Nuclear Magnetic Resonance

Nuclear magnetic resonance gave data concerning the aliphatic structure in the radiolyzed polyphenyl high boiler. The following conclusions have been drawn from NMR data:

- (1) No olefinic unsaturation was found in the radiolyzed products from OMRE high boiler or in products from the electron irradiation of biphenyl and the terphenyls. Evidently any olefins which formed during radiolysis reacted quickly as hydrogen scavengers or by polymerization.

(2) NMR showed that higher-molecular-weight fractions (in the sublimation of high boiler) contained more aliphatic hydrogen. This supports the theory that olefins disappeared by polymerization and/or hydrogenation. This result accounts for the fact that G (polymer) is about an order of magnitude greater than G_{H_2} . Part of the hydrogen generated during radiolysis reacts with polymeric material. This finding also indicates the irradiation mechanism involves some reactions more complicated than simple dimerization.

(3) The lack of naphthene structures in all irradiated samples (except o-terphenyl) indicated a ring-opening mechanism for non-fused structures. Ring opening may occur prior to ring saturation followed by rupture because no naphthenes were detected. Only partially hydrogenated triphenylenes were found in the o-terphenyl irradiation products. Therefore, rupture may occur in partially saturated structures. Scission was indicated by the presence of alkylated side chains.

(4) Chemically hydrogenated OMRE high boiler did not resemble irradiated high boiler. Thus, hydrogenation in the reactor favored ring scission while chemical hydrogenation favored ring saturation.

(5) NMR showed only small amounts of methyl groups adjacent to aromatic rings in the irradiation of the terphenyls. Longer alkyl groups predominated.

(6) Sublimed cuts from the irradiated terphenyls gave broad NMR signals which increased with molecular weight. Electron spin resonance confirmed the presence of free radicals in the sublimed cuts. The ESR signal resembled those from carbon black and asphaltenes.

(7) NMR was useful in determining the type of linkages in a single, pure polyphenyl. Also, mixtures of linear polyphenyls could be analyzed by the various linkages present.

Most of the experimental details and results were given in three quarterly reports [24 - 26].

8.2 Infrared Correlations in Polyphenyl Structure

The systematizing of polyphenyl infrared spectral data leads to certain observations about structure. The generalizations have been reported [25] previously and the details more recently [23 - 27].

In summary, the following spectral changes occurred with structural changes:

(1) As the number of consecutive para linkages increased in a molecule, the infrared band shifted to longer wavelengths: 11.7 microns for one para linkage to 12.25 microns for four.

(2) A band at 13.7 to 14.8 microns due to mono-substituted aromatics varied according to the position of the terminal substituent.

(3) Increasing successive meta linkages caused the wavelength to shift from 12.4 to 12.9 microns as the meta chain grew.

(4) A low meta band due to the single hydrogens between the meta branches was displaced to longer wavelength in trisubstituted meta structures.

8.3 Number Average Molecular Weight

The molecular weight of the high boiler in the coolant was formed to change with irradiation. Fractional sublimation of OMRE high boiler (541 average molecular weight) indicated that after 50 percent sublimation the residue had a number average molecular weight of 1160. Additional electron irradiation raised the molecular weight to 580 while the 50 percent residue was 1440. This represents a great increase in the heavier ends.

Maintaining the OMRE high boiler at 700°F for seven hours failed to change the molecular weight profile. Evidently, pyrolysis of high boiler does not occur at this temperature.

When OMRE high boiler was treated with Wyex carbon black, the higher ends were preferentially adsorbed. The average molecular weight decreased to 500 and the 50 percent residue was 900.

These experiments provided information about the radiolysis process in high boiler. PCFT experiments have shown that high-molecular-weight components in the high boiler gave increased fouling. Carbon black selectively removed these components. Thus, the molecular weight profile could be used to monitor reactor coolant for fouling potential.

8.4 Weight Average Molecular Weight

The data from the Static Pyrolytic Capsule experiments indicated fouling was more severe when high boiler was present [28]. Also, certain higher-molecular-weight fractions appeared to be more active in fouling. Data from the radiation of aromatic mixtures showed higher polyphenyls scavenged free radicals more efficiently than low-molecular-weight molecules.

Both these results indicated the molecular weight of the high boilers was important, and specifically, the higher ends contained. Number average molecular weight is relatively insensible to changes occurring to the higher-weight molecules. Weight average molecular weight is more sensitive to changes in the molecular weight of the higher fractions. Weight average molecular weight, $\bar{M}_w$, can be determined by light scattering or centrifugation methods. However, the dark color of the high boiler prevents the use of these methods.

A method was developed whereby a high-boiler profile was prepared by determining the number average weight of successive sublimation fractions and the corresponding residue. The number average molecular weight, $\bar{M}_n$, of each fraction was determined on a Mechrolab Osmometer. About 10 fractions

were needed to form the profile. Mathematical equations and graphs were used to determine $\bar{M}_w$. Table X shows how certain treatments greatly affected $\bar{M}_w$ but $\bar{M}_n$ showed little change.

TABLE X
AVERAGE MOLECULAR WEIGHT COMPARISONS

	$\bar{M}_n$	$\bar{M}_w$
OMRE high boiler	541	1296
Same as above plus additional irradiation	573	2118
Same as original but treated with carbon black	504	852

The results show how $\bar{M}_w$ better reflects the changes occurring in the high boiler. Not only does this method solve the problems at hand but makes possible the determination of $\bar{M}_w$ for similar systems.

9. NEW ANALYTICAL METHODS

In some problem areas, new analytical procedures had to be developed where old procedures could not be modified. For example, in the study of the products from biphenyl and terphenyl radiolysis, ordinary gas chromatographic columns would not elute the quaterphenyl, quinquephenyl, and hexaphenyl products. Therefore, new types of column packing were required.

9.1 Gas Chromatography

In the analysis of the many high-boiling isomeric polyphenyls, only gas chromatographic analysis was feasible. Ordinary columns which contained an organic phase bled badly and would not elute higher polyphenyls. Similar limitations were found with liquid eutectic inorganic salts. Lithium chloride on Chromosorb P was found to give good separations up to 500°C [29, 30]. This column operated on an adsorption-desorption principle between the solid and gas phase rather than by the usual liquid-gas phase process.

Other salt columns of the alkali metals and alkaline earth metals were investigated [23]. It was found that different salts affected the elution temperature and elution order of the polyphenyls. For example, the most difficult separations were between o,p-quaterphenyl and 1,2,4-triphenylbenzene (quite similar structurally), and 1,3,5-triphenylbenzene and m-quaterphenyl. In the latter pair, the branched compound eluted ahead of the linear one on a CsCl column, while on LiCl the two almost coincided, and the order was reversed on a CaCl₂ column. Other changes of this type were noted and correlated with polyphenyl structure. Thus, the structure of many unknown hexaphenyl isomers was tentatively established by the type of shift they exhibited on different columns. Two columns, LiCl and CaCl₂, were most useful in separating the

hexaphenyl radiolysis products from each of the terphenyl isomers (10 from para, 21 from meta, and 15 from ortho).

From a correlation of structure and elution temperature, it was possible to predict the elution temperature for each hexaphenyl isomer based on structure. Each polyphenyl was assigned an elution number. The number for each hexaphenyl was calculated from the type of bonds in the molecule. A straight-line function was found to exist between elution number and elution temperature. Branched structures were given numbers based on an equivalence with a linear form which eluted at the same temperature. Each polyphenyl family (quaterphenyl, quinquephenyl, hexaphenyl) had its own series of elution numbers. Also, the system had to be changed for columns other than LiCl. The elution numbers are tabulated for each family in Table XI.

Polyphenyl Type	Linkage Values		
	<u>o</u>	<u>m</u>	<u>p</u>
ϕ_3	20	44	13
ϕ_4	32	32	12
ϕ_5	35	25	11
o- ϕ_6	36	18	10
m- ϕ_6	26	29	8
p- ϕ_6	21	32	10

Branched structure equivalents are:

1,2 substitution = ortho

1,3 substitution = meta

1,2,4 substitution = o,p-linear, designated (o,p)

1,3,5 substitution - m,m-linear, designated (m,m)

1,2,3 substitution - o,m-linear, designated (o,m)

The single linkages have the following correlation:

one meta = two ortho

one para = 1,2,3-branched

Elution numbers were useful in establishing hexaphenyl isomer structure. An unknown hexaphenyl eluting at a certain temperature would be assigned an elution number (from graph of elution number vs elution temperature). Structures would be proposed which corresponded to the elution number. In addition, the peak shift would be noted on a different type of salt column and more structural detail deduced. Finally, calculation from partial rate factors [1] indicated the relative size of the peak. These techniques in addition to chromatographic trapping established many of the hexaphenyl isomers from the radiolysis of the individual terphenyls.

In conclusion, the development of salt columns for studying high-molecular-weight polyphenyls permitted analyses previously not possible. Much of the fundamental work on radiolysis mechanism in the program would have been impossible without this tool.

9.2 High-Boiler Sublimation

Analysis for high boiler was found to be most satisfactorily carried out by a micro-sublimation technique. While the method adopted was essentially that of Bates [31], considerable development was done on the apparatus used. Calibrations were run which established that different sublimation conditions were required for accurate analysis of samples in several different concentration ranges [32, 33]. It also was established that chromatographic analysis of both the sublimate and the residue is necessary for precise determination in any case.

III. STABLE COOLANT STRUCTURES (W. M. Hutchinson, R. C. Doss)

1. GENERAL PROGRAM

1.1 Objectives and Scope

The objective of these investigations was to find or develop coolants whose molecular structures are very stable when subjected to radiolysis at elevated temperature, exceeding those of the currently used terphenyls, and approaching the ideal of complete stability under proposed reactor conditions.

The objective of the study, it was conceived, would be met primarily by application of knowledge and principles to be developed in the preceding basic investigation of radiolysis. Thus, a logical, scientific method could be used in searching for and selecting compounds for evaluation, or in designing and subsequently synthesizing structures which should approach ideality. In addition, however, the investigation was to include evaluation of compounds selected from certain classes which earlier theory suggested should be stable but which had been neglected in the extensive but rather random studies heretofore completed.

Stability would be judged of course primarily by disappearance of the coolant molecules as such. The appearance of polymer as evidence of this disappearance probably would be the most important way in which it would be measured. Gas and light liquids formation would be less important parameters. Freedom from deposition of a film of decomposition products became a practical and very important criterion of coolant stability during this period.

1.2 Theoretical Development

When benzenoid compounds such as terphenyl are radiolyzed they form hydroaromatic compounds as a consequence of addition of hydrogen atoms and aryl radicals to benzene rings. For example:

Gas chromatographic analysis of extensively radiolyzed benzene showed that only about three percent of the hydroaromatic products expected from addition of phenyl radicals and hydrogen atoms to benzene were present. This suggested that these hydroaromatics were preferentially converted to polymer. For example:

This polymer may be a source of organic film deposit.

These hydroaromatic compounds are readily aromatized by air but some oxygenation is usually observed. Certain oxygenated compounds capable of forming chelates with iron have been associated with deposition of iron compounds, particularly the percarbide, on hot metal surfaces [34]. Terphenyl exposed to air after irradiation also develops the property of dissolving

iron [35]. Thus, it appears desirable to eliminate hydroaromatic compounds from coolants.

Two approaches to the elimination of hydroaromatic compounds from coolants have been considered. One is to hydrocrack radiolyzed coolant over a solid-contact catalyst in the presence of hydrogen [36]. This treatment removes iron and oxygenated compounds and aromatizes hydroaromatics because the temperature-pressure regime is on the dehydrogenation side. It is primarily a reclamation process to recover coolant from the polymer. The other approach is to eliminate radiolysis of C-H bonds in a coolant by substituting a weaker bond that ruptures into two radicals that are so inactive that they can only dimerize back to the starting material; ie, are "self-healing".

1.3 Evaluation

A concept of "self-healing" coolants has been developed. Together with a type of hydrogen-donor coolant derived from hydrogenated condensed-ring compounds, first noted in working with stabilizers, and with certain types of heterocyclics, several profitable fields for study have been opened up. The undesirability of hydrogenated polyphenyls in the coolant has been pointed out.

Terphenyl has excellent thermal stability and no coolant superior to it in this property was demonstrated during this study. Several compounds generated polymer more slowly than terphenyl while under simultaneous and equal radiation from a 6-Mev linear electron accelerator at 600 to 650°F. Lower polymer yield in one clear-cut case was found to be due to changing the course of reaction subsequent to radiolysis into reactive fragments. In other less definite cases, low polymer yield probably was due to greater internal conversion of excitation energy.

2. HYDROGEN-DONOR COOLANTS

The object of this study was to examine certain hydrogenated polycyclics, particularly dihydrophenanthrenes, to determine whether by serving as hydrogen donors, they might inhibit attack by generated free radicals on aromatic rings. Evidence of an action of this sort had been developed in the researches in stabilizers.

9,10-Dihydrophenanthrene was found to yield only 17 weight percent of the polymer formed in terphenyl (Santowax OMP) under simultaneous and equal irradiation [37]. Phenanthrene also was formed. Direct dehydrogenation of 0, 10-dihydrophenanthrene was observed to occur thermally at 750°F and higher temperatures and presumably occurred to some extent at 650°F under electron irradiation.

The low yield of polymer is believed to be due to the preferential formation by at least two processes of a radical (A) with its odd electron at the 9 (and 10) position but so associated with the π electron system of neighboring rings that the radical (A) is incapable of substituting an aromatic ring:

The coefficient (actually, relative probabilities) $P_a = 0.48$ and $P_s = 0.52$ were evaluated from data on secondary hydrogen abstraction from toluene and ethylbenzene by phenyl radicals [38]. These were used to interpret the radiolysis of toluene into benzyl and tolyl radicals [39] to yield values of $P_c = 0.67$, $P_n = 0.33$. This resulted in a calculated yield of radiolytic polymer ($=P_n P_s$) from 9,10-dihydrophenanthrene relative to phenanthrene of 0.17, which compared well with the experimental relative yield of 0.22. Direct dehydrogenation reactions prevented similar interpretations of relative yields of hydrogen gas and phenanthrene from 9,10-dihydrophenanthrene.

9,10-Dihydrophenanthrene yielded little polymer on pyrolysis up to 800°F. Dehydrogenation was almost complete after 48 hours at this temperature. Means of hydrogenation of phenanthrene back to 9,10-dihydrophenanthrene would be necessary should the latter be used as a coolant.

3. HETEROCYCLIC COOLANTS

The objective of this project was to test the idea that some aromatic heterocyclic systems might not form reactive hydroaromatics on radiolysis. Most nitrogen-containing heterocyclics had been subjected to test in earlier surveys, but certain obvious gaps existed. The pyridine series was one very obvious one insufficiently studied. Other rings containing several nitrogen atoms, or nitrogen in condensed-ring structures were of interest also.

To test this idea benzene, imidazole, pyridine, and thiophene were extensively irradiated with 6-Mev electrons. These materials generated approximately equal amounts of gas (mainly hydrogen) during radiolysis. Imidazole formed no polymeric products other than carbon. Radiolyzed benzene, pyridine, and thiophene contained first- and second-generation polymer (dimer and trimer) but apparently little hydroaromatic products. The low yield of hydrogen gas indicated that hydroaromatic products had been formed, but their low final concentration suggested that they were preferentially converted into higher polymers under irradiation.

These results did not promise much advantage in cleanliness or stability for these heterocyclic systems over benzenoid coolants. Several heterocyclics had already been tested or prepared for testing. 2,4,6-Triphenyl-s-triazine produced only one-third as much polymer as terphenyl under equal electron irradiation at 650°F and was very stable thermally up to at least 750°F. Interestingly, 2,4,6-tri-(m-toyl)-s-triazine possessed no outstanding radiolytic or thermal stability. 1,5-Naphthyridine had an initial rate of polymer formation that was 0.2 percent that of m-terphenyl at 180°F. This compound itself is too volatile for coolant use. Quinoline was about equal to terphenyl and 2,2'-bipyridyl and 1,2-bis-(4-pyridyl) ethylene were inferior to terphenyl in radiolytic stability. Phenanthridine and 7,8-benzoquinoline were slightly superior to terphenyl.

4. SELF-HEALING COOLANTS

The objective was to find and show the efficiency of "self-healing" coolants. This is an undemonstrated concept in which the radiolytic generation of hydro-aromatic as well as high-boiling products in moderator-coolant would be eliminated. The concept is as follows:

where N is an aromatic, heterocyclic ring. The concept rests on three assumptions:

- (1) The N-N bond is sufficiently weaker than the C-H bonds in the ring system so that no radiolysis of the latter occurs.
- (2) The radical formed by radiolysis of the N-N bond is too inactive to substitute the aromatic rings of the coolant or to react with oxygen. Instead, the radiolytic fragments can only dimerize to regenerate the coolant.
- (3) A suitable aromatic, heterocyclic system can be found. The nitrogen must be in the ring system to prevent disproportionation characteristic of substituted hydrazines.

The first ring system investigated was imidazole. The preparation or properties of 1,1'-biimidazole were not found in the literature. Instead of spending time in its preparation, assumption 2 was tested by radiolysis of imidazole. Here radiolysis of C-H as well as N-H bonds would be expected. However, if the 1-imidazolyl radical were inactive then 1,1'-biimidazole should be formed by its dimerization. Only carbon, ammonia, nitrogen, and hydrogen could be identified as products from the irradiation of imidazole. The feasibility test was repeated with pyrrole. A material that may have been 1,1'-bipyrrole eluted from a chromatograph shortly after pyrrole itself and much before the other (more polar N-H containing) bipyrroles that were formed as a result of C-H radiolysis and subsequent ring substitutions. Time did not permit

identification of the radiolysis products. None of the assumptions have therefore yet been demonstrated to be true. The self-healing concept remains an undemonstrated but intriguing idea.

IV. STABILIZATION AGAINST RADIOLYSIS

(R. B. Regier and H. A. Hartzfeld)

1. PURPOSE AND SIGNIFICANCE OF STABILIZATION STUDIES

Since a significant portion of the direct operating cost in current designs of organic-cooled and -moderated nuclear power reactor comes from replacing terphenyl coolant that has been converted to polymer, and no other organic compounds were known which gave less polymer, interest was naturally high in means for reducing the rate of radiolysis of the coolant. Finding additives, that in low concentration and at reasonable cost might stabilize terphenyl and reduce the rate of radiation damage to it, would constitute one obviously attractive solution to the problem of replacement cost.

Some earlier studies had been completed searching for such additives. West [40] has reported results from work done by California Research Corp. in which the effects of seven additives on stability of polyphenyls to pile radiation was studied, and Gercke [41] reported a survey of 94 additives in terphenyl subjected to gamma radiation at elevated temperature. Selection of the additives to be studied was made on the basis of earlier observations of molecular stabilities and postulates concerning radiolysis mechanisms; nevertheless, lack of adequate basic knowledge of radiolysis necessarily introduced a considerable degree of randomness into the selection of compounds to be tested.

The objective of this assignment was to make a further search for effective stabilizers, basing the selection of compounds on the basic knowledge of radiolysis to be developed in the fundamental studies. It was expected that this would eliminate the random character of the selection of candidate additives.

This investigation was therefore planned largely for the later stages of the contract work, following developments in radiolytic theory. However, it is not implied that no theories of radiolytic mechanisms existed at the onset of the program nor that they had all been applied to stabilizer selection. Some consideration had been given to the problem in a study by Schmidt et al [42] and by Burton and Lipsky [43]. Moreover, there appeared to be several areas in which present knowledge had not been fully applied and some attractive possibilities remained untried. Investigation, therefore, was started in these areas concurrently with the radiolysis mechanism studies basic to it.

2. EVALUATION OF ADDITIVES

2.1 Objective

The objective of this part of the investigation was to survey the field of organic compounds and evaluate the effect of all those which existing knowledge and hypotheses of radiolysis suggested might have a stabilizing effect against radiolytic decomposition of terphenyl coolants. In particular, irradiations were to be made on additive-containing samples at high doses and dose rates, and by this means obtain a much better evaluation of the efficiency of the additives

including those which had been studied in the earlier programs [61, 62]. Compounds of a few additional types, indicated by theory but not previously tested, would extend the scope of the survey of proposed additives.

2.2 Experiments and Results

The additives that were selected for evaluation were tested under irradiation at about 650°F with 6-Mev electrons from the Linac, to a dosage of 0.5 to 1.0 x 10¹⁰ rads. Generally, an additive concentration of 3 mole percent was taken, but for some of the more effective ones a wide range of concentrations was examined [44, 45]. The evaluation of additives was based on comparison with control samples that were always irradiated simultaneously; their effectiveness was judged primarily by relative polymer production, but relative gas production also was always determined [46].

In this study 44 separate irradiations were made in which 93 individual additives were investigated, some of them at a number of concentrations or in combination with other additives [47 - 52]. From the results of these irradiations some correlations between chemical structure and stabilizing action have been deduced. With a few exceptions, the best stabilizers comprise three classes of substances:

(1) Elemental sulfur or compounds containing di- or tetravalent sulfur reduce polymer production to 0.75 to 0.88 percent of that in a control sample. More than 20 markedly different sulfur-containing compounds provided substantially equal stabilization, indicating that the effect is not critically dependent upon the molecular arrangement in which sulfur is introduced into the system [53].

(2) Fused-ring compounds structurally related to anthracene reduce polymer production to 0.73 to 0.89 percent of that in a control sample. These compounds have one of the following general formulas:

where A and B may be sulfur, nitrogen, carbon, and in a few cases oxygen [54].

(3) Hydrogenated or partially hydrogenated fused ring compounds that do not necessarily have the structure of anthracene reduce polymer production to 0.75 to 0.93 percent of that in a control sample. These include partially hydrogenated anthracene, phenanthrene, acenaphthene, and pyrene. In general, an increase in the degree of hydrogenation resulted in greater protective action; in contrast, partially hydrogenated terphenyls at the same concentration were ineffective [54].

Compounds in group 2 were only slightly concentration-dependent, while groups 1 and 3 were very concentration-dependent. None of the better stabilizers was very temperature-dependent. No synergistic effects were noted [54].

2.3 Evaluation

An evaluation of these experiments in terms of the objectives set forth at the beginning of the program shows that significant progress has been made. Materials have been found which in low concentration (3 mole percent or less) will substantially reduce radiolytic damage to terphenyls under high-temperature electron irradiation. Several of these materials are of low enough cost, or have potential for low-cost production, so that economics are not prohibitive. It is recognized that the observed reduction in damage must be confirmed by in-pile irradiations where the much-more-damaging fast neutron irradiation is present.

The reduction in polymer formation obtained by the best additives was 20 to 25 percent. The very dramatic reductions which had been hoped for were not observed, which is not surprising in view of the remarkable radiolytic stability of terphenyl itself.

Several of the more effective compounds contained sulfur, and their use can therefore be questioned. Objections to the presence of sulfur in organic reactor coolant are based principally on the production of 87-day S-35 and 14.3 day P-32 (by n,p reaction with S-32) which complicate the disposal of waste coolant by incineration. Feasible methods to circumvent this objection are now available [55], so that sulfur and sulfur-containing additives are considered acceptable in coolants.

Two areas for research which could help elucidate the fundamental radiolysis process and the behavior of stabilizers have been suggested by the results. One is the observation that partially hydrogenated fused-ring compounds are more effective than the corresponding aromatics. The failure of partially hydrogenated terphenyls to produce the same effect requires explanation. Conceivably, the fused-ring compounds serve as hydrogen donors which can compete successfully against dimerization of terphenyl. The most interesting of these, particularly 9,10-dihydrophenanthrene, were investigated further as new coolants, not merely additives.

The other area of research suggested would try to explain why sulfur and its compounds are effective inhibitors of polymer formation. Since both elemental sulfur and many markedly different sulfur compounds are effective, the effect is not critically dependent on the molecular structure. The mechanism by which in all cases most of the sulfur is converted to hydrogen sulfide should be explained.

3. STABILIZATION BY ELEMENTAL SULFUR

3.1 Objective

The objective of this portion of the stabilizer program was to make a more intensive study of the action of sulfur as a stabilizer. Because of its extremely

low cost and good stabilizing action, elemental sulfur was one of the most interesting materials revealed in the survey.

3.2 Experiments and Results

A series of irradiation tests established that the stabilizing action of elemental sulfur was concentration dependent, and that the optimum concentration was close to 0.7 mol percent S-8 [44]. Tests were then initiated to determine the course of the reaction involving the sulfur atoms and their ultimate fate. Using the optimum 0.7 mol percent concentration, good material balances were obtained. It was shown that most of the sulfur was converted to hydrogen sulfide, reaching two-thirds at higher doses, and much of the remainder being in the heavy polymer. No elemental sulfur was detectable in the residues [48].

3.3 Evaluation

The efficiency of sulfur as a stabilizer was well established and delineated [53]. Its conversion largely to hydrogen sulfide, which could be absorbed readily from the small volume of radiolytic gases, with much of the rest in the heavy polymer wherein, using the recommended hydrocracking process for polymer reclamation, it would remain as a catalyst deposit, shows that radioactivity will not be a serious problem in its use. The mechanism of the formation of H_2S remains to be elucidated [55].

4. CONVERSION OF CONDENSED-RING STABILIZERS

The purpose of this phase of the stabilizer program was to learn something of the mechanism of stabilization by studying the disappearance of acid products from some condensed-ring aromatic stabilizers.

4.1 Experiments and Results

Tests were made to determine the rate of disappearance of anthracene in terphenyl in irradiations of different lengths. While most of the anthracene disappeared rather quickly, protection against polymer formation continued. Effects on gas product were erratic [48].

Studies of the products of irradiation of 9,10-dihydrophenanthrene alone showed that the major reaction was dehydrogenation to phenanthrene [47]. Similarly, dihydroanthracene was converted to anthracene.

4.2 Significance of the Findings

These experiments suggest that the successful hydrogenated condensed-ring structures may function as hydrogen donors. Formation of the rather easily hydrogenated aromatic analogues in the irradiation suggests the possibility of regeneration of the stabilizer in a recycle process [55].

V. HEAT TRANSFER SURFACE FOULING
(P. S. Hudson, W. M. Hutchinson, R. B. Regier,
R. A. Mengelkamp, H. A. Parker, A. J. Moffat, and P. W. Solomon)

1. INTRODUCTION

The deposition of films, which markedly reduced heat transfer, on the surfaces of the fuel elements in the OMRE and in certain test loops was recognized as a serious threat to the economic success of the organic reactor concept before the work in Phillips' laboratories had been started. This film was generally a hard, black, adherent varnish, with very poor heat conductivity. At times there also was observed the buildup of a loose, carbonaceous deposit which interfered with flow or even blocked off narrow channels. To avoid burnout in this situation, reactor power had to be reduced. The film had a high ash content, primarily iron, with the organic portion relatively rich in carbon.

The phenomenon has been discussed by Trilling [56] and Parkins [57].

In order to understand and prevent this fouling, studies were initiated to discover the significant variables in the process. These studies involved the chemistry of organic precursors of film, the role of soluble and insoluble contaminants, and the effect of various operating parameters on the film deposition.

Specific goals of the program were:

- (1) To develop experimental equipment and techniques which would evaluate the significant variables in film formation
- (2) To evaluate various hypotheses of film formation with the above techniques
- (3) To develop and test means of preventing or minimizing film formation

2. DEVELOPMENT OF EXPERIMENTAL EQUIPMENT AND TEST TECHNIQUES

Ideally, film studies should be conducted in nuclear reactor in-pile loops under service conditions. The coolant technology loop planned for the EOGR would have provided a facility suitable for such studies. However, facilities of this type are expensive, require long test periods, and their availability was quite limited at the initiation of this study.

In order to study fouling in a laboratory test apparatus, the nuclear environment should be simulated as closely as possible to obtain valid results. This simulation involves the following important factors: (a) intense radiation, preferably nuclear; (b) reactor fuel element geometry and resultant coolant hydrodynamics; (c) non-corrosive materials of construction; (d) capability of generating nuclear-reactor-type film in a reproducible manner; (e) means

for quantitative measurement of fouling; (f) maximum in-radiation volume to out-of-radiation volume; and (g) ease of assembly and cleaning.

2.1 Circulating Loops

Out-of-pile electron irradiation circulating loops were the closest approach to meeting these criteria. They were used in conjunction with an Applied Radiation Corp. 4-kw, 6-Mev electron linear accelerator. Several loops of various sizes and different functions were fabricated. The first loop, designated as EPL, utilized an electron irradiation cell which simulated the geometry of a fuel element channel of the OMRE and had a 5150-ml coolant charge. A comprehensive description of this loop has been reported [58].

The second loop designated REPL, also was used extensively and had a radiation cell 1.75 inches deep with a 3500-ml coolant charge. This cell had a channel deep enough to absorb the entire electron beam. It could be fitted with an electrode unit for studying the effect of electrostatic fields. This loop also has been described fully in a topical report [58].

For rapid screening work a "Micro-Loop" with a 730-gram coolant capacity was employed in conjunction with the Linac. This device was more fully described in a previous report [59]. Another device known as a "Rocking Irradiation Cell" also was successfully employed for screening work [60].

2.2 Pyrolytic Capsules

Two pyrolytic capsules were employed for screening work on film deposition. The pyrolytic procedure was predicated on the assumption that excess temperature would produce film deposition equivalent to that which radiation would have produced. The first capsule test, designated as the "SF" test procedure, used a coolant charge of 1200 grams of coolant. A description of this test capsule may be found in IDO-16713 [61]. The second capsule had a 600-gram coolant charge and was designated the "SBF". This capsule is described in IDO-16807 [62].

2.3 Coolant Analysis

Isomeric composition of the test coolants was determined by the gas chromatographic method, iron content by X-ray fluorescence and colorimetric techniques, ash by standard ashing procedure, high boiler by micro-sublimation, and carbon and hydrogen by normal combustion techniques.

2.4 Film Measurement

Measurement of film required the utmost care. Various techniques were employed, depending on the apparatus being used. For the circulating loops the film was measured primarily by thickness, weight, and photomicrographic techniques. Chemical analysis of the film for carbon, hydrogen, ash, iron, X-ray diffraction, and magnetic properties also were used. Color photographs were used to compare various runs with each other.

For pyrolytic capsules film analysis, the above techniques were employed. In addition the change in heat transfer was estimated from the reduction in maximum power which could be supplied to the heater without increasing its temperature.

3. RADIOLYTIC AND PYROLYTIC EXPERIMENTS ON FILM DEPOSITION

The irradiated circulating loops and the pyrolytic capsule experiments were employed in initial experiments to observe the effect on fouling of certain operating variables and components of coolant. These tests were supplemented by other miscellaneous experiments from time to time. As information accumulated, apparently conflicting results began to appear. Proposed theories or mechanisms of film deposition were contradicted by some of the experimental evidence. Later, it was strongly indicated that two quite different mechanisms were acting simultaneously to produce films. Evidence for these two routes to film which was collected is presented in the following sections. Most of the loop and capsule work was devoted to the first of this laboratory's hypotheses on the mechanism.

3.1 A Proposed Mechanism of Film Formation

Based on a limited number of test observations this mechanism of film formation is proposed as one possibility. This mechanism is not new, as it was proposed by early automotive fuels and lubricant investigators and more recently by Trilling [57] and Parkins [58]. Basically, it proposed that the fouling film is formed from inorganic particles which are bound together by an organic "glue" or adhesive. In a nuclear reactor the inorganic particles may have been formed from either soluble or insoluble iron removed from the iron piping by acids or by erosion due to high coolant velocities. Other inorganic contaminants which have been found in film comprise a large variety of metals, sand, glass wool, etc. The organic binder for these particles is believed to be high-molecular-weight degradation products, formed from the irradiation of the terphenyl coolant. It should be noted that both inorganic contaminants and high-molecular-weight organic compounds are necessary in this mechanism of film formation. Table XII illustrates the film-formation effects due to (1) high boiler and (2) high boiler with additional iron.

In the first test series (SFB-7, -34, -30, -29, and -41), various concentrations of Core III-A high boiler were added to Santowax OMP. The iron content was very low and fouling was light. However, in tests SFB-33, -31, -16, and -40, in which magnetite was an additive, film weight was very high. This indicated high boiler alone did not form film, but when combined with iron, fouling was heavy. Pure Santowax OMP which contained 100 ppm iron in the form of magnetite (SF-17) gave only 5.4 mg of film. When the same amount of iron was added to Core II coolant in test SF-7, 25 mg of film were formed. In test SF-17 the film that did form was not very adherent and flaked off with handling. In test SF-7 when high boiler was present the large amount of film was tightly adherent. These results indicate the effectiveness of the organic binder found in the high boiler.

With low coolant velocities, zero to two feet per second, the optimum amount of high boiler required for maximum film formation was quite low. For the rocking cell it was about six percent; for the Micro-Loop with about two feet per second coolant velocity, the optimum high boiler concentration was nearly the same. Static film test data (Table XII) indicated a maximum film formation at four percent high boiler. However, optimum high-boiler concentration for maximum film formation in the large loops occurred at higher concentrations. No simple explanation for this phenomenon is apparent

TABLE XII
EFFECT OF OMRE CORE III-A HIGH BOILER
AND IRON CONCENTRATION ON FILM FORMATION

Static Film Test	Coolant	Net High Boiler* (%)	Iron (ppm)	Film Weight (mg)	Film Formation Rate (mg/hr)	Power Reduction (%)
SFB-7	OMP	0	16	0.2	0.01	0
SFB-34	OMP	1.65	17	0.1	0.04	1
SFB-30	OMP	4.12	18	0.5	0.02	3
SFB-29	OMP	19.0	25	0.4	0.02	0
SFB-41	OMP	33.0	31	0.3	0.01	0
SFB-33**	OMP	1.65	117	10.3	0.43	23
SFB-31**	OMP	4.12	113	12.0	0.50	14
SFB-16**	OMP	19.0	125	4.9	0.24	6.5
SFB-40**	OMP	33.0	131	6.8	0.28	8

* OMRE Core III-A high boiler removed from the reactor October 8, 1961, contained 82.5% net high boiler, 455 molecular weight, and 37 PPM iron.

** 100 PPM iron added in the form of magnetite.

other than scale and hydrodynamic factors. Data on test EPL-10 given in Table XIII show twice the film with the final high-boiler concentration of 26.6 percent than was obtained in test EPL-15 where only 4.3 percent final high boiler was available. Coolant velocity past the window was six feet per second in the EPL

TABLE XIII
EFFECT OF IRON AND HIGH BOILER IN FILM FORMATION

Test	Coolant	Additives	Final HB (%)	Iron (ppm)	Film Thickness (mils)	Film Weight (mg)
EPL-15	OMP	0.2% Ferrocene	4.3	615	0.1	7.4
EPL-10	Core II	0.2% Ferrocene	26.6	650	0.2	-
REPL-14	OMP	0.2% Ferrocene	3.5	615	-	9.0
REPL-11	OMP	0.2% Ferrocene + 25% net Core III-A HB	25.1	610	-	18.5
REPL-19	OMP	0.2% Ferrocene + 33% net Core III-A HB	32.9	615	-	7.4

tests. In addition, in test REPL-11 maximum film was formed at 25.1 percent high boiler. Coolant velocity was only 0.5 foot per second past the window in the REPL tests.

In summary, a combination of both high boiler and iron are required to form film. To a limited degree, certain higher-molecular-weight high boilers were more effective in fouling.

3.2 Effect of Inorganic Particle Concentration on Fouling

The data shown in Table XIV were obtained to show the effect of particulate iron concentration on film formation. Various concentrations of ferrocene were added to Santowax OMP and tested in the SF capsule. It has been shown that ferrocene rapidly decomposes to give a suspension of very fine uniform spheres of iron particles.

TABLE XIV
EFFECT OF IRON PARTICULATES ON FILM DEPOSITION

<u>Test</u>	<u>Coolant</u>	<u>Iron (ppm)</u>	<u>Film Weight (mg)</u>	<u>Power loss (%)</u>
SF-8	OMP	16	0	0
SF-26	OMP	66	1.9	12
SF-21	OMP	116	7.7	25
SF-15	OMP	216	6.3	38
SF-37	OMP	616	21.5	69

The film binder for the above tests was believed to be dicyclopentadiene, the degradation product of ferrocene. REPL and EPL circulating loop tests confirmed the above data. For instance, in test REPL-18 when 0.1 percent ferrocene (300 ppm iron) was added to a blend of 33 net percent Core III-A high boiler and Santowax OMP, 3.3 mg of film were formed. When the concentration of ferrocene was increased to 0.2 percent (600 ppm iron) 7.4 mg of film were formed. In general, as the iron concentration in the coolant increased, the amount of film formed increased linearly providing binder was available for cementing it to the heat transfer surface. While ferrocene was originally soluble in the coolant, this was not a prerequisite for fouling. A suitable preparation of magnetite was shown to cause film formation very easily.

Other materials found on the heat transfer surfaces were carbon, quartz, glass wool, beta zinc sulfide, aluminum, zinc, chromium, copper, nickel, lead, manganese, molybdenum, and tin. However, ferromagnetic materials formed film more rapidly than non-ferromagnetic materials.

3.3 Effect of Temperature

Very early in the test program it became apparent that film weight or thickness was a function of maximum surface temperature. In general, film thickness was found to increase exponentially with temperature measured

along the SF and SFB capsule heater tubes. Two typical examples are shown in Figure 1. With the electron irradiation loop no extensive study of the effect of window temperature vs dose rate could be included due to the early termination

FIG. 1 EFFECT OF TEST ELEMENT TEMPERATURE ON FILM THICKNESS.

of the contract. However, the first test indicated that even with dosages of 10^8 rads, only trace film was obtained when bulk coolant temperatures were less than 650°F and electron window temperatures were less than 900°F . Also, very short period (less than one minute) temperature spikes greatly increased the film-formation rate, which tended to make the tests non-reproducible and thus unreliable.

Surface temperature had a strong influence on the ash content of the film formed. Fouling films were composed of various layers or strata. Layers adjacent to the heater surface had the lowest ash content. In general, higher surface temperatures gave films with lower ash content.

Bulk coolant temperature was important in the SFB test. When magnetite was added to a blend of Santowax OMP and 4.12 percent Core III-A high boiler, more film was formed at a bulk temperature of 445°F than at 603°F or 695°F . Apparently the particles of magnetite were suspended better in the more viscous coolant. Also, convection may have been more pronounced due to greater temperature differences between the bulk coolant and the heater element.

When dissolved ferrocene was added to the above coolant blend (iron concentration 118 ppm in both cases) maximum film formed at 698°F while less film was formed at 461°F and 595°F bulk coolant temperatures. The usual 950°F heater surface temperature was used in all SF and SFB tests. In the above case, the higher bulk temperature probably caused the pyrolytic decomposition of ferrocene which gave iron particles. Thus, at least a threshold bulk coolant temperature was an important parameter in film formation in convective flow systems.

In general, both surface and bulk coolant temperature appear important factors in film formation.

3.4 Effect of Velocity

The role of velocity in fouling was investigated early in the program because test equipment and procedures had to be standardized. Three velocities were studied in the EPL loop with the OMRE coolant channel. These velocities were three, six, and nine feet per second past the electron window. Results showed 0.4 mil of film at three feet per second, 0.2 mil at six feet per second, and 0.1 mil at nine feet per second. These results indicated that film thickness was inversely proportional to coolant velocity. OMRE Core II coolant with 0.2 percent added ferrocene was used for the above tests.

In the EPL and REPL irradiation cells a maximum amount of film collected in areas of lower velocity. Also, surface asperities or projections into the coolant stream tended to act as centers for film growth.

3.5 Beta Current Effect

It has been postulated [57, 58] that current from beta decay in the fuel elements would enter the coolant and generate a potential between coolant and fuel element. This potential would drive charged particles in the coolant to the fuel element where they would be discharged on the surface. A study of this phenomenon was attempted by inserting grounded and non-grounded plates 0.8 in. below the window in the REPL deep cell. The electron beam current

to the grounded plate was about 30 microamp for a flux density of about 0.5 microamp/cm².

Test results from REPL-3, -4, and -5 showed that two to three times more film formed on the grounded plates than on the ungrounded plates.

The effect of film deposition on plates outside the radiation zone also was studied in REPL-6. Both grounded and ungrounded plates were assembled downstream of the radiation field in the exit portion of the cell. Results have indicated no significant difference in the amounts of film collected on the grounded and ungrounded plates. The electron beam current to the grounded condenser plate was only 0.5 microamp during the test.

Possibly if the fuel elements in the reactor could be insulated, less fouling would occur. However, this would be difficult to accomplish in a nuclear reactor.

3.6 Effect of a Hydrogen Blanket

It is commonly reported that a hydrogen atmosphere inhibits fouling in hydrocarbon heat exchangers under refinery conditions. The effect of hydrogen on fuel element fouling was studied in two electron loops. Test EPL-15 was a control test in which a nitrogen blanket was employed. The coolant was Santowax OMP plus 0.2 percent ferrocene. The film on the window was 0.1 mil thick and weighed 7.4 milligrams. The iron found in the window film was principally magnetite with the balance alpha-iron. In test 16, under identical conditions except that a hydrogen blanket was used, the film on the window measured 0.1 mil thick, weighed 9.0 milligrams, and the iron was principally alpha-iron with minor amounts of cementite, magnetite, and austenite. It was concluded that no significant benefit resulted from the use of a hydrogen blanket. Tests also were conducted in the SF capsule. When a hydrogen blanket was used the inorganic part of the film was alpha-iron. However, when a nitrogen blanket was used the inorganic part of the film was magnetite. In the hydrogen blanket tests a heavier film was always formed. However, the thermal conductivity of the film with a hydrogen blanket was always higher than the film formed under nitrogen because the metal conducted heat better than the oxide. A hydrogen atmosphere in a reactor might improve heat transfer characteristics of fouling film and permit operation without power reduction.

3.7 Effect of Blanket Pressure

In a series of SF tests, the effect of blanket pressure was briefly investigated. Tests were conducted on Core II coolant at 400, 470, 600, and 700 psig. Film weights obtained were 28.9, 24.9, 28.8, and 22.0 milligrams, respectively. These results suggested that pressure did not greatly affect film formation. Nucleate boiling was extensive at all pressures except 700 psig. One percent decalin added to Core II coolant did not reduce film formation, although nucleate boiling occurred which improved heat transfer.

3.8 Conclusions from Radiolytic Experiments

The following conclusions regarding film formation may be drawn from the experimental data on loop and capsule tests in the preceding sections:

- (1) Electron irradiation loop tests and pyrolytic capsule tests were developed which were capable of evaluating significant variables in the film formation.

(2) One mechanism of film formation involves the binding of inorganic particles with organic high-molecular-weight degradation products of terphenyl coolants. Both inorganic particles and degradation products such as high boiler are required in order to form fouling film by this mechanism.

(3) The optimum high-boiler concentration for maximum film formation varied with the test device used. For capsules and the Micro-Loop this was about four to six weight percent, but it was about 27 percent in the electron irradiation loops.

(4) As iron concentration increased in the coolant, the amount of film formed increased linearly providing organic binder was available to attach it to the heat transfer surface. Substantially all the iron was in the form of insoluble particulates in these tests.

(5) Film thickness increased exponentially as surface temperature increased.

(6) Film thickness or film weight was inversely proportional to coolant velocity with a stainless loop system. In a steel loop system this may be reversed due to mass transfer of iron from the piping.

(7) Two or three times more film was transported to grounded surfaces compared to ungrounded surfaces under the electron beam. This suggests the existence of a beta current.

(8) At a given surface temperature no reduction in film weight was obtained when a hydrogen blanket was used. However, better heat transfer through the film was noted with the hydrogen blanket, evidently resulting from reduction of the iron compounds in the film to alpha-iron.

(9) Blanket pressure did not affect film formation to a large extent.

4. SOLUBLE COOLANT CONTAMINANTS IN FILM FORMATION

4.1 Introduction

A considerable body of evidence has accumulated in the work on the organic-cooled reactor concept pointing toward a rather different mechanism for the deposition of film, in which neither particulate matter in the coolant or heavy "sticky" degradation products of organic matter is particularly important. In some tests, and with some coolants, the usual correlation between insoluble inorganic particulate matter and film deposition fell down. Much heavier deposits were observed than expected from certain clean coolants. These films were very high in ash (iron) and had really almost no organic binder. Similar films have been observed in water reactors where there is no organic to form a "glue". Also, the amount of iron deposited in the film was many times that present as particulate matter circulating in the coolant. Increased coolant

velocity increased rather than decreased the film rate in these cases. All these observations pointed toward a mass transport of iron, in solution, from the external piping to the fuel element surfaces where it is deposited as an insoluble film adhering to the surface without the aid of an organic binder. The chemistry of the attack and solubilization of the iron by coolant and its subsequent re-deposition may involve other trace constituents of coolant, such as oxygen and its compounds, water, chlorine, etc.

Experiments in the capsules and in other chemical apparatus and irradiations were devised to study these possible effects of oxygen and the other contaminants leading to iron transport in solution.

4.2 Mechanism of Film Formation

The importance of iron in producing fouling films that have appeared on fuel elements or organic-cooled reactors has been discussed in quarterly reports [35, 36]. The last report [64] summarized the results from a series of PCF bomb tests in which both dissolved and particulate iron in Santowax were studied, under atmospheres of nitrogen, hydrogen, or a hydrogen-carbon monoxide mixture. In these tests it was noted that in every case the form of iron deposited on the test heater was different from its form in the bulk fluid. This observation prompted the generalization that iron becomes attached to a heat transfer only when it can and does undergo a change in phase from that in which it is present in the bulk fluid. Because iron is fairly reactive chemically, and has two different valence states in which it can combine in compounds, in addition to existence as the element, changes in iron are readily effected. The consequence of this is that iron in almost any form in the organic fluid is potential film-forming material if conditions permit it to change chemical form; eg, precipitation of dissolved iron, reduction of oxide particles, carburization of metal and/or oxide, etc.

4.3 Experiments on Film Deposition

To test this idea further, two PCF bomb experiments were performed in which aluminum was used instead of iron. Aluminum was selected because, in the sense discussed above, it is much less reactive than iron is under the conditions that obtain in the PCF bomb tests. Its oxide cannot be reduced with hydrogen, so about the only change possible is a change of phase from one form of oxide to another. The idea underlying these two experiments, under identical test conditions, was to perform the first one using aluminum dissolved in Santowax after determining the form in which it was deposited on the test heater, and to start the second with a suspension of that form in Santowax.

In the first test, the bomb was charged with a solution of Santowax OMP containing 200-ppm aluminum as its acetylacetonate. The test heater was maintained between 825 and 850°F while the bulk fluid temperature was between 400 and 450°F for 55 hours under 700 psig of hydrogen. A substantial deposit collected on the test heater: thick, rough, and light colored at the top, and smooth and dark on the lower part. Its weight was equivalent to 117 percent of the weight of aluminum initially taken, calculated as aluminum oxide. It was subsequently shown, by heating a small portion in a glass tube, that it contained some volatile material, but the observed weight suggests that the dissolved aluminum was collected essentially quantitatively as alumina during the test. Three portions of the deposit that were markedly different in appearance were subjected to X-ray diffraction analysis, but all three were found to be amorphous.

Since no finely divided amorphous alumina was available, the second test was made using a suspension containing 378 ppm (= 200 ppm aluminum) of Cabot's Alon C. This is extremely fine eta-alumina having a particle size range of 0.01 to 0.04 micron, and is reported to be stable against phase change (to theta-alumina) to at least 930°F. This suspension was stirred vigorously before introducing it to the bomb, but no special treatment was given to insure a permanent dispersion. The bomb test was made under conditions identical to those given above for the first test, but was of 101 hours duration. During this experiment the test heater collected no visible deposit. Upon removal it was bright and shiny and had not become at all discolored. If the colloidal alumina particles remained in suspension during the test, they showed no tendency to collect on the test heater, in marked contrast to the behavior of colloidal iron oxide under similar conditions.

These two tests support the idea that was deduced from the experiments using iron: that a change in phase or form is required to produce an adherent inorganic fouling film on heat transfer surfaces. The next experiments that were planned for this area of interest were not performed because of the termination of this project. It had been planned to make Linac irradiations using the dynamic pumping loop with Santowax containing radioactive dissolved iron and "cold" particulate iron oxide to determine their relative importance as sources of the iron that invariably appears in fouling films. The static PCF tests had indicated that dissolved iron was much more important, but experimental confirmation in a dynamic heat transfer loop is required.

4.4 Corrosion of Iron by Terphenyls

One of the advantages of aromatic hydrocarbons as coolant-moderators for nuclear reactors is their compatibility with mild steel, which is the material of construction for coolant containment. Although mild steel is reported to be satisfactorily resistant to attack by virgin terphenyls, some complications arise when these are used together in a nuclear reactor. The iron which invariably comprises a substantial part of fouling films that appear on fuel plates presumably is introduced into the coolant fluid by corrosion. Identification of the causes of corrosion would be an important step to minimize or possibly prevent fuel fouling.

Some experiments have been completed that were intended to help elucidate the types of foreign compounds in terphenyl that cause corrosion. These were an extension of tests reported previously [65] in which virgin and irradiated terphenyls under air or an inert atmosphere were exposed to radioactive iron for over 1100 hours at 300°C. During that test the organic phase was sampled periodically, then analyzed to determine the rate of iron dissolution. It was shown that irradiated terphenyl subsequently exposed to air was significantly more corrosive to iron than the other samples were.

The present experiments were performed in a manner different than the earlier ones to eliminate periodic exposure to air of samples that were intended to be under an inert atmosphere only. This time 32 separate glass tubes were charged with approximately 4-g portions of the organic mixture being examined. These mixtures were of two kinds: derived from irradiated terphenyl subsequently altered by various treatments, or from virgin terphenyl containing a known concentration of different organic compounds. Into each of the 32 tubes a known weight of irradiated iron wire was introduced; the tubes were warmed sufficiently

to melt their contents and permit the wire to sink, then were outgassed by pumping, the vacuum was released with argon, and the samples were frozen. Finally, each tube was sealed with a torch while being evacuated with a mechanical pump; this pretreatment removed essentially all the oxygen from the systems for their subsequent thermal exposure.

The iron used in these tests was J. T. Baker Chemical Co. reagent iron wire (0.009 inch diameter). A helix weighing 0.27 g was sealed in quartz and irradiated for one cycle (≈ 15 days) in a high thermal neutron flux ($\approx 2 \times 10^{14}$ neutrons $\text{cm}^{-2} \text{sec}^{-1}$) in the MTR. Unfortunately, the quartz capsule containing the wire became filled with water during the irradiation, and when it was returned here the wire was covered with a black deposit and fine black powder was present in the water in the capsule. An attempt to clean the wire was made by washing it in hot, dilute citric acid. This restored a metallic luster to its surface, but subsequent handling showed that the wire had lost much of its tensile strength, and it is felt that iron containing some oxide was being used in the tests even though analysis by XRD showed only the presence of α -iron.

In these corrosion studies, 21 different organic mixtures were tested, as shown in Table XV.

The sealed glass tube containing accurately weighed quantities of the above organic mixtures and irradiated iron wire were exposed at 288°C (550°F) for the times shown in Table XVI. The entire tube was maintained at this temperature to prevent fractionation of components of differing volatility. Although the samples were not stirred during the test, they were shaken to mix their contents at the end, and the wire was separated from the organic phase by slowly inverting the tubes and permitting the liquid sample to drain to the end away from the wire. After the samples solidified the two ends were cut apart. Analyses for iron-59 were made by placing the organic phase, still in its original container, directly against a 1-inch-long $\times$ 1.5-inch-diameter NaI scintillation detector and counting with a single-channel analyzer operated to accept all counts above 0.4 Mev. A known aliquot of the original iron, counted in the same geometry as the samples, related counting rate to weight of iron. For this experiment the relation was 226 c/m-microgram of iron. This method of analysis revealed the total quantity of radio-iron that had been removed from the wire source, but gave no information about its final form in the system.

Table XVI summarizes the times of exposure of the individual samples at 288°C and the results of the radiometric analyses. Each sample comprised about 4 g of organic, and the weights of iron wire used ranged from 5.3 to 13.4 mg. Results have been normalized by reporting the total weight of iron per gram of organic per milligram of wire that had separated during the indicated test period.

Tests 1 through 22 involved organic phases that were mostly obtained by subjecting irradiated terphenyl to various treatments, while tests 23 through 32 used organic phases consisting of virgin terphenyl containing various organic solutes. Interpretation of the results is clouded by the observation noted above, that the iron wire very probably retained traces of oxide either on its surface or from intergranular corrosion. This could have permitted traces of iron activity to be sloughed off to the organic phase without representing chemical attack on the iron. After studying the data, the rather arbitrary decision has

TABLE XV
DESCRIPTION OF ORGANIC MIXTURES USED IN CORROSION TESTS

A	Virgin Santowax OM, distilled in all-glass apparatus
B	From sample A, irradiated by the Linac under argon to contain 9.2% HB; estimated dose 2.3×10^9 rads
C	From sample B, maintained 163 hours at 80°C in air
D	From sample B, plus 0.10 wt% benzoyl peroxide; maintained 163 hours at 80°C in air
E	From sample B, plus 100 ppm dissolved "cold" iron as ferric benzoylacetate; maintained 163 hours at 80°C in air
F	From sample B, maintained 44 hours at 170°C in air
G	From sample B, plus 100 ppm dissolved "cold" iron as ferric benzoylacetate; maintained 44 hours at 170°C in air
H	Reclaimed coolant prepared by hydrocracking used OMRE coolant that contained 30% HB. This sample contained 82% terphenyl, 6% biphenyl, 9% alkyl biphenyl and alkyl terphenyl, 1% triphenylene, and 2% quaterphenyl
I	Irradiated reclaimed coolant. Initially this sample was similar to H, but was irradiated with the Linac at 650°F to contain 30% HB. This sample was exposed to the air at ambient temperatures for about 5 months before being used in this experiment.
J	From sample F, plus ≈ 1 mol % n-tributyl amine
K	From sample G, plus ≈ 1 mol % n-tributyl amine
L	0.96 mol% p-chlorobiphenyl in sample A
M	1.02 mol% benzyl chloride sample A
N	0.97 mol% 3-phenylsalicylic acid in sample A
O	0.95 mol% 1-hydroxy-2-naphthoic acid in sample A
P	1.00 mol% 2,3-naphthalenediol in sample A
Q	0.94 mol% benzoylacetone in sample A
R	1.00 mol% benzil (dibenzoyl) in sample A
S	0.97 mol% 8-quinolinol in sample A
T	1.02 mol% fluorenone in sample A
U	0.98 mol% anthraquinone in sample A

been made that levels below 0.2 and 0.3 microgram per g sample per mg wire for 24- and 166-hour exposures, respectively, do not constitute significant chemical attack, and the following observations are based on that criterion.

Neither virgin nor clean irradiated Santowax OMP (mixtures A and B) were corrosive. Mixtures C, D, E, F, and G were exposed to conditions in which autoxidation of the irradiated material might be expected. Test 6, and particularly

TABLE XVI
RESULTS FROM CORROSION TESTS

<u>Test Number</u>	<u>Organic Component</u>	<u>Micrograms Fe (g Sample)⁻¹ (mg Wire)⁻¹</u>	<u>Time at 288°C. (hr)</u>
1	A	0.15	24
2	A	0.08	166
3	B	0.06	24
4	B	0.14	166
5	C	0.16	24
6	C	0.33	166
7	D	0.20	24
8	D	0.14	166
9	E	0.11	24
10	E	1.13	166
11	F	0.37	24
12	F	0.57	166
13	G	0.30	24
14	G	0.63	166
15	H	0.14	24
16	H	0.28	166
17	I	0.35	24
18	I	0.52	166
19	J	0.21	24
20	J	0.43	166
21	K	0.33	24
22	K	0.45	166
23	L	0.24	166
24	M	0.54	166
25	N	0.62	166
26	O	0.32	166
27	P	0.01	166
28	Q	25.6	166
29	R	0.12	166
30	S	108.	166
31	T	0.06	166
32	U	0.08	166

test 13 (autoxidation at 80°C), were positive, but the latter may have been partially because of residual benzoylacetone, which is discussed below. Autoxidation at 170°C (mixtures F and G) yielded consistently corrosive material, but the presence of soluble iron did not significantly affect the results. Virgin reclaimed coolant (mixture H) gave negative results whereas the irradiated reclaimed material (I) was definitely corrosive. This may have been due to the fact that the material had been exposed to the air for months after the irradiation, as mentioned above. Mixtures J and K containing n-tributyl amine were tested because it had been anticipated that mixtures F and G, from which they were prepared, would be corrosive and the latter tests were to observe the effect of an organic base on acids that may have been present. The amine reduced corrosion only slightly, and probably not significantly.

Of the solutes examined in tests 23 through 32, two were several orders of magnitude more corrosive than the others. These two, benzoylacetone and 8-quinolinol, are known to form very stable complexes with iron; apparently, under the conditions used, reaction went appreciably toward completion. The final form of the iron that was dissolved is not known, but the very dark color of these two samples suggested that it remained in solution. This observed behavior of 8-quinolinol provides an explanation of results that were reported by AECL in 1961 that is fully consistent with the explanation of the mechanism of fuel fouling proposed by this laboratory. In an experiment in AECL's X-7 loop at Chalk River, coolant containing 8-quinolinol was tested, and they reported that it was necessary to shut the test down after only 48 hours because of severe fouling on the heat transfer surface. Apparently the 8-quinolinol dissolved iron from their loop which was subsequently precipitated by heat and/or radiation on their fuel elements.

The other solutes that were tested in this experiment gave less dramatic results. With two organic chlorides, chlorobiphenyl gave negative results while benzyl chloride was definitely corrosive. The two organic acids studied, salicylic and naphthoic derivatives, were both definitely corrosive, but four other oxygen-containing aromatic compounds gave negative results. Fluorenone and anthraquinone were tested because they have been found in measurable concentration in commercial Santowax OMP.

Except for the results with two substances, benzoylacetone and 8-quinolinol, which were not anticipated, this experiment has provided general confirmation of results that have been reported previously from this and other AEC contractor laboratories. Clean terphenyls, irradiated or unirradiated, are not corrosive to iron, but they become so after exposure to conditions that permit air oxidation. It would be very interesting to know whether this change which can be effected in irradiated terphenyls is due to the formation of moderate amounts of organic acids, or to the formation of only traces of strong complexing agents such as the 1,3-diketones.

5. PREVENTION OF DEPOSITION BY ADDITIVES

The objective of this work was to determine whether an additive could be found, acceptable for use in the coolant, which would remove the adhering film, or prevent its deposition. The resemblance of the films found on the fuel

elements to those deposits and varnishes observed in automotive engines suggested that the detergent-type additives widely used in engine oils might be effective in organic reactors.

Many of these additives contain calcium, zinc, or other metals completely unacceptable in the organic reactor concept where coolant-moderator activity ideally is to remain essentially zero. "Ashless" detergents, however, should be acceptable in this respect. The acceptability of sulfur, which is almost sure to be present, is the same problem discussed in Section IV, Stabilization Against Radiolysis, and may not constitute a real objection. The first tests were merely to establish whether any effect could be produced by substances of this type, and therefore it was not necessary that they be ashless.

Two automotive motor oil detergents, Phil-Ad (Phillips Detergent Additive) and Rohm and Haas' Acryloid 917, were tested in two percent concentrations in Core II coolant [66]. In the case of Phil-Ad, there was no reduction in film formation but power loss decreased 50 percent. With Acryloid 917 film weight was reduced 50 percent but no reduction in power loss was noted. In addition, some benzene insoluble polymer was found on other parts of the capsule which were at about a 620°F temperature. Further work on the motor oil detergent approach was postponed because of these unfavorable first indications and because even when free of metals, the polymeric material contained also tended to accelerate fouling. This approach is still considered to have possibilities, but it will undoubtedly require much work to develop, which was not possible within the term of the contract.

6. DISCUSSION

At the conclusion of the work, and in surveying the accumulated knowledge from the efforts of all the investigators here and abroad, it is felt that sufficient progress has been made so that fouling can be controlled adequately to insure reactor operation. It need no longer be considered a serious problem; its causes and mechanism are sufficiently well understood so that effective control measures have been devised and can be practically applied.

It is believed that evidence collected here and which has been accumulating in other laboratories indicates that fouling of fuel elements is proceeding by at least two distinct mechanisms. Decomposition of coolant into polymer, tar, or even carbon particles furnishes an adherent material which can form a film on the heat transfer surfaces. Solid particulate matter becomes coated with similar material, and in time is likely to be collected by and adhere to the surface film. Films containing 20 to 25 percent ash result from this process. The film deposition rate is an inversed function of the velocity of the coolant flow. It also should be affected by the beta current flow across the coolant channel since the particulate matter can become charged.

Operations in the OMRE, at the MIT reactor, and in the AECL loops, have shown that this type of fouling can be controlled to very low rates of buildup by: (a) maintaining a very low level of high boiler in the coolant and, in turn, maintaining the little which is present at a low average molecular weight by operation of the purification facilities at high rates; (b) maintaining the solid

particulate matter at a very low concentration by filtration and/or distillation; and (c) maintaining other harmful constituents, possibly polymer initiators, intermediates, or even colloidal-size insoluble matter at a very low level by an adsorption treatment, such as with Attapulgate.

Should a need arise for an organic moderator-coolant incapable of depositing fouling film on heat exchanger surfaces, the self-healing concept should be tested. Alternatives such as exclusion of oxygen or aromatization of hydroaromatics in a side stream are incomplete solutions since they do not eliminate radiative conversion of low concentrations of hydroaromatics into polymers much higher in molecular weight than obtainable by the doubling reaction (by which hexa- and nona-phenyls are made from terphenyl).

Fouling, it is believed, also can result from precipitation and phase change of a soluble ion, usually iron, occurring at the surface of a fuel plate. When this precipitation occurs in the bulk liquid particulate matter is formed, which contributes to fouling only in a secondary manner if the particles are of a correct size to function by the first mechanism detailed in the preceding sections. This second mechanism is therefore tied to mass transport of iron from the external piping to the reactor core. Fouling rate is therefore a direct function of the coolant flow velocity, and the films resulting are very high in iron content.

Evidence has been obtained in this laboratory's reported work and in that of others, that iron can be dissolved from the system and transported in the terphenyl coolant by oxygen-containing compounds which are formed from coolant which has been exposed to irradiation. Some evidence was obtained that chlorine may be a contributing element in this mechanism. Charlesworth of AECL [67] has presented clear evidence that organic chlorine can be responsible for the dissolved iron, but has less clear evidence that oxygen is involved. Fouling by this mechanism also can be controlled by maintaining high purity of the coolant. Water, oxygen, and chlorine contents in added coolants must be very low. Exposure to air of the coolant after irradiation must be avoided. Treatment with Attapulgate adsorbant is very helpful.

VI. LOW-COST COOLANTS

(W. M. Hutchinson, L. V. Wilson, Jr., L. E. Gardner)

1. OBJECTIVE

The aim of the low-cost coolant program was to reduce significantly the inventory and replacement cost for organic coolant for nuclear power reactors. The current and projected price for terphenyl coolant is 15¢ per pound (17¢ delivered). Several industrial organic materials are known whose composition includes the known more stable organic molecules and which are available in quantity at prices near one cent per pound. Very marked savings are thus possible if a liquid can be found in this group which is usable at the conditions of temperature and radiolysis existing in a reactor core. Substantial savings still are possible even though decomposition rates with such a coolant should rise to several times that of terphenyl.

A further aim of this investigation was to find means of improving the candidate coolants while still preserving much of their economic advantage. Reactor operating conditions and the mere logistics of handling and replacement of coolant limit the allowable decomposition rate to two or three times that of terphenyl, probably to much less than this. However, rather extensive processing, such as fractionating, desulfurizing, dealkylating, etc, should be possible without raising these coolant costs to five cents per pound.

2. EXPERIMENTS AND RESULTS

A large group of high-boiling distillates from petroleum sources was assembled. These represented fractions which were known to be high in aromatic content, primarily condensed-ring systems. They included recycle oils from various catalytic cracking operations, in which the condensed-ring aromatics are among the more resistant molecular types, and other highly aromatic fractions prepared by solvent extraction or other processes for feed to furnace-process carbon black production [68]. Coal tar distillates from the "middle oil" or "anthracene oil" range also were included [68].

These oils were subjected to further fractionation, to eliminate low- and particularly high-boiling materials that might be unacceptable in reactor operation [69]. They were then subjected to radiolysis with 6-Mev electrons under the Linac beam in direct comparison with Santowax, using the same apparatus described in Section IV for testing stabilizers [53]. The results showed that a number of these materials were equal to or even slightly superior to Santowax in polymer formation. Others were inferior in various degrees [13, 69 through 71]. Gas liberation was generally greater than with Santowax, often much greater [69 through 72]. Thermal stability tests were carried out on these samples also, using an apparatus comprising small sample holders, with gas-sampling devices in large metal constant-temperature blocks [68]. In general, thermal stabilities were entirely unsatisfactory above 650°F [70, 72, 73].

Processing studies were then instituted on a few of the more promising materials. De-waxing made relatively little difference in the cases studied [69]. Solvent extraction, or re-extraction produced some favorable effects, [70, 71] but was not studied extensively. It was concluded that the petroleum-based stocks must be hydrodealkylated to reduce the average number of methyl and higher alkyl groups on each aromatic ring and that coal tar stocks must be hydrodesulfurized. When applied these processes produced coolants that have a pyrolytic threshold temperature about 50°F less than terphenyl, form radiolytic polymer at from one-half to three-fourths the rate of terphenyl, but still form radiolytic gas at several times the rate of terphenyl. Viscosities, vapor pressures, density, and proton densities similar to terphenyl are attainable. Tendency to form film has not been tested but no coking has been observed at temperatures up to 750°F. These are theoretical grounds for predicting that alkyl-condensed aromatic coolants would have less tendency to form radiolytic film than terphenyl.

A topical report [74] summarizing the status of this program has been prepared. Coolants have been processed and tested on a lab scale that are so promising that they should be prepared on a larger scale and tested in an in-pile loop when the need arises for such a coolant. Tables XVII, XVIII, and XIX compare general properties, radiolytic stability, and thermal stability of two of the better low-cost coolants with terphenyl. Inventory and makeup costs with these coolants should be less than one-third that of terphenyl in a conventional steam plant operation where the bulk temperature does not exceed 700°F and the maximum coolant temperature is 750°F.

TABLE XVII
COMPARISON OF PROPERTIES OF TWO LOW-COST COOLANTS AND TERPHENYL

Coolant	Boiling Range °F/760 mm Hg	C/H Ratio	Molecular Wt. (No. Avg.)	Sulfur, (Wt%)
Hydrodealkylated Phillips Borger SO ₂ Extract				
Sample A	650-750	1.24	185	<0.03
Sample B	650-750	1.18	188	<0.03
Hydrodesulfurized Pittsburgh Coal Tar	620-650	1.11	199	<0.05
Terphenyl (o,m,p)	630-710	1.29	230	

3. CONCLUSIONS

Considerable promise exists in low-cost coolants derivable from petroleum or coal tar distillates, but considerable further development work is necessary. Starting with a distillate of suitable boiling range from cycle oils from fluid

TABLE XVIII

COMPARISON OF RADIOLYTIC STABILITY OF TWO LOW-COST COOLANTS
AND TERPHENYL UNDER 6-MEV ELECTRONS AT 650°F (5.6×10^9 RADS)

Coolant	Molecular Wt (No. Avg.)		Relative Polymer Generated	Relative Gas Generated
	Before	After		
Hydrodealkylated Phillips Borger SO ₂ Extract				
Sample A	185	229	0.6	6
Sample B	188	209	0.7	5
Hydrodesulfurized Pittsburgh Coal Tar	199	215	0.8	6
Santowax OMP*	230	258	1.0	1

* Mixture of o-, m-, and p-terphenyl

TABLE XIX

COMPARISON OF THERMAL STABILITY OF TWO LOW-COST COOLANTS AND TERPHENYL

Coolant	(48-HR TESTS)			
	High Boiler Formed (Wt%)			
	650°F	700°F	740°F	750°F
Hydrodealkylated Phillips Borger SO ₂ Extract - Sample B	0.1	0.6	4.2	4.8
Hydrodesulfurized Pittsburgh Coal Tar	1.0	2.2	6.9	8.7
Santowax OMP*	-	-	-	0.0
	Molecular Weight (No. Avg)			
	Before	650°F	700°F	750°F
Sample B	188	197	194	199
Coal Tar	199	206	208	214
Santowax OMP*	230	-	-	235

* Mixture of o-, m-, and p-terphenyl

catalytic cracking of gas oils from typical North American crudes, a coolant can be produced which has better stability toward radiolytic polymer formation than Santowax. This is accomplished by the relatively inexpensive operations

of desulfurizing and hydrodealkylating. Gas formation in radiolysis is relatively high, but within operable limits. The materials are thermally stable up to 700 or 725°F but break down rapidly at higher temperatures. It is believed that, had time permitted, further studies in hydrodealkylation would have resulted in marked improvements in both these respects.

VII. RECLAMATION OF COOLANTS

(W. M. Hutchinson, L. E. Gardner)

1. OBJECTIVE

The objective of this project was to find an economical method of re-constituting damaged coolant (high boiler) into usable coolant. This is considered essential to the economic success of the organic reactor concept, for the expense of high-boiler disposal and makeup with fresh terphenyl coolant has been estimated to total 18.5 cents per pound of makeup required. High-boiler production rates are in the range of 25 to 100 pounds per megawatt-day (thermal) operation. Coolant replacement therefore will account for 0.6 mil per kilowatt hour or more in the cost of electric power generated. Worthwhile savings are thus possible in a reclamation process.

Reclamation of high boiler might be carried out by methods which would segregate still-usable fractions from the total high-boiler waste, or by methods which would chemically reconstitute a usable coolant fluid from the polymeric waste. Segregation of material which is sufficiently fluid, stable to heat and radiation, and non-fouling might be accomplished by flash or deep-cut distillation, by molecular distillation, or by solvent extraction. In the latter case, processes could be devised which make a separation between molecular types rather than on a molecular-weight or boiling-point basis. These methods are limited, however, in the amount recoverable to the relatively small proportion of material contained which would be directly usable as coolant. The recovered material, being of higher molecular weight, is likely to be more susceptible to further polymerization. Reclamation by breaking down the polymer into the original terphenyls, or to other stable structures in the right molecular weight range, offers the chance for a higher recovery, although some loss to low-boiling compounds and to coke must be expected.

Since distillation and extraction methods are being investigated by others, the proposed investigations in these two areas were held in abeyance. Efforts were directed to reconstitution by chemical means. The method selected was catalytic hydrocracking.

The bench-scale study of this method of reclamation was completed, and results and recommendations have been reported [36, 75 through 77] in topical reports as well as in the quarterly reports.

2. SUMMARY OF RESULTS

An initial screening program [75] indicated the catalyst requirements and operating conditions for selective hydrocracking of the carbon-carbon linkage between benzene rings in polyphenyls. The main catalyst requirements were found to be a small degree of cracking activity along with a component which promotes the reaction of cracked fragments with hydrogen to prevent undesirable side reactions such as polymerization, isomerization, and coke formation. Low-surface alumina was found to be an optimum base for metals

and metal oxide components. Catalysts containing acidity, ie, silica-alumina, boria, or fluorine, were non-selective and also gave excessive rate of coke formation. Of 35 catalysts evaluated the following were found to be most efficient:

- (1) $\text{CoMoO}_4\text{-Al}_2\text{O}_3$
- (2) $\text{NiO-Al}_2\text{O}_3$
- (3) $\text{Pt-Al}_2\text{O}_3$
- (4) $\text{CoO-V}_2\text{O}_5\text{-Al}_2\text{O}_3$

Surface areas of the above catalysts were in the range 25 to 100 square meters per gram, and they were stable, active, and selective after repeated air-regenerations to remove carbonaceous deposits.

Using the above catalysts OMRE high boilers (Cores II and III-A) were converted into products which were similar to terphenyls^[76]. The most favorable route for hydrocracking neat high boiler was a low-conversion process with recycle of unconverted material. Reclaimed coolants were in a molecular weight range of 210 to 230 and were stable to electron irradiation at 650°F and 10¹⁰ rads dosage, and were thermally stable up to 750°F. Typical reaction conditions and results are shown in Table XX. Data reported here were for processing Core II high boiler. Core III-A hydrocracking gave coking rates of about one-fourth those found with Core II high boiler which should lead to very long process cycles, possibly in excess of 400 hours.

TABLE XX

CONDITIONS AND RESULTS USED IN CATALYTIC
HYDROCRACKING OF HIGH BOILER (HB)

<u>Conditions:</u> 1000 psig	
900°F	
0.5 vol (HB) per vol (catalyst) per hr	
10 to 30 moles H ₂ per mole high boiler	
$\text{CoMoO}_4\text{-Al}_2\text{O}_3$ (low surface area)	
<u>Typical Results:</u>	
Conversion of HB per pass	25
Coolant yield per pass (wt%)	24.
Product recovery per pass (wt%)*	98
Ultimate yield (wt%)	80
Coke yield (wt of HB charged)	0.5
Hydrogen consumption (moles/mole HB charged)	1.5
Process cycle length (hr)**	>100

* Including unconverted HB

** Between catalyst regeneration

A more efficient process was found [36] in which total coolant was hydrocracked, thus eliminating vacuum distillation of coolant side streams and hydrocracked products. The selective conversion was possible since polyphenyls were found to be more susceptible towards hydrocracking as the phenyl chain length increased. Data were obtained for coolant containing 5 to 30 weight percent high boiler. Typical data from this method of coolant reclamation are listed in Table XXI.

TABLE XXI

HYDROCRACKING TERPHENYL COOLANT CONTAINING
30 PERCENT CORE III-A HIGH BOILER (HB)

A. <u>Reaction Conditions:</u> 1000 psig, 900°F, 0.8 vol coolant per vol catalyst per hr, 25 moles hydrogen per mole coolant, CoMoO ₄ -Al ₂ O ₃ catalyst, and 30 hr run time.	
B. <u>Typical Results:</u>	
HB conversion (wt%)	52
Product recovery (wt%)	99
Total net yield (wt%)	92
Coke yield (wt% of HB charged)	1.5
Net yields (wt%)*	
Lighter than ϕ_2 + coke	8
Alkyls (ϕ_2 and ϕ_3)	25
Biphenyl	27
Terphenyls	34
Triphenylene + ϕ_4	6
C. <u>Product Properties:</u> Analysis (in wt%) - alkyls (4), biphenyl (4), terphenyls (77), triphenylene + ϕ_4 (1), and unconverted HB (14). Molecular weight - 243 compared to 296 for charge.	

* Based on HB converted

The only data not reported in topical reports were obtained from a micro-loop irradiation test [59] of reclaimed coolant from hydrocracking Core III-A coolant. Test conditions were 900°F (top tube), 750°F (bottom tube), 700°F (bulk), and 8 hours under a linear electron accelerator. During the test 3.2 percent high-boiler formation was reported with no film formation on the tube. The operator reported that the heat transfer properties of the sample appeared to be better than clean Santowax OMP.

Sufficient data were obtained to recommend the above two processes as economically feasible [36, 76]. Laboratory data are available for projecting

these methods into use in either pilot plant operation or demonstration units. Reclaimed products were shown to be stable to electron irradiation and stable thermally up to 750°F. A potential additional benefit of a downflow, catalytic process in the presence of hydrogen lies in the removal of precursors to film formation such as particulate and soluble iron compounds, partially saturated aromatics, and oxygenated species.

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