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CONTRACT NO. NAS 8-25318

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**DEVELOPMENT AND CHARACTERIZATION OF LUBRICANTS  
FOR USE NEAR NUCLEAR REACTORS IN SPACE VEHICLES**

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R. I. Akawie  
M. N. Gardos  
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AEROSPACE GROUP

**HUGHES**

HUGHES AIRCRAFT COMPANY  
CULVER CITY, CALIFORNIA

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July 1972

Approved:

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## FOREWORD

This report was prepared by Hughes Aircraft Company under NASA Contract No. 8-25318 entitled "Development and Characterization of Lubricants for Use Near Nuclear Reactors in Space Vehicles" for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Astronautics Laboratory, Materials Division of the George C. Marshall Space Flight Center with Mr. Keith E. Demorest acting as Project Manager.

The Program Manager is Mr. Glenn L. Robinson, Manager of the Materials Application Department. The authors acknowledge professional assistance from Dr. Normal Bilow, Mr. Darryl Brittain, Dr. Daniel A. Demeo, and Mr. John R. Jones.

This report covers work conducted between 15 May 1971 and 15 May 1972 and is the final report covering the second year's work on this contract. Results of the first year's effort were presented in a summary report issued in January 1971 (Reference 1).

## SUMMARY

This 12-month synthesis and evaluation program was conducted to develop wide-temperature range lubricants suitable for use in space vehicles particularly in the vicinity of nuclear reactors. Based on the extensive synthesis and evaluation program of the first year's effort, additional novel synthetic approaches resulted in non-polymeric, large molecular weight materials, all based on some combination of siloxane and aromatic groups.

Evaluation of these materials indicated that 1,3-disubstituted, 1,1,3,3-tetramethyl- and 1,5-disubstituted-1,1,3,3,5,5-hexamethyl-disiloxanes containing phenylthiophenyl substituents are extremely promising with respect to radiation stability, wide temperature range, good lubricity, oxidation resistance and additive acceptance.

This work discusses the synthesis of fluids and describes the equipment and methods used in evaluation, some of which were specially designed for this program to evaluate micro-quantities of the synthesized lubricants.

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## 1. INTRODUCTION

Prior to 1970 there was no lubricative base fluid whose characteristics approached all those necessary for the various systems of nuclear powered space vehicles, such as the NERVA gimbal, liquid hydrogen valves, pneumatic control valves, pumps, alternators and generators. The only chemical families possessing appreciable radiation resistance, the polyphenyl ethers and polyphenyls, have such high pour points that they are practically useless at low temperatures. Even the modified polyphenyl ethers (C-ethers) display only a limited improvement in low-temperature properties. At the opposite extreme, the silicones, with the widest available temperature range (-100°F to +550°F), have very poor lubricity, low radiation resistance, and poor additive acceptance. Other synthetics and petroleum oils fall in between these two categories: mineral oils lack radiation resistance and temperature range; phosphate esters lack radiation resistance and high-temperature stability.

For the past two years Hughes has been involved in synthesizing and evaluating new classes of nonpolymeric chemical compounds that combine the excellent low-temperature properties and low volatility of silicones with high radiation resistance and good high-temperature stability of polyphenyl ethers. This task has been accomplished by incorporating the basic structural features of both of the above types of lubricants.

During the first 12 months of the synthesis and evaluation program over forty base fluid materials and intermediates have been synthesized and purified; several novel synthetic approaches have been developed; and two unique additives have been made. All of the synthetic materials are based on some combination of siloxane and aromatic groups. This portion of the program is described in detail elsewhere (Reference 1). The present report encompasses the description of the second year's effort to meet the modified environmental and dynamic lubrication requirements for nuclear rocket vehicle components (see Table 1), describing the work accomplished under Contract No. NAS 8-25318 during the period of 15 May 1971 through 15 May 1972.

The primary objectives of the program in this period were to:

- Provide at least one bearing oil and one valve grease capable of withstanding the combined effects of space and nuclear reactor environments
- Fully characterize the lubricants submitted for final testing, and demonstrate their suitability for the intended applications.

In the first year's effort two families of fluids were investigated and found potentially capable of yielding fluids meeting the program objectives. These are:

- 1, 3-disubstituted-1, 1, 3, 3-tetramethyldisiloxanes
- bis [ 4-(3-substituted-1, 1, 3, 3-tetramethyldisiloxanyl)aryl] ethers.

Table 1. Nuclear rocket vehicle component lubrication requirements

ENVIRONMENTAL

1. Temperature: -50 to +500<sup>o</sup>F
2. Medium:
  - Air, 0 to 100 percent relative humidity
  - Helium gas, dry
  - Hydrogen gas, dry
  - Vacuum
3. Radiation: 0 to 10<sup>10</sup> ergs gram<sup>-1</sup> (C)

DYNAMICS

1. True Contact Stress: 10 to 200 ksi
2. Mode for gimbals and valves:
  - Oscillation and hold under load:
    - Frequency: 0.001 to 5 Hz
    - Velocity: 0 to 20 fps
    - Life: 5000 cycles
3. Mode for rotating equipment:
  - Start-up and continuous rotation velocity: 0 to 32,000 rpm
  - Life: 2 years

The substituted groups were usually phenyl or chlorophenyl. Pour points as low as -35<sup>o</sup>F were obtained on non-volatile, radiation-resistant fluids (Reference 1).

During the current period, further introduction of novel synthetic approaches, e.g., substitution of sulfur for the phenoxy group oxygen in 1,3-bis(3-phenoxyphenyl)-1,1,3,3-tetramethyldisiloxane and the eventual

replacement of the tetramethyldisiloxane "backbone" of the molecule with a hexamethyltrisiloxane linkage, has resulted in a low pour point (-53°F), radiation stable lubricant with lubricity properties on a par with those of a commercially available polyphenyl ether (OS-124). In addition, several new additives have been synthesized.

It is generally recognized that in a synthesis research program directed toward a commercial objective it is, indeed, difficult to determine when the objectives have been satisfactorily met, unless an outstanding candidate is obtained. The final fluid, 1,5-bis[3-(phenylthio)phenyl]-1,1,3,3,5,5-hexamethyltrisiloxane is considered to be the outstanding candidate capable of meeting the requirements set forth in Table 1.

Selection of this fluid was aided by specially developed evaluation tests requiring only micro-quantities of lubricant samples. These special tests have been shown to be repeatable and to correlate well with established test methods needing sample quantities that may suit the requirements of the evaluating technologist but far exceeding the capabilities of the research chemist.

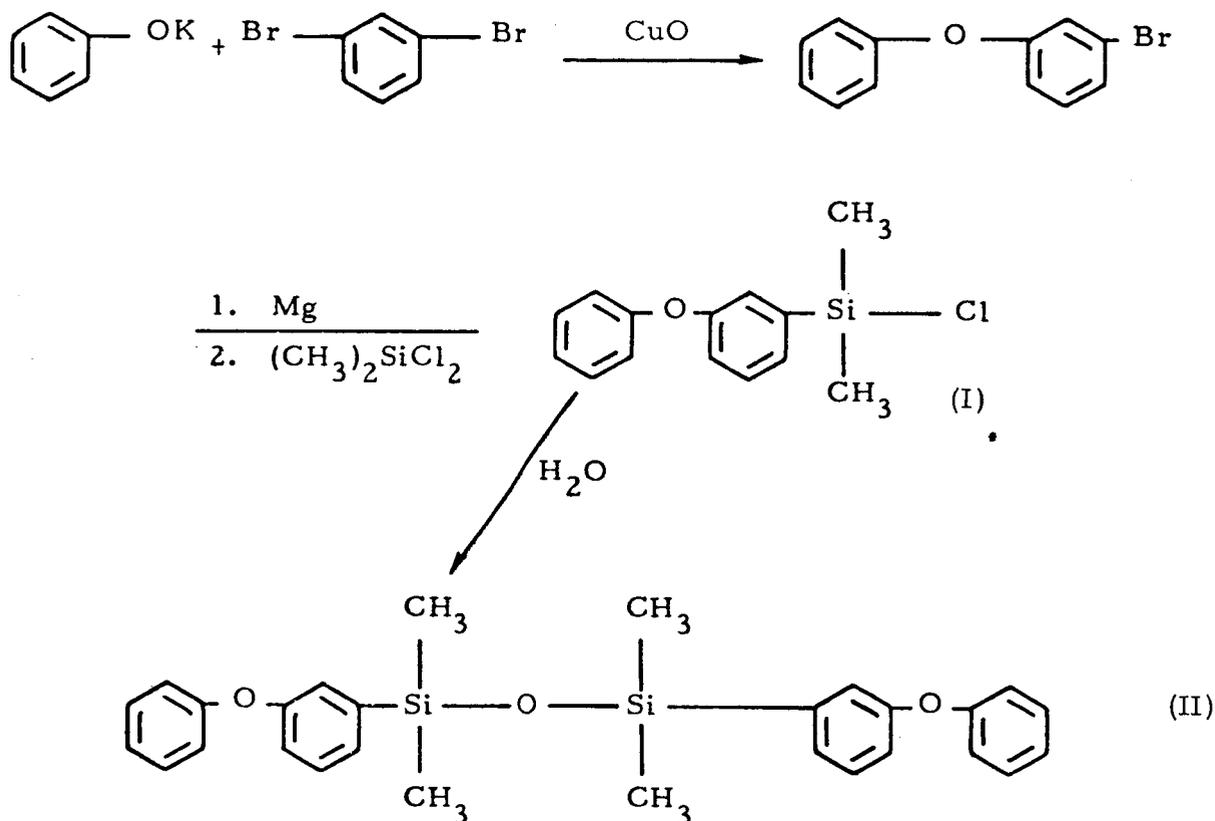
Whenever applicable, physical properties of the Hughes fluids are compared to those of OS-124, which at this time is one of the most widely available radiation resistant commercial lubricants. It was, therefore, selected as the baseline fluid of the current investigation.

## 2. CHEMICAL SYNTHESSES

The synthesis effort was a continuation of that conducted during the previous program. Some of the compounds prepared this year had already been made previously, and the new compounds were chemically analogous. Usually the new compounds contained sulfur atoms in place of some of the oxygen atoms of the original compounds.

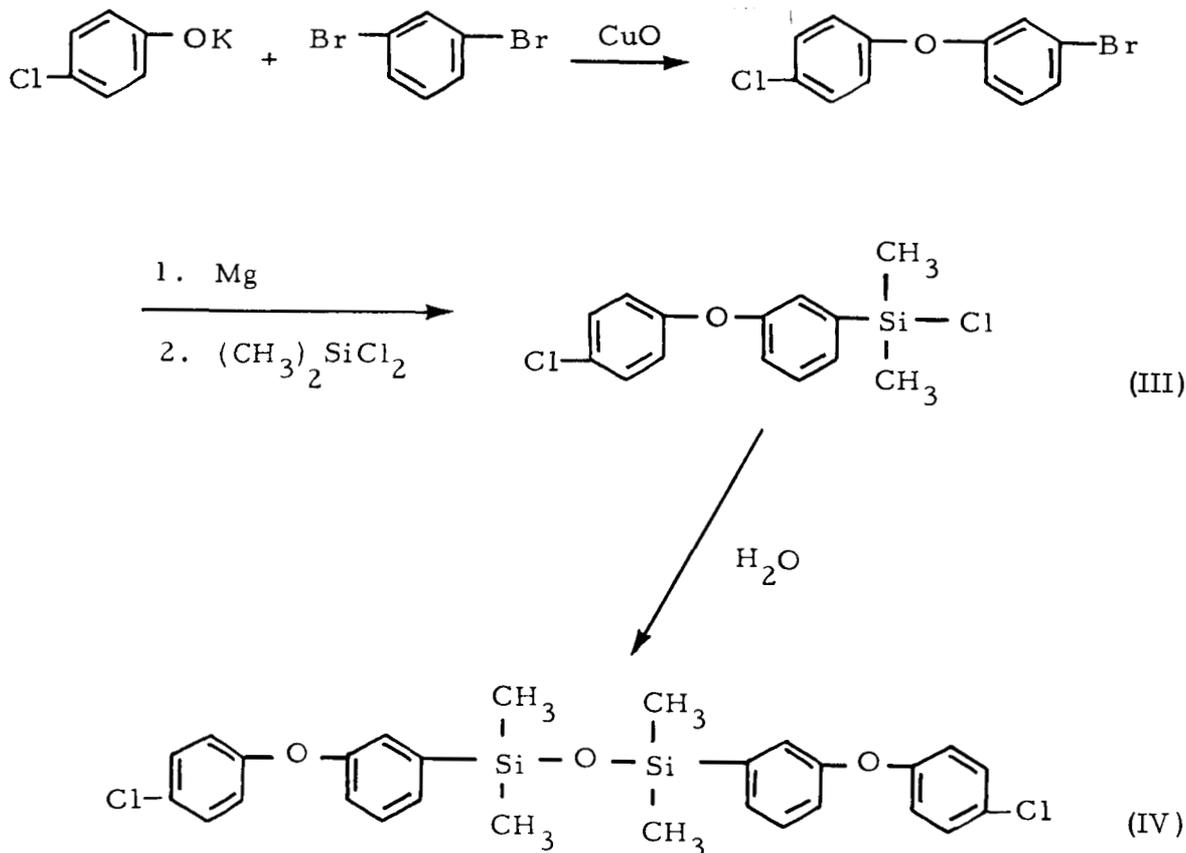
### A. 1,3-Bis(aryloxyphenyl)-1,1,3,3-tetramethyldisiloxanes

The first compound prepared was HCP-1500, 1,3-bis(3-phenoxyphenyl)-1,1,3,3-tetramethyldisiloxane (II). The method used is shown below.



Potassium phenoxide and m-dibromobenzene were condensed in the presence of cupric oxide to form 1-bromo-3-phenoxybenzene. The latter compound reacted with magnesium in tetrahydrofuran to form the Grignard reagent, which was treated with dimethyldichlorosilane in ethyl ether to form (3-phenoxyphenyl)dimethylchlorosilane (I). This chlorosilane was hydrolyzed with water in dioxane to the desired HCP-1500 (II). The product was purified by treatment with activated alumina and charcoal.

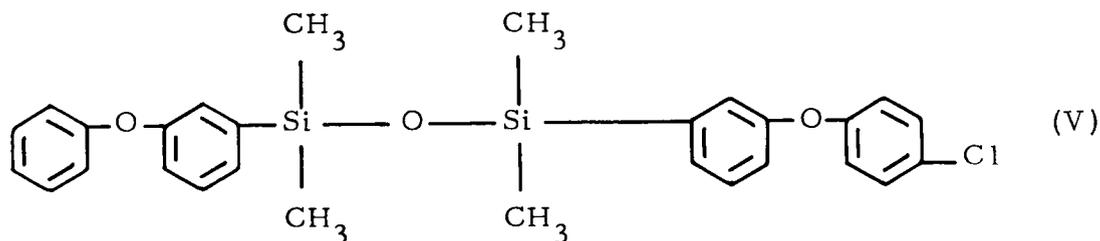
The second of this class of compounds, HCP-1600, 1,3-bis[3-(4-chlorophenoxy)phenyl]-1,1,3,3-tetramethyldisiloxane (IV), is the chlorinated analog of HCP-1500. Its synthesis was carried out as before, starting with 4-chlorophenol and m-dibromobenzene.



4-Chlorophenol was converted by potassium hydroxide to the potassium salt. The salt was condensed with m-dibromobenzene in the presence of cupric oxide. After refluxing the mixture, the product 1-bromo-3-(4-chlorophenoxy)benzene, was isolated and distilled. This was converted to its Grignard reagent, 3-(4-chlorophenoxy)phenylmagnesium bromide. After this reagent was added to an excess of dimethyldichlorosilane, the mixture was worked up, and the [3-(4-chlorophenoxy)phenyl]dimethylchlorosilane (III) was distilled. Another batch of this chlorosilane was made from 1-bromo-3-(4-chlorophenoxy)benzene through the corresponding lithium compound and reaction with dimethyldichlorosilane. The chlorosilane was then hydrolyzed in dioxane to give the desired HCP-1600 (IV), which was shown by infrared spectrophotometry to be identical to the HCP-1600 previously synthesized.

In order to determine the effect of mixing similar disiloxanes on the melting points of the mixtures, several blends of (3-phenoxyphenyl)dimethylchlorosilane (I) and [3-(4-chlorophenoxy)phenyl]dimethylchlorosilane (III) were prepared and hydrolyzed to disiloxane mixtures. The mixtures contained

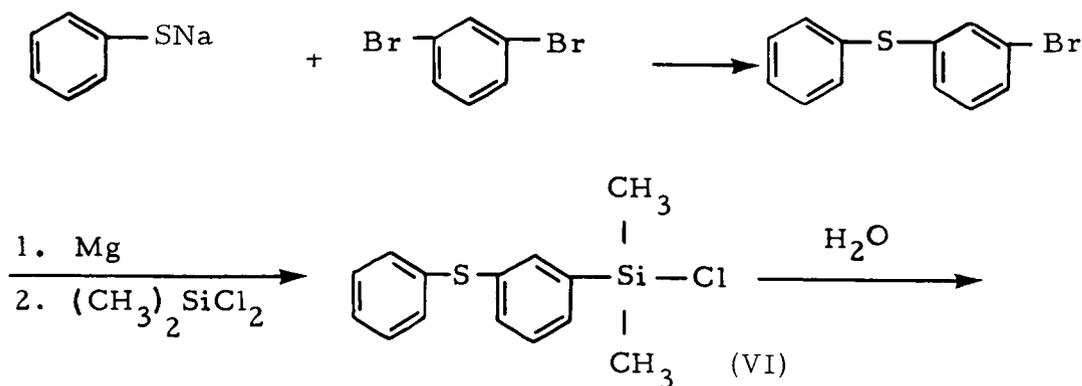
the symmetrical disiloxane II, formed from 2 molecules of chlorosilane I plus water, and the symmetrical disiloxane IV, formed from 2 molecules of chlorosilane III plus water, along with the unsymmetrical disiloxane 1-(3-phenoxyphenyl)-3-[3-(4-chlorophenoxy)phenyl]-1,1,3,3-tetramethyldisiloxane (V), formed from 1 molecule of chlorosilane I and 1 molecule of chlorosilane III plus water. The amounts of II, IV, and V in the disiloxane mixtures depended on the amounts of the two chlorosilanes I and III in the original blends.

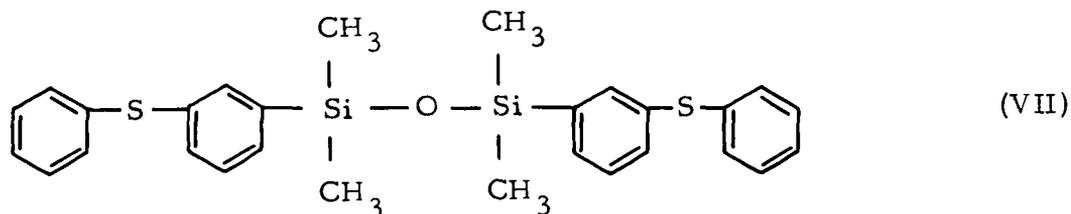


Four different blends of the two chlorosilanes were hydrolyzed. These were, on a molar basis, 9 parts of I to 1 part of III, designated HCP-C1500/1600(9/1), 3 parts of I to 1 part of III (2 batches of this blend were prepared), designated HCP-C1500/1600(3/1), 3 parts of I to 2 parts of III, designated HCP-C1500/1600(3/2), and 1 part of I to 3 parts of III, designated HCP-C1500/1600(1/3). The various blends were hydrolyzed with water in dioxane, and then purified by treatment with charcoal or alumina. The physical properties of the products are given elsewhere in this report.

#### B. 1,3-Bis(arylthiophenyl)-1,1,3,3-tetramethyldisiloxanes

The next series of compounds prepared varied from those above in that the oxygen atoms between the aromatic rings were replaced by sulfur atoms. The first of these, 1,3-bis[3-(phenylthio)phenyl]-1,1,3,3-tetramethyldisiloxane (VII), HCP-1800, is the sulfur-containing analog of HCP-1500. It was prepared by the following method:



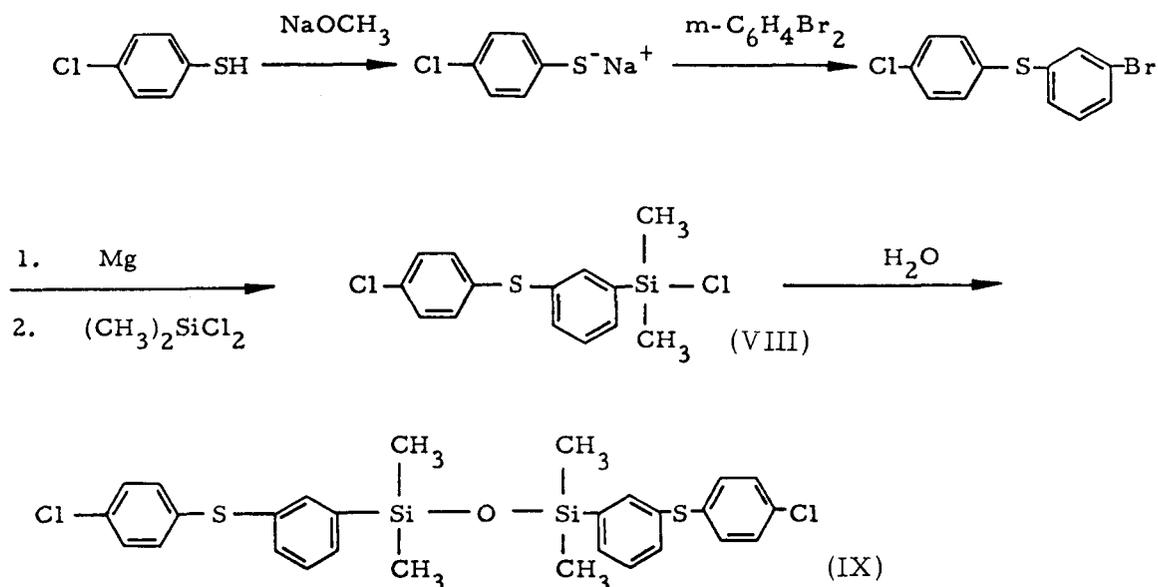


Sodium thiophenoxide was prepared by treating benzenethiol with sodium methoxide in anhydrous ethanol and then distilling the solvent. A 99 percent yield of the salt was obtained. It was condensed with *m*-dibromobenzene by refluxing the mixture in bis(2-methoxyethyl) ether to form 1-bromo-3-(phenylthio)benzene. The Grignard reagent of this last compound was formed in tetrahydrofuran and added to an excess of dimethyldichlorosilane. The [3-(phenylthio)phenyl]dimethylchlorosilane (VI) thus formed was hydrolyzed in the usual manner with water in dioxane. The resulting product was purified by chromatography on a neutral alumina column to a clear yellow liquid, which was batch No. 1 of HCP-1800. Batch No. 2 of HCP-1800 was prepared in a similar manner. Elemental analysis and molecular weight showed that neither of these batches was pure HCP-1800, so the chlorosilane VI was made once more by the same procedure and purified by distillation under very low pressure.

A portion of the distillate was dissolved in dioxane and treated with water in dioxane to form batch No. 3. The disiloxane was washed with methanol and then purified by chromatography on a neutral alumina column. The remainder of the distillate was similarly treated to give batch No. 4. Both of these batches were analyzed for elemental composition, and the analyses indicated that the compounds were pure.

However, the physical properties of batch No. 3 and batch No. 4 were different, even though the procedure for synthesis was almost identical. Hence, another batch of the chlorosilane VI was prepared and distilled, and it was divided in three parts. These were converted by hydrolysis to batches 5, 6, and 7 of HCP-1800. Hydrolysis of VI to form batch No. 5 was carried out at room temperature, while hydrolyses to form batches 6 and 7 were carried out at reflux temperature. Nevertheless, batches 5, 6, and 7 had the same physical properties as batch No. 4. There is no obvious explanation for the different properties which batch No. 3 had, even though its elemental analysis agreed with the theoretical values for pure HCP-1800.

The second compound in this series that was synthesized was HCP-1900, 1, 3-bis[3-(4-chlorophenylthio)phenyl]-1, 1, 3, 3-tetramethyldisiloxane (IX). This is the chlorinated analog of HCP-1800, and the sulfur-containing analog of HCP-1600. It was synthesized by the procedure below.

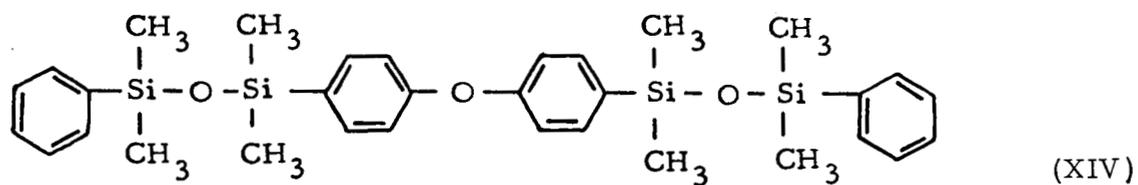
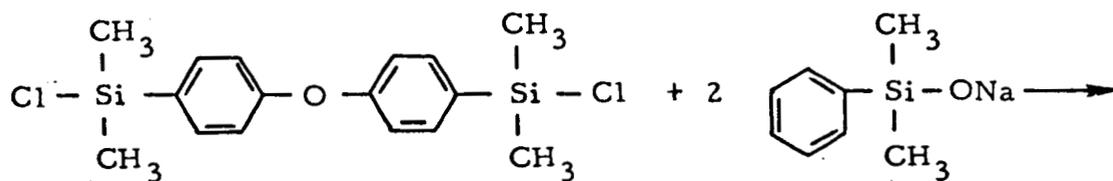
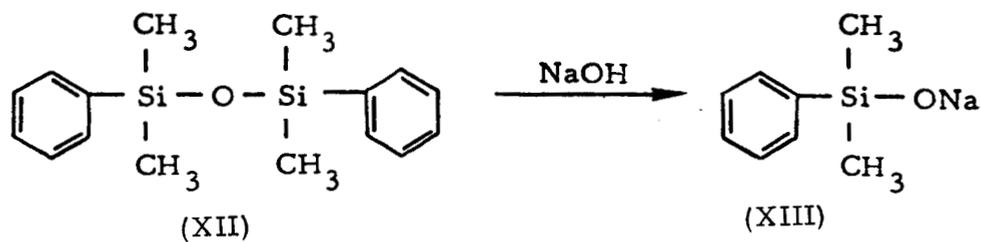
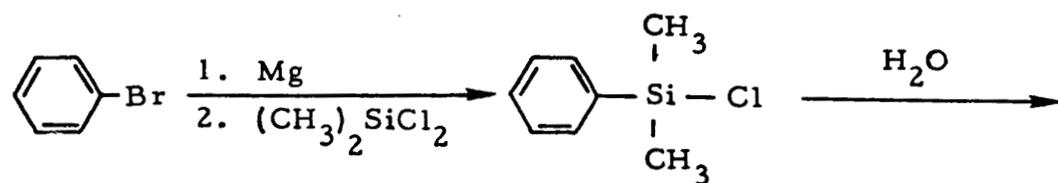
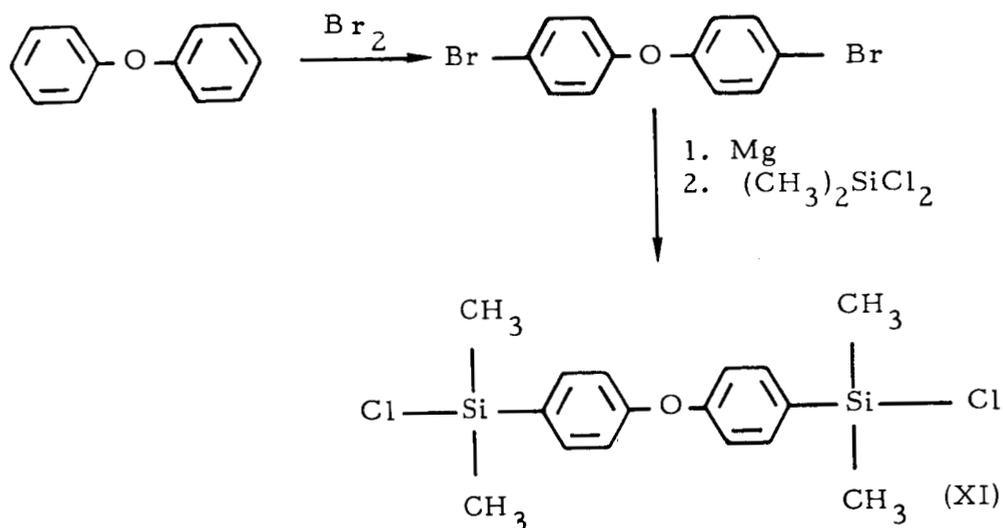


The reaction of 4-chlorobenzenethiol with sodium methoxide in refluxing anhydrous ethanol gave sodium 4-chlorothiophenoxide in almost quantitative yield after removal of the solvent. This salt was then condensed with m-dibromobenzene. The reaction mixture was refluxed 41 hours, and was worked up to yield 1-bromo-3-(4-chlorophenylthio)benzene. It was treated with magnesium in tetrahydrofuran to give the Grignard reagent and this was then added to an excess of dimethyldichlorosilane. The 3-[4-chlorophenylthio]phenyl]dimethylchlorosilane (VIII) was isolated by distillation. The chlorosilane, dissolved in dioxane, was hydrolyzed by water in dioxane and the product, HCP-1900, was purified by column chromatography on neutral alumina. Elemental analysis showed it to be pure.

### C. 1,5-Bis(arylthiophenyl)-1,1,3,3,5,5-hexamethyltrisiloxanes

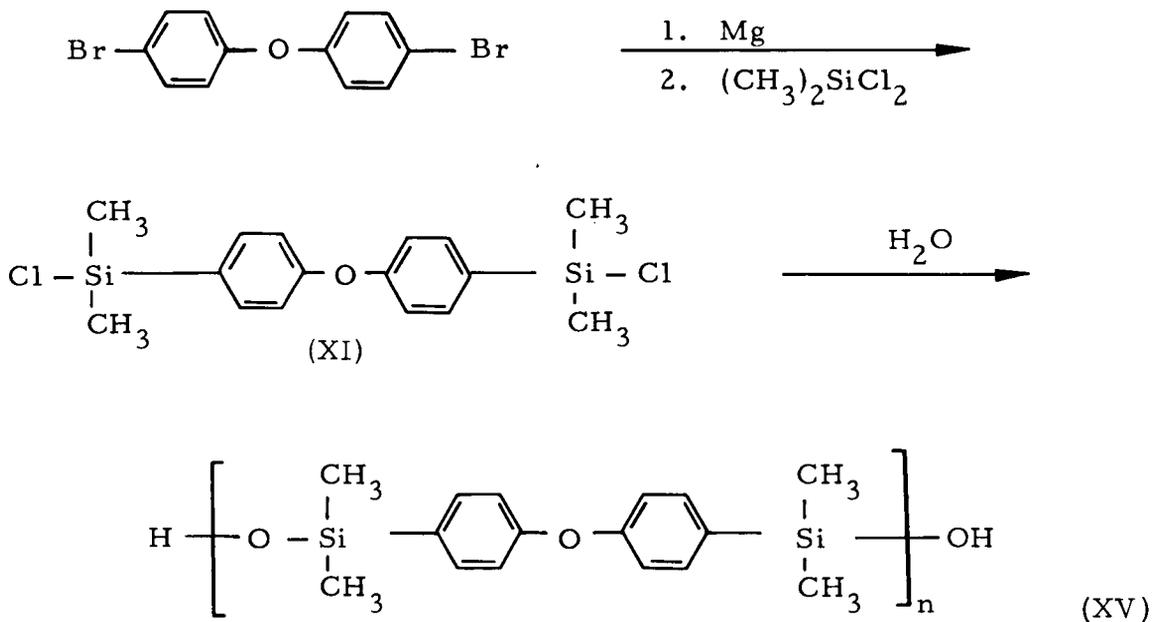
In order to measure the effect on physical properties of lengthening the center portion of the molecule to a trisiloxane group, the compound 1,5-bis[3-(phenylthio)phenyl]-1,1,3,3,5,5-hexamethyltrisiloxane (X), HCP-2800, was synthesized by the procedure below.





Phenyl ether was brominated to form bis(4-bromophenyl) ether. This was converted to the di-Grignard reagent or the dilithium derivative, which was treated with dimethyldichlorosilane to form bis[4-(chlorodimethylsilyl)phenyl] ether (XI). However, difficulty was encountered in preparing the sodium salt of phenyldimethylsilanol (XIII). The Grignard reagent from bromobenzene was treated with dimethyldichlorosilane in ethyl ether, and a 78 percent yield of phenyldimethylchlorosilane was isolated. This was hydrolyzed in the presence of barium carbonate to keep the reaction mixture from becoming acid. The product, which was thought to be phenyldimethylsilanol, was treated with sodium metal in refluxing toluene, but only a negligible reaction occurred. It was then found that the hydrolysis had formed 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane (XII) instead of the silanol; this disiloxane will not react with sodium. However, since the disiloxane will react with sodium hydroxide in boiling isopropyl alcohol to form the sodium salt of phenyldimethylsilanol (reference 3), the disiloxane was treated with sodium hydroxide in a mixture of isopropyl and methyl alcohols, and the sodium salt (XIII) was isolated. The sodium salt was then condensed with the bis[4-(chlorodimethylsilyl)phenyl] ether to give HCP-4270 (XIV).

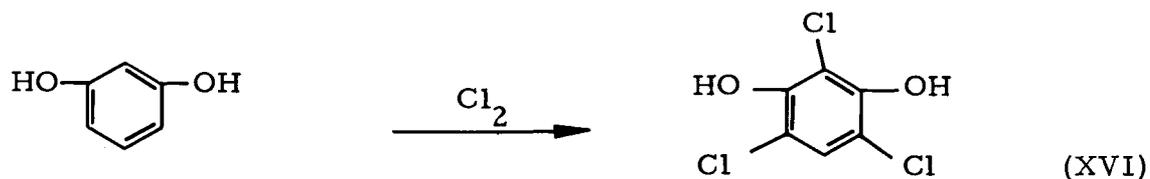
A high molecular weight analog of HCP-4270, designated HCP-4270P (XV), was synthesized for testing as an additive. The reactions are shown below.



Bis(4-bromophenyl) ether was allowed to react with magnesium in tetrahydrofuran to form the corresponding di-Grignard reagent, which was then treated with excess dimethyldichlorosilane. The product, bis[4-(chlorodimethylsilyl)phenyl] ether, was isolated and hydrolyzed in dioxane. Unfortunately, much heat was evolved during the hydrolysis, and almost none of the desired polymer was obtained. From the amount of phenyl ether isolated, it was evident that scission of aryl-silicon bonds had taken place because of the high temperature. The hydrolysis was therefore repeated at 0°C, and the HCP-4270P was isolated. The average molecular weight was found to be 1108, which indicates that n in the above formula (XV) was 3 to 4.

#### E. MISCELLANEOUS

The compound 2,4,6-trichlororesorcinol (XVI) was synthesized for use as an additive. Resorcinol, dissolved in glacial acetic acid, was treated with excess chlorine until the product crystallized out of the mixture. The crude product was purified by recrystallizing it from aqueous ethanol.



### 3. SYNTHETIC PROCEDURES

#### 1-Bromo-3-phenoxybenzene (G1211-04)

A solution of 157 g (1.19 moles) of potassium phenoxide in 413 ml of bis[2-(2-methoxyethoxy)ethyl] ether was prepared by warming. It was added with stirring during 7 hours to a mixture of 559 g (2.37 moles) of m-dibromobenzene, 13.6 g of cupric oxide, and 177 ml of bis[2-(2-methoxyethoxy)ethyl] ether held at 210-215°C. The mixture was then stirred at this temperature for 7 hours, cooled, filtered with suction, and diluted with 2000 ml of benzene. The solution was washed twice with 4 percent aqueous potassium hydroxide solution, twice with 4 percent aqueous sodium chloride solution, and three times with water. It was dried over anhydrous potassium carbonate and distilled. The fraction boiling at 125-145°C at 4 torr was redistilled, giving 148 g (0.594 mole) of product distilling at 105-110°C at 1 torr. The yield was 50 percent of the theoretical.

#### (3-Phenoxyphenyl)dimethylchlorosilane (G1211-06)

A solution of 74.7 g (0.300 mole) of 1-bromo-3-phenoxybenzene in ethyl ether was added slowly to 15.0 g (0.62 g-atom) of magnesium. Formation of the Grignard reagent was initiated with a small amount of 1-iodobutane. When the addition was completed, the mixture was refluxed and stirred for 1 hour. The solution was decanted and added slowly to 122 ml (130 g, 1.00 mole) of dimethyldichlorosilane in ethyl ether. A second phase separated, but disappeared when 500 ml of tetrahydrofuran was added. After the mixture was refluxed for 5 hours, the solvent and excess dimethyldichlorosilane were distilled and the salts filtered off. The product distilled at 120-145°C at 2-4 torr. The yield of 51.7 g (0.197 mole) was 66 percent of the theoretical.

#### 1,3-Bis(3-phenoxyphenyl)-1,1,3,3-tetramethyldisiloxane, HCP-1500 (G1211-09)

A solution of 10 ml of water in 30 ml of dioxane was added dropwise with stirring to a solution of 23.6 g (0.0898 mole) of (3-phenoxyphenyl)-dimethylchlorosilane in 100 ml of dioxane. The mixture was refluxed 3 hours, and then the solvent and excess water were distilled at 3 torr. The residue was dissolved in tetrahydrofuran, decolorized with charcoal, dried over potassium carbonate, and heated up to 110°C at 2 torr to remove volatile material. The residue was stirred with neutral alumina and then with charcoal, and filtered once more. The yield of 16.5 g (0.0351 mole) of product was 78 percent of the theoretical.

#### 1-Bromo-3-(4-chlorophenoxy)benzene (G1211-25)

A solution of 252 g (1.96 moles) of p-chlorophenol in 350 ml of ethanol was treated with a solution of 129 g of 85 percent pure potassium hydroxide (109.5 g pure, 1.96 moles) in water. After stirring for 30 minutes, the solvent was distilled under vacuum until the potassium

p-chlorophenoxide was dry. It was dissolved in 700 ml of bis-[2-(2-methoxyethoxy)ethyl] ether. The solution was heated to 115°C and added at this temperature during 3-4 hours to a refluxing mixture of 867.5 g (3.677 moles) of m-dibromobenzene, 20 g of cupric oxide, and 300 ml of bis[2-(2-methoxyethoxy)ethyl] ether. The mixture was refluxed 42 hours with stirring, cooled, and filtered. The excess m-dibromobenzene and the solvent were distilled from the filtrate, after which 303.7 g (1.071 moles) of 1-bromo-3-(4-chlorophenoxy)benzene, distilling at 150-158°C at 2 torr, and 58.1 g (0.175 mole) of 1,3-bis(4-chlorophenoxy)benzene, distilling at 190-210°C at 2 torr, were obtained. The yield of the monochloro product was 55 percent of the theoretical.

[3-(4-Chlorophenoxy)phenyl]dimethylchlorosilane (G1211-31, F2783-36)

A solution of 141.7 g (0.500 mole) of 1-bromo-3-(4-chlorophenoxy)benzene in anhydrous tetrahydrofuran was added slowly to 12.2 g (0.50 g-atom) of magnesium. Formation of the Grignard reagent was initiated with a small amount of iodoethane. The reaction started slowly, but was completed in 3.5 hours. The Grignard reagent was added dropwise to 150 ml (160 g, 1.23 moles) of dimethyldichlorosilane in 400 ml of anhydrous tetrahydrofuran over 1.5 hours. The heat of reaction caused the mixture to reflux. Stirring was continued for 2 hours, after which the solvent and excess dimethyldichlorosilane were distilled and the salts were filtered off. The product distilled at 175-185°C at 1-2 torr. The yield of 75.8 g (0.255 mole) was 51 percent of the theoretical.

In another run, a cooled solution of 137 g (0.483 mole) of 1-bromo-3-(4-chlorophenoxy)benzene in 500 ml of ethyl ether was treated during 1.5 hours with 212 ml of 2.28 Molar n-butyllithium in ethyl ether (Alfa Products). The mixture was stirred for 1 hour at room temperature, and then was added to 196 g (1.52 moles) of dimethyldichlorosilane in 1500 ml of ethyl ether. A precipitate formed and heat was evolved. The mixture was stirred 1 hour at room temperature and then was filtered. The ethyl ether and excess dimethyldichlorosilane were distilled. The product distilled at 175-182°C at 4 torr.

1,3-Bis[3-(4-chlorophenoxy)phenyl]-1,1,3,3-tetramethyldisiloxane, HCP-1600 (F2783-36)

The [3-(4-chlorophenoxy)phenyl]dimethylchlorosilane above was dissolved in dioxane and added dropwise with stirring to a solution of water in dioxane. After stirring for a while at room temperature the excess water and solvent were distilled under vacuum. Material distilling up to 200°C at 7 torr was separated. The residue was purified by treatment with charcoal.

Hydrolysis of (3-Phenoxyphenyl)dimethylchlorosilane and [3-(4-Chlorophenoxy)phenyl]dimethylchlorosilane Blends, HCP-C1500/1600 (G1211-11, F2783-51, G1211-35, 33, F2783-52)

1. (9/1). A mixture of 28.1 g (0.107 mole) of (3-phenoxyphenyl)-dimethylchlorosilane and 3.5 g (0.0118 mole) of [3-(4-chlorophenoxy)-

phenyl]dimethylchlorosilane in 100 ml of dioxane was treated dropwise with stirring with a solution of 20 ml of water in 40 ml of dioxane. The mixture was refluxed for approximately 1 hour. The solvent and excess water were distilled at 3 torr. The residue was dissolved in carbon tetrachloride and treated with neutral alumina. The solvent was then distilled under vacuum. The yield of 25.5 g of mixed disiloxanes was 90 percent of the theoretical.

2. (3/1). A mixture of 39.3 g (0.1495 mole) of (3-phenoxyphenyl)-dimethylchlorosilane and 14.8 g (0.0498 mole) of [3-(4-chlorophenoxy)phenyl]-dimethylchlorosilane was dissolved in dioxane, and a solution of 25 ml of water in more dioxane was added with stirring. The mixture was refluxed overnight. Material boiling up to 165°C at 5 torr was distilled off. The residue was dissolved in ethyl ether and benzene, washed several times with water, dried over anhydrous magnesium sulfate, filtered, decolorized several times with charcoal, and concentrated. The liquid was finally filtered through activated charcoal. The yield of 34.5 g of mixed disiloxanes was 71 percent of the theoretical.

3. (3/1). A mixture of 16.6 g (0.0632 mole) of (3-phenoxyphenyl)-dimethylchlorosilane and 6.3 g (0.0212 mole) of [3-(4-chlorophenoxy)phenyl]-dimethylchlorosilane was dissolved in 50 ml of dioxane, and a solution of 10 ml of water in 30 ml of dioxane was added with stirring. The mixture was refluxed for 30 minutes, and then the excess water and dioxane were distilled under vacuum. The residue was taken up in carbon tetrachloride and passed through neutral alumina. After the solvent was distilled, the residue was filtered through a fiberglass filter. The yield of 15.9 g of mixed disiloxanes was 77 percent of the theoretical.

4. (3/2). A mixture of 23.7 g (0.092 mole) of (3-phenoxyphenyl)-dimethylchlorosilane and 17.8 g (0.0599 mole) of [3-(4-chlorophenoxy)phenyl]-dimethylchlorosilane was dissolved in 30 ml of dioxane, and a solution of 15 ml of water in 25 ml of dioxane was added with stirring. The mixture was refluxed for 30 minutes, and then the excess water and dioxane were distilled under vacuum. The residue was taken up in carbon tetrachloride and passed through neutral alumina. After the solvent was distilled, the residue was filtered through a fiberglass filter. The yield of 31.8 g of mixed disiloxanes was 85 percent of the theoretical.

5. (1/3). A mixture of 6.0 g (0.023 mole) of (3-phenoxyphenyl)-dimethylchlorosilane and 20.7 g (0.0696 mole) of [3-(4-chlorophenoxy)phenyl]-dimethylchlorosilane was dissolved in dioxane, and a solution of 25 ml of water in more dioxane was added with stirring. The mixture was refluxed for 2 hours. Material boiling up to 185°C at 6 torr was distilled off. The residue was dissolved in ethyl ether, decolorized with charcoal, and the solvent was distilled. The yield of 15.0 g of mixed disiloxanes was 62 percent of the theoretical.

#### Sodium Thiophenoxide (G1211-47)

To a solution of 108 g (2.00 moles) of sodium methoxide in 750 ml of absolute ethanol was added 220 g (2.00 moles) of benzenethiol. After refluxing

with stirring for 4 hours, the solvent was distilled under vacuum, leaving 261.5 g (1.98 moles) of white product. The yield was 99 percent of the theoretical.

#### 1-Bromo-3-(phenylthio)benzene (G1211-08)

A solution of 132 g (1.00 mole) of sodium thiophenoxide in 800 ml of bis(2-methoxyethyl) ether was added dropwise during 2 hours to a refluxing solution of 236 g (1.00 mole) of m-dibromobenzene in 200 ml of bis(2-methoxyethyl) ether. The mixture was refluxed 22 hours longer, and poured into a large amount of water. The brown oil which separated was washed several times with water, decolorized with charcoal, dried over potassium carbonate, and distilled. After unreacted m-dibromobenzene was collected, the product distilled at 157-160°C at 3 torr. The yield of 121.5 g (0.458 mole) of product was 46 percent of the theoretical.

#### [3-(Phenylthio)phenyl]dimethylchlorosilane (G1211-19)

A solution of 115 g (0.433 mole) of 1-bromo-3-(phenylthio)benzene in 100 ml of tetrahydrofuran was added with stirring during 3 hours to 17 g (0.70 g-atom) of magnesium suspended in tetrahydrofuran. Formation of the Grignard reagent was initiated with a small amount of 1-iodobutane. After stirring for 3 hours longer, the Grignard reagent was decanted and added slowly during 2 hours to 122 ml (130 g, 1.00 mole) of dimethyldichlorosilane. After stirring overnight, the tetrahydrofuran and excess dimethyldichlorosilane were distilled. Carbon tetrachloride was added, and the insoluble salt was separated by filtration. The filtrate was then heated up to 185°C at 3 torr to remove volatile components from the product. The yield was 73 percent of the theoretical.

#### 1,3-Bis[3-(phenylthio)phenyl]-1,1,3,3-tetramethyldisiloxane, HCP-1800 (G1211-29, 43)

To a solution of 41.5 g (0.149 mole) of [3-(phenylthio)phenyl]-dimethylchlorosilane in 70 ml of dioxane was added dropwise with stirring a solution of 10 ml of water in 30 ml of dioxane. After refluxing for 1.5 hours, the excess water and dioxane were removed under vacuum. The residue was washed with water and with methanol and then was dissolved in carbon tetrachloride. This solution was passed through a column of neutral alumina. The solvent was evaporated under vacuum, and the residue was filtered through a fiberglass filter. The yield of 28.7 g (0.0571 mole) of product was 77 percent of the theoretical. This was batch No. 3.

In another run, a solution of 20 ml of water in 25 ml of dioxane was added dropwise with stirring to a solution of 27.9 g (0.100 mole) of [3-(phenylthio)phenyl]dimethylchlorosilane in 75 ml of dioxane. After the mixture was stirred for 1 hour at room temperature and refluxed for 1 hour, the excess water and dioxane were distilled under vacuum. The residue was washed with water and with methanol, dissolved in carbon tetrachloride and passed through two successive columns of neutral alumina. The solvent was evaporated under vacuum, and the residue was filtered through a fiberglass

filter. The yield of 20.6 g (0.0410 mole) of product was 82 percent of the theoretical. This was batch No. 4.

Sodium 4-Chlorothiophenoxide (G1211-27)

To a solution of 108 g (2.00 moles) of sodium methoxide in 750 ml of absolute ethanol was added 289.3 g (2.00 moles) of 4-chlorobenzenethiol. After refluxing with stirring for 6 hours, the solvent was distilled from the product under vacuum.

1-Bromo-3-(4-chlorophenylthio)benzene (G1211-28)

A solution of 333 g (2.00 moles) of sodium 4-chlorothiophenoxide in 700 ml of bis[2-(2-methoxyethoxy)ethyl] ether was added slowly during 4 hours to a refluxing solution of 944 g (4.00 moles) of m-dibromobenzene in 800 ml of the same solvent. The mixture was refluxed with stirring for 41 hours. It was cooled, diluted with 1000 ml of benzene, and washed twice with 4 percent aqueous sodium hydroxide solution, twice with 4 percent aqueous sodium chloride solution, and three times with water. The benzene and excess m-dibromobenzene were distilled. The product distilled at 170-175°C at 2 torr. The yield of 350.2 g (1.169 moles) was 58 percent of the theoretical.

[3-(4-Chlorophenylthio)phenyl]dimethylchlorosilane (G1211-34)

A solution of 150 g (0.500 mole) of 1-bromo-3-(4-chlorophenylthio)benzene in 500 ml of anhydrous tetrahydrofuran was added slowly to 12.2 g (0.50 g-atom) of magnesium. Formation of the Grignard reagent was initiated with a small amount of iodoethane, and was completed in 6 hours. The reagent was then added to 122 ml (130 g, 1.00 mole) of dimethyldichlorosilane in tetrahydrofuran. After stirring for an hour, the excess dimethyldichlorosilane and tetrahydrofuran were distilled, and the salts were filtered off. The product distilled at 195-205°C at 3 torr. The yield of 57.6 g (0.184 mole) was 37 percent of the theoretical.

1,3-Bis[3-(4-chlorophenylthio)phenyl]-1,1,3,3-tetramethyldisiloxane, HCP-1900 (G1211-42)

To a solution of 57.6 g (0.184 mole) of [3-(4-chlorophenylthio)phenyl]dimethylchlorosilane in 100 ml of dioxane was added dropwise with stirring a solution of 20 ml of water in 25 ml of dioxane. After refluxing for 1.5 hours, the excess water and dioxane were removed under vacuum. The residue was washed with methanol and then dissolved in carbon tetrachloride. This solution was passed through a column of neutral alumina. The solvent was evaporated under vacuum, and the residue was filtered through a fiberglass filter. The yield of 42.1 g (0.0736 mole) was 80 percent of the theoretical.

1,5-Dichloro-1,1,3,3,5,5-hexamethyltrisiloxane (G1211-44)

A solution of 53 g (2.94 moles) of water in 60 ml of dioxane was added dropwise with stirring during 2 hours to a solution of 750 g (5.81 moles) of dimethyldichlorosilane in 750 ml of anhydrous ethyl ether. The solution was

then distilled through a short Vigreux column to separate the solvents. The higher boiling material was then redistilled through a 16-inch Vigreux column. The fraction distilling at 136-140°C at 760 torr (1,3-dichloro-1,1,3,3-tetramethyldisiloxane) weighed 136.6 g (0.672 mole), and the fraction distilling at 174-178°C at 760 torr (1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane) weighed 76.7 g (0.277 mole). The yield of the disiloxane was 23 percent of the theoretical, and the yield of the trisiloxane was 19 percent of the theoretical.

1,5-Bis[3-(phenylthio)phenyl]-1,1,3,3,5,5-hexamethyltrisiloxane, HCP-2800 (G1211-58)

A solution of 115.8g (0.437 mole) of 1-bromo-3-(phenylthio)benzene in 500 ml of anhydrous tetrahydrofuran was added slowly to 10.6g (0.436 g-atom) of magnesium. Formation of the Grignard reagent was completed in approximately 5 hours. The reagent was then added dropwise over 1.5 hours to a solution of 57.7g (0.208 mole) of 1,5-dichlorohexamethyltrisiloxane in 500 ml of anhydrous tetrahydrofuran. The mixture was refluxed 2 hours, cooled, and treated with water (heat was evolved). The solvent in the organic phase was removed by heating under vacuum. The residue was dissolved in carbon tetrachloride and passed through a column of neutral alumina. The solvent was evaporated under vacuum, leaving 108.5g (0.188 mole) of product, batch No. 3. The yield was 90 percent of the theoretical.

Batch No. 3 and batch No. 4 were combined and heated up to 150°C at 0.035 torr. The residue, dissolved in carbon tetrachloride, was passed through a column of neutral alumina, after which the solvent was evaporated under vacuum and the product was filtered through a fritted glass filter.

Bis(4-bromophenyl) Ether (F2783-67)

Phenyl ether (50 g, 0.29 mole) in one dish and bromine (105 g, 0.66 mole) in another dish were placed in a desiccator left open to the atmosphere. After 3 days at room temperature all the bromine had disappeared. The crude product was taken out of the desiccator and left at room temperature overnight. After recrystallization from hexane it melted at 59-60°C. The yield of 92 g (0.28 mole) was 97 percent of the theoretical.

Bis[4-(chlorodimethylsilyl)phenyl] Ether (G1211-32, F2783-53)

Bis(4-bromophenyl) ether (164 g, 0.500 mole) was converted to the di-Grignard reagent by refluxing 5.5 hours with 24.3 g (1.00 g-atom) of magnesium in anhydrous tetrahydrofuran. The di-Grignard was only partially soluble in the solvent, and the mixture was added with difficulty during 2 hours to 150 ml (160.5 g, 1.244 moles) of dimethyldichlorosilane in tetrahydrofuran. The tetrahydrofuran was distilled off and carbon tetrachloride was added to facilitate removal by filtration of the inorganic salts. The filtrate was then fractionated. The product distilled at 145-153°C at 0.065 torr. The yield of 55.0 g (0.155 mole) was 31 percent of the theoretical.

To 78.7 g (0.24 mole) of bis(4-bromophenyl) ether in 500 ml of ethyl ether was added 220 ml of 2.28 Molar n-butyllithium (0.50 mole) (Alfa). After stirring for 2 hours, the reaction mixture was added to 129 g (1.00 mole) of dimethyldichlorosilane in ethyl ether. White solid separated quickly. After stirring and refluxing for several hours, the liquid was decanted and the excess ethyl ether and dimethyldichlorosilane were distilled. The product distilled at 230°C at 9 torr.

#### Phenyldimethylchlorosilane (G1211-05)

A solution of 157 g (1.00 mole) of bromobenzene in ethyl ether was added to 36.5 g (1.50 g-atom) of magnesium with stirring and refluxing over 4 hours. The Grignard reagent was then added to 366 ml (390 g, 3.00 moles) of dimethyldichlorosilane in ethyl ether and the mixture was refluxed for 1.5 hours. The solvent was distilled, the solids were filtered off, and the filtrate was distilled. The product boiled at 196 to 203°C at 760 torr. The yield of 134 g (0.785 mole) of product was 78 percent of the theoretical.

#### 1,3-Diphenyl-1,1,3,3-tetramethyldisiloxane (G1211-13)

A solution of 20 ml of water in 40 ml of dioxane was added dropwise with stirring to 51.3 g (0.301 mole) of phenyldimethylchlorosilane in 80 ml of dioxane. The mixture was stirred 2 hours at room temperature, refluxed 2 hours, and distilled. The product boiled at 135-145°C at 3 torr. The yield of 32 g (0.11 mole) was 74 percent of the theoretical.

#### Phenyldimethylsilanol Sodium Salt (G1211-16)

To a solution of 8 g of sodium hydroxide in 70 ml of isopropyl alcohol and 30 ml of methyl alcohol was added 28.6 g (0.100 mole) of 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane. The temperature was held at 40 to 50°C during the addition. The hot solution was filtered to remove sodium carbonate, and then concentrated by heating to 115°C. Three times the residue was treated with 5 ml of methyl alcohol and concentrated by heating to 140°C at 15 torr. The residue was dissolved in toluene, heated to boiling, filtered, and concentrated under vacuum. The yield of viscous oil was 28.4 g (0.163 mole), or 81 percent of the theoretical.

#### Bis[4-(3-phenyl-1,1,3,3-tetramethyldisiloxanyl)phenyl] Ether, HCP-4270 (G1211-18)

A mixture of 58.0 g (0.163 mole) of bis[4-(chlorodimethylsilyl)phenyl] ether, 56.9 g (0.327 mole) of phenyldimethylsilanol sodium salt, and 325 ml of dioxane was refluxed 6 hours with stirring, filtered, and concentrated by distillation. The residue was treated with neutral alumina and charcoal. The yield of 85.7 g (0.146 mole) of product was 90 percent of the theoretical.

Poly[oxy(dimethylsilylene)-1,4-phenyleneoxy-1,4-phenylene(dimethylsilylene)], HCP-4270P (G1211-46A)

A solution of 17.0 g (0.0478 mole) of bis[4-(chlorodimethylsilyl)phenyl] ether in 100 ml of dioxane was cooled in an ice bath. To it was added dropwise with stirring a solution of 10 ml of water in 25 ml of dioxane. After stirring for 1 hour, the mixture was left overnight at room temperature. The solvent was removed under vacuum. The residue was dissolved in carbon tetrachloride and passed through a column of neutral alumina. The solvent was evaporated under vacuum, leaving 9.9 g (0.033 mole) of very viscous material. The yield was 69 percent of the theoretical.

2,4,6-Trichlororesorcinol (G1211-24)

A rapid stream of chlorine gas was passed into a stirred solution of 150 grams (1.36 moles) of resorcinol in 625 ml of glacial acetic acid. The solution became quite warm and dark red, but then the color gradually lightened. After several hours the reaction was stopped. Crystals which separated on standing overnight were filtered off, recrystallized twice from water, and then decolorized in aqueous ethanol. The yield of white crystals was 91.7 grams (0.430 mole), or 32 percent of the theoretical.

## 4. EVALUATION

### A. LUBRICANT DESIGNATION

The code for designating the Hughes synthesized lubricants is printed below because certain molecular structures have been found attractive and certain others will probably never be used again. Due precisely to this reason, the code presented herein differs significantly from that established in Reference 1.

1. The first three letters (HCP) indicate a Hughes material synthesized for the Engineering Physics Branch of NASA-ASTN-MEL.
2. The first digit indicates the chemical family:
  - 1 - 1,3-disubstituted-1,1,3,3-tetramethyldisiloxanes
  - 2 - 1,5-disubstituted-1,1,3,3,5,5-hexamethyltrisiloxanes
  - 3 - bis[4-(3-substituted-1,1,3,3-tetramethyldisiloxanyl)aryl]thioethers
  - 4 - bis[4-(3-substituted-1,1,3,3-tetramethyldisiloxanyl)aryl]ethers
3. The second digit designates the  $R_1$  group indicated in various structural formulae. Similarly the third digit designates the  $R_2$  group (if different from  $R_1$ ). Both groups will use the following numerical designations:
  - 0 = none (hydrogen atom)
  - 1 = not in use
  - 2 = phenyl
  - 3 = chlorophenyl
  - 4 = 2,4-di(4-chlorophenoxy)phenyl
  - 5 = 3-phenoxyphenyl
  - 6 = 3-(4-chlorophenoxy)phenyl
  - 7 = 1,4-phenylene
  - 8 = 3-(phenylthio)phenyl
  - 9 = 3-(4-chlorophenylthio)phenyl

4. The fourth digit was originally reserved to designate blends formulated with a particular chemical (additive). Although numerous additives have received attention in the present program, none has been singled out as a prime candidate for a specific additive function. For sake of simplicity, therefore, each blend is designated without the use of the fourth digit (or more precisely, the digit "0" is used throughout) but with the inclusion of the type and weight percent of the additive in question.
5. The letter P appearing after the fourth digit designates a polymeric material derived from the type of fluid described by the first three HCP digits.

Examples of the coding system are:

HCP-1500	1,3-bis(3-phenoxyphenyl)-1,1,3,3-tetramethyl-disiloxane.
HCP-1600	1,3-bis[3-(4-chlorophenoxy)phenyl]-1,1,3,3-tetramethyldisiloxane.
HCP-4270	bis[4-(3-phenyl-1,1,3,3-tetramethyldisiloxanyl)-phenyl] ether.
HCP-4270P	poly[oxy(dimethylsilylene)-1,4-phenyleneoxy-1,4-phenylene(dimethylsilylene)]

The compounds that have been synthesized by Hughes during the second year's effort are listed, with their structures, in Appendix II.

## B. PURITY

The primary objective of the first year's effort was to prepare the greatest possible number of synthetic combinations in order to establish the effects of various substituent groups on fluid pour points. The structures and purity were confirmed by infrared spectroscopy only. Since the purification methods did not include vacuum distillation of the intermediates, the product obtained were necessarily impure, and were not consistent from one batch to the next. Note that in the past it was decided not to distill these intermediates prior to the final stage of synthesis because of concern that they would decompose at the high temperatures required even at reduced pressures (1-5 torr).

During the second year's synthesis work, however, since basic synthesis methods became well established and familiar, all of the compounds were prepared to analytical purity as shown by elemental analyses. Their structures were established by infrared, as well as nuclear magnetic resonance spectroscopy. Essentially all of the intermediates and final products

were purified by high-vacuum ( $2-3 \times 10^{-2}$  torr) distillations and column chromatography on neutral alumina. The distillates and final products were closely monitored for constant refractive indices.

### 1. Elemental Analyses

A comprehensive compilation of elemental analysis data on nearly all of the HCP fluids is presented in Table 2.

The data in Table 2 indicate that

1. The key step in improving the purity of these fluids (with the exception of HCP-2800 and HCP-4270) is the careful high-vacuum distillation of the chlorosilane intermediate. Note the dramatic improvement in the accuracy of the values from HCP-1500, Batch No. 1 to Batch No. 3 (although all of these batches still contain some high-molecular weight, if not polymeric material), from HCP-C1500/1600 (3/1) Batch No. 1 to Batch No. 2 and from HCP-1800, Batch Nos. 1 and 2 to Batch Nos. 4, 5, 6 and 7. In fact, the preparative procedure has become so effective that the first attempt to synthesize HCP-1900 (the last product in a series of synthesized disubstituted tetramethyl disiloxanes) has immediately resulted in a chemically pure product, as shown in Table 2 elemental analyses and N. M. R. spectroscopy (Figure I-2).
2. The rather difficult synthesis and poor performance characteristics of HCP-4270, coupled with the fact that the analyses do not correspond to those of the theoretical structure have eliminated this compound from further considerations.
3. The analysis of the HCP-4270P polymer indicates that approximately 4 monomer units are linked together to form each molecular chain.
4. The extremely low volatility of the dichlorosilane intermediate of the hexamethyltrisiloxane HCP-2800 did not permit even high-vacuum distillation, due, again, to concern over decomposition even at  $\sim 2 \times 10^{-2}$  torr pressures. This lack of intermediate purification resulted in a certain degree of "impurity," with the possible presence of tetrasiloxanes and, perhaps, some even higher homologs. In addition, during synthesis of HCP-2800, a considerable amount of phenyl sulfide is generated in side reactions. Phenyl sulfide can, however, be effectively removed from the final products by high vacuum distillation and further by ultra-high vacuum degassing of  $\sim 5 \times 10^{-5}$  torr. Incidentally, this compound is the prevalent high-volatility "contaminant" in all of the thioether siloxane fluids and rather easily detected by its characteristic odor, even in trace quantities.

Table 2. Elemental analyses of HCP fluids

Compound Designation	Batch No.	C%	H%	Si%	S%	Cl%	Mol. Wt.
HCP-1500	theory	71.4	6.38	11.9	-	-	470
HCP-1500	1	65.75	5.88	13.03	-	-	624
HCP-1500	2 <sup>(1)</sup>	67.12	6.01	13.83	-	-	540
		65.65	5.88	14.04	-	-	560
HCP-1500	3	70.75	6.16	10.63	-	-	529
HCP-C1500/1600 (1/3)	theory	64.37	5.51	10.75	-	10.18	522
HCP-C1500/1600 (1/3)	1	60.63	5.62	12.78	-	9.80	556
HCP-C1500/1600 (3/1)	theory	68.91	6.11	11.51	-	3.63	488
HCP-C1500/1600 (3/1)	1	61.25	6.50	16.06	-	4.45	550
HCP-C1500/1600 (3/1)	2	68.61	6.40	11.50	-	3.91	503
HCP-1600	theory	62.4	5.2	10.38	-	13.15	539
HCP-1600	1	-	-	-	-	-	-
HCP-1800	theory	66.88	6.01	11.17	12.75	-	503
HCP-1800	1 <sup>(1)</sup>	60.85	5.82	14.13	-	-	556
HCP-1800	1	63.13	5.97	11.66	12.82	-	504
HCP-1800	2 <sup>(1)</sup>	68.65	5.34	6.15	-	-	377
HCP-1800	2	70.86	5.59	5.58	15.66	-	333
HCP-1800	3	67.08	5.73	11.44	12.80	-	491
HCP-1800	4	66.80	5.89	11.21	12.60	-	488
HCP-1800	5+6+7	66.92	6.00	11.45	12.57	-	517
HCP-1900	theory	58.82	4.94	9.82	11.22	12.40	572
HCP-1900	1	58.88	5.23	10.02	10.91	12.35	562
HCP-2800	theory	62.45	6.29	14.60	11.11	-	577
HCP-2800	1	-	-	-	-	-	587
HCP-2800	2+3+4	60.01	6.80	17.41	10.27	-	642
HCP-4270	theory	65.47	7.21	19.14	-	-	587
HCP-4270	2	58.43	6.41	19.10	-	-	423
HCP-4270P	1	61.69	6.72	-	-	-	1108

<sup>(1)</sup> Duplicate values were obtained to assess the repeatability of the method. Both values are reported.

## 2. Spectroscopy

I.R. and N.M.R. spectroscopy have proved invaluable in determining the structure and confirming the purity of the compounds in question. A Beckman IR-5 infrared spectrophotometer and a Varian Model No. A-60 N.M.R. spectrometer were utilized in obtaining the spectra combinations of selected fluids before and after irradiation, shown in Appendix I. In addition, several facets of synthesis and evaluation steps were monitored by spectroscopic methods (e. g., batch uniformity of the HCP-2800 fluid, identification of the volatile products in vapor pressure and evaporation rate measurements, etc.).

Examination of these figures clearly indicates that I.R. spectroscopy is far from adequate in determining either purity or structural changes, especially where no pure standards are available. Although the presence of the required characteristic bands, e. g., the broad siloxane band from  $\sim 1020$  to  $1100\text{ cm}^{-1}$ , the silicone-phenyl band at  $\sim 1110\text{ cm}^{-1}$ , the meta-substituted aromatic band at  $\sim 750\text{ cm}^{-1}$  and the mono-substituted aromatic band at  $\sim 690\text{ cm}^{-1}$ , is the prime prerequisite for the correct structure, N.M.R. spectroscopy is needed for the final structural determination. With this prerequisite in mind, the following observations can be made by examining the figures presented in Appendix I, Figures I-1 through I-17.

1. Neither purity nor structural change effects can be detected with certainty between batches of the same compound or after irradiation of any given product by I.R. alone. Since all of the spectra were obtained between salt crystals with variable sample thickness, interpretation of any relative changes in band intensities is difficult. At any rate, these changes appear to be negligible in nearly all cases.
2. N.M.R. spectroscopy is not nearly as dependent on the availability of standard spectra as infrared spectroscopy. On basic theoretical considerations alone one would expect only two characteristic peaks with pure disubstituted siloxanes: one attributable to the aromatic protons at  $\delta \approx 7.0$  and the other due to the methyl protons of the disiloxane group upfield, quite close to the TMS (tetramethylsilane) reference peak at  $\delta = 0$ .

This characteristic peak arrangement is indeed found with the pure batches of HCP-1800 and HCP-1900 (see Appendix I, Figures I-10 and I-12), positively confirming the purity and correct chemical structure of these preparations. It is also evident, however, that the third batch of HCP-1800 which displays rather good elemental analytical results (see Table 2) is in fact a mixture (most likely an isomer and homolog mixture), as indicated by the two upfield multiplets (see Appendix I, Figure I-8). Actually, the presence of this set of two multiplets is characteristic not only of the "impure" batches (No. 1, 2 and 3) of HCP-1800 (note: no vacuum distillation of the chlorosilane intermediate

performed), but with the HCP-1500 batches, and all batches of HCP-2800 (spectra of the phenyl sulfide-contaminated first batch and the final product are shown in Figures I-14 and I-16 of Appendix I). It should be noted, again, that no vacuum distillation of the HCP-2800 chlorosilane intermediate is performed during synthesis. It will be shown later that the formation of mixtures has a profound effect on the pour point of a given fluid.

3. Very little change in fluid structure due to irradiation is indicated by N.M.R. Since the unusual splitting of the methyl proton multiplets can not be definitely interpreted on the non-irradiated products themselves at this time (i. e., these multiplets could arise from non-equivalence through steric effects, due to some unexpected structural changes in the siloxane linkage that otherwise do not affect the results of elemental analyses, or to the presence of some higher siloxane homologs) determination of radiation damage is confined to the qualitative, visual observation of the variations in multiplet splitting only.
4. The relative peak areas were integrated only in the cases of pure products, e. g., HCP-1800, Batch Nos. 4, 5, 6, and 7 and HCP-1900, Batch No. 1. Due to the frequent malfunctioning of the NMR integrator, integration was accomplished by the "paper doll" method (preparing copies of the spectra, cutting out the respective peaks forms and weighing the sections), and in one case (see Appendix I, Figure I-8) by machine integration. In the cases of the pure compounds, integration confirms the presence of 18 aromatic and 12 methyl protons (HCP-1800) and 16 aromatic with 12 methyl protons (HCP-1900) with fair accuracy. Peak integration of Figure I-8 (HCP-1800, Batch No. 3) is not interpreted due to the presence of the multiplets.

In certain cases, e. g., with HCP-2800 (Batch No. 1) which was irradiated while contaminated with phenyl sulfide (see Appendix I, Figures I-14 and I-15), the relatively large aromatic proton peak area (as compared to that of the methyl proton peak(s)) clearly indicated the phenyl sulfide contamination. This peak area is reduced in the case of the final, vacuum distilled batches of HCP-2800 (Figure I-16).

## C. POUR POINT

### 1. Description of the Apparatus and Test Method

One of the difficulties associated with development of low-temperature aerospace lubricants is the lack of suitable definition of low-temperature flowing characteristics. The long-established Cloud and Pour Point Test (in accordance with ASTM method D97) is rather inconvenient for use in testing experimental quantities of low pour-point products, because

1. ~60 ml of product is required for the test. More often than not significantly smaller quantities were available for characterization.

2. The repeatability of this method is  $\pm 5^{\circ}\text{F}$ , the reproducibility between laboratories is  $\pm 10^{\circ}\text{F}$ . At low temperatures (below  $-40^{\circ}\text{F}$ ) the accuracy is further reduced by increased difficulty in observing the pouring tendencies through the rapidly icing pour point jar wall. Any attempt at improving visibility by preventing the deposition of frozen atmospheric moisture on the outer surface of the jar is in direct contradiction of the prescribed test conditions. The original and maintenance costs of a multi-well pour point apparatus are high. On the other hand, the cost of a single well apparatus is low and the bath temperature adjustment is simple: testing, however, is very time consuming, since only a single determination can be performed at any one time.

During the first year of the program, modified pour point tests were performed in a single well Cloud and Pour Test Apparatus (in accordance with ASTM Method D97), whenever 30 ml of the fluid was available. These tests were performed in weighing bottles (used as pour point jars as well as irradiation and storage containers). The amounts used were approximately half of that prescribed by ASTM D97-57, but the I. D. of the container was the same (1-3/16 inches). In order to establish the effect of reduced volume on the pour point value, three determinations were made on nonirradiated OS-124 using an ASTM jar and the required quantity of oil. In all three cases the pour point was  $+40^{\circ}\text{F}$ . The same value was obtained using the modified test procedure.

Since all the products of this program were initially synthesized in even smaller quantities, a decision was made later to utilize a "freezing point" or melting point test. The liquid product was heat-sealed in a small glass capillary and the capillary was tied either to the bulb of a low-temperature thermometer or to a thermocouple. The thermometer (thermocouple) was lowered into a transparent Dewar flask filled with a solvent or solvent mixture. The system was cooled to within a pre-determined temperature range or until the product froze. The capillary was observed with a magnifying glass to detect the point of crystallization.

At this time the entire system was permitted to warm up through heat conductance from the surroundings. The product remained under constant observation to detect the melting point.

Experiments indicated, however, that the families of fluids represented by HCP-1500 and HCP-1800 do not assume a crystalline lattice on freezing, but rather they vitrify. Stationary aliquots of these and similar compounds do not exhibit any visible sign of crystallization, or other phase change (e. g., haziness) or glassification. The capillary micro-sample method of stationary freezing-melting point determination, therefore, could not be utilized with confidence. This method was modified so that a sealed capillary, charged with the frozen fluid, was inverted and re-attached to the thermometer bulb; the bulb was then warmed and, on melting at the capillary glass/product interface, the downward movement of the still-frozen core was observed. In many cases, however, due perhaps to the high surface tension

of the fluids and the back-pressure of the air plug, the core movement was extremely slow. In some instances it was even non-existent, especially if the diameter of the capillary was too small.

During the second year's effort these difficulties prompted the development of a hitherto unreported micro-sample pour point method. The method permits observation of the "melting" of vitrified fluids, and correlates well with the pour point (ASTM Method D97).

Essentially, the desolidification temperature of a product was determined by (1) rapidly freezing a small, predetermined amount of the liquid to the side of a small test tube, to form a frozen drop; (2) immersing duplicates of the charged, stoppered tubes, tied vertically to the low-temperature thermometer, into a transparent Dewar cold bath brought to a temperature below the expected desolidification point; and (3) measuring the temperature when the drop front had moved a predetermined distance as the bath was warmed up. The sample may be fully recovered after the test. The detailed testing procedure is presented in Appendix III.

The bases for the validity of the new method are constituted by the following assumptions:

1. The large rate of change in viscosity during the melting process, coupled with the effect of gravity on the large, melting drop, are the controlling factors in drop-front movement on a vertically positioned, clean glass surface.
2. The change in the surface energy of glass, and the degree of wetting by the fluid as functions of gradually increasing temperature (especially in the low-temperature range of interest) affect short-distance front movement much less than viscosity change. These factors may be neglected in view of the fact that the fluid families under study tend to exhibit similar wetting behavior on glass.
3. Rapid freezing of fluids that crystallize on freezing can significantly affect the apparent freezing (or melting) point and can lead to erroneous results. The same cannot be stated with fluids that vitrify, since no orderly process of molecular movement to a definite crystalline lattice is involved.
4. The effect of the hydrated glass surface may be neglected, since no hydrolysis, and consequently no significant change in surface tension of the subject fluids, can occur due to their hydrolytic stability. At any rate, as stated earlier, the degree of wetting is considered to be a minor factor in vertical drop movement.

In order to prove the soundness of the above discussion, a correlation study was conducted using OS-124, FS 1265 (300 cs), a low-pouring fluoro-silicone), HCP-1500 Batch No. 2, and HCP-2800 Batch Nos. 3 and 4. The pour point data obtained in accordance with the new method and per ASTM D97 (Pour Point) are presented in Table 3. The data indicate a very satisfactory correlation, even on cooling the bath to temperatures considerably below the expected pour point.

Note that since good correlation was established between this new method and ASTM Method D97 and, on "melting", the droplet frozen to the side of the stoppered test tube (immersed in a warming cold bath) simply begins to flow (to "pour") down the side of the glass, the test is aptly designated as a modified pour-point determination and, hereafter, will be referred to as such.

Table 3. New pour point method correlation study

Product	Initial Bath Temp. (°F)	Modified Pour Point (°F)	Pour Point (°F)*
OS-124	30	39	40
OS-124	10	41	40
FS-1265	-80	-50	-55
FS-1265	-60	-52	-55
HCP-1500 (Batch No. 2)	-20	-9	-10
HCP-1500 (Batch No. 2)	-40	-7	-10
HCP-2800 (Batch No. 3 and 4)	-80	-56	-55
HCP-2800 (Batch No. 3 and 4)	-65	-57	-55

\*Per ASTM Method D97. Initial bath temperature well above pour point. Repeatability of this method is considered to be  $\pm 5^{\circ}\text{F}$ .

The test results of the modified procedure are reported to the nearest degree Fahrenheit and its repeatability and reproducibility have been established to be  $\pm 2^{\circ}\text{F}$  (See Table 4). Results per ASTM Method D97 are given to the nearest five degrees Fahrenheit and the reported repeatability is  $\pm 5^{\circ}\text{F}$ .

The original goal of this program in 1970 was to develop radiation-resistant lubricants capable of functioning from  $-100^{\circ}$  to  $+500^{\circ}\text{F}$ . Since the pour point determination is designated as primary screening test for most of the synthesized lubricants, it follows that the method must encompass the lowest boundary of the temperature range of interest.

The modified pour-point procedure is limited only by the low-temperature capability of the Dewar cold bath charge. This is only  $-94^{\circ}\text{F}$  with the present cooling system, (acetone/dry ice in an unsilvered Dewar flask) because of the need for visual observation of the tubes. One prime prerequisite of the micro-sample method is the immersion of the frozen droplet-containing test tube into a cold bath already at a temperature significantly below the melting point of the sample. Consequently, much colder bath mixtures would have to be prepared in order to check melting points of  $-100^{\circ}\text{F}$ . Although a specially distilled petroleum ether/liquid nitrogen system is capable of producing a temperature as low as  $-256^{\circ}\text{F}$ , its preparation is expensive and time consuming. The micro-sample melting point method has therefore been extended to temperatures below  $-100^{\circ}\text{F}$  without utilizing cumbersome, two-phase cooling systems. Modification of the method consists of the following steps:

1. Charge the 800 ml transparent Dewar flask with 200-300 ml liquid nitrogen. Immediately after the initial partial boil-off, replenish the charge to its original volume.
2. Prepare the sample tube per the prescribed procedure (see Appendix III) with the following exceptions:
  - a. To accomplish complete rapid freezing of the test drop to the side of the sample tube, carefully pour liquid nitrogen over the horizontally positioned, charged and stoppered test tube.
  - b. Instead of utilizing a low-temperature thermometer, fasten the prepared sample tubes to a 0.1-inch I. D. Pyrex glass tube (sealed at one end) containing a thermocouple.
  - c. Immediately lower the thermocouple-tubes assembly in a vertical position into the Dewar flask, placing the bottom of the test tubes slightly above the liquid nitrogen surface. The thermocouple bead (inserted all the way into the sealed tube) must be in the immediate vicinity of the two frozen test drops. Cover the Dewar flask top with a sheet of aluminum foil to minimize condensation of moisture.

- d. When the sample tube bottom is ~1 cm away from the liquid nitrogen surface, thermal equilibrium at the sample level is ~-220°F. Raising the sample tube increases this equilibrium temperature 18-27°F for every centimeter of height. For example, if the melting point of a fluid is known to be below -94°F, the tube may be lowered to within 1.0 cm of the surface of the liquid nitrogen and kept there for a period of time to reach thermal equilibrium. For a rapid, preliminary determination, the thermocouple stem may then be raised slowly in small increments, and the melting point may be recorded per the prescribed criterion. The temperature is measured with a millivolt potentiometer. For a slower, more accurate determination, the distance and temperature increase should be achieved simply by permitting the liquid nitrogen to evaporate from the flask.

Following the development of the improved method described above, it was determined in discussion with the Project Manager that low-temperature requirements for radiation-resistant space lubricants are approximately -50°F rather than the originally specified -100°F. The above method was checked, however, on some recently developed, experimental grade fluorinated polyethers and gave the following results:

<u>Fluid</u>	<u>Melting (pour) point</u>
Light fraction	-105°F
Medium fraction	-96°F
Heavy fraction	-54°F

The method is considered suitable for any extended development of any non wax-containing fluids that still flow in the lower temperature regions.

## 2. Results and Discussion

Modified pour-point determinations were performed on all products prepared during the second year of this program. The data obtained are presented in Table 4. Examination of these pour point values indicate the following:

1. Early indications for the probability of reducing the pour points of both "parent" compounds by synthesizing unsymmetrical molecules by cohydrolysis of various HCP-1500 and HCP-1600 intermediates were proved wrong when pure cohydrolysis products were synthesized (see Table 2). These pure preparations had significantly higher pour points than the first year's impure counterparts. The phenomenon is rather dramatically shown in Figure 1. Note that the second

Table 4. Modified pour point data on HCP fluids

Lubricant Designation	Modified Pour Point (°F)	
	Trial #1	Trial #2
HCP-1500 (Batch No. 3)	-23	-24
HCP-C1500/1600 (9/1) (Batch No. 1)	-17	-17
HCP-C1500/1600 (3/1) (Batch No. 2)	-16	-14
HCP-C1500/1600 (3/2) Batch No. 1	-10	-10
HCP-C1500/1600 (1/3)	-20	-20
HCP-1600 (Batch No. 2)	54	52
HCP-1800 (Batch No. 2)	-51	-50
HCP-1800 (Batch No. 3)	-53	-52
HCP-1800 (Batch No. 4)	-22	-24
HCP-1800 (Batch No. 5)	-13	-15
HCP-1800 (Batch No. 6)	-15	-15
HCP-1800 (Batch No. 7)	-14	-15
HCP-1900 (Batch No. 1)	+3	+1
HCP-2800 (Batch No. 1)	-50	-48
HCP-2800 (Batch No. 2)	-56	-54
HCP-2800 (Batch No. 3 + 4)	-56	-56
HCP-4270 (Batch No. 2)	-40	-39

batch of HCP-1500/1600 (3/1), as well as the first batch of (3/2), were hydrolyzed from purified intermediates, and are therefore much more likely to be representative of the theoretical mixture of products than were the first batches of cohydrolysis products. The strong indication is that cohydrolysis of mixtures of the HCP-1500 and HCP-1600 intermediates cannot be expected to produce materials having lower pour points than HCP-1500.

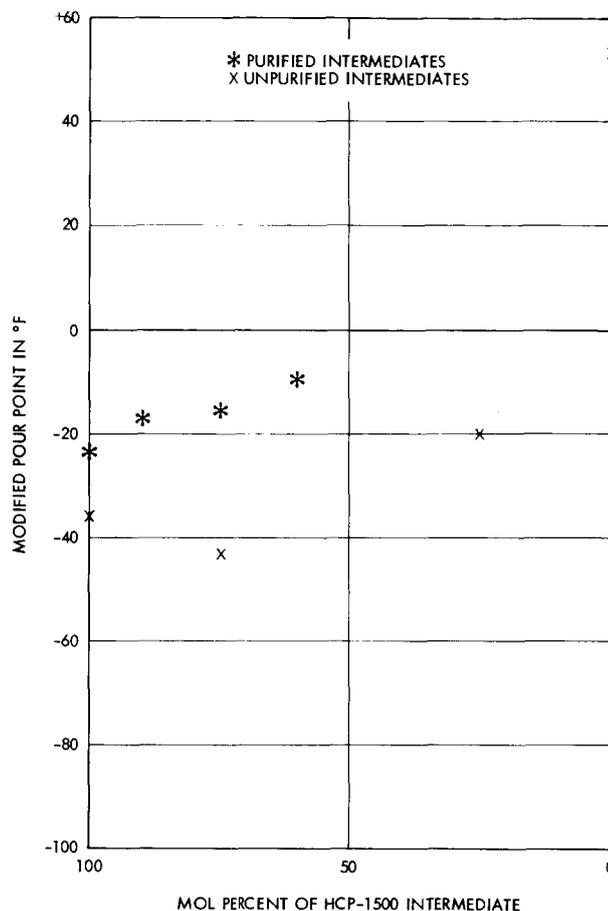


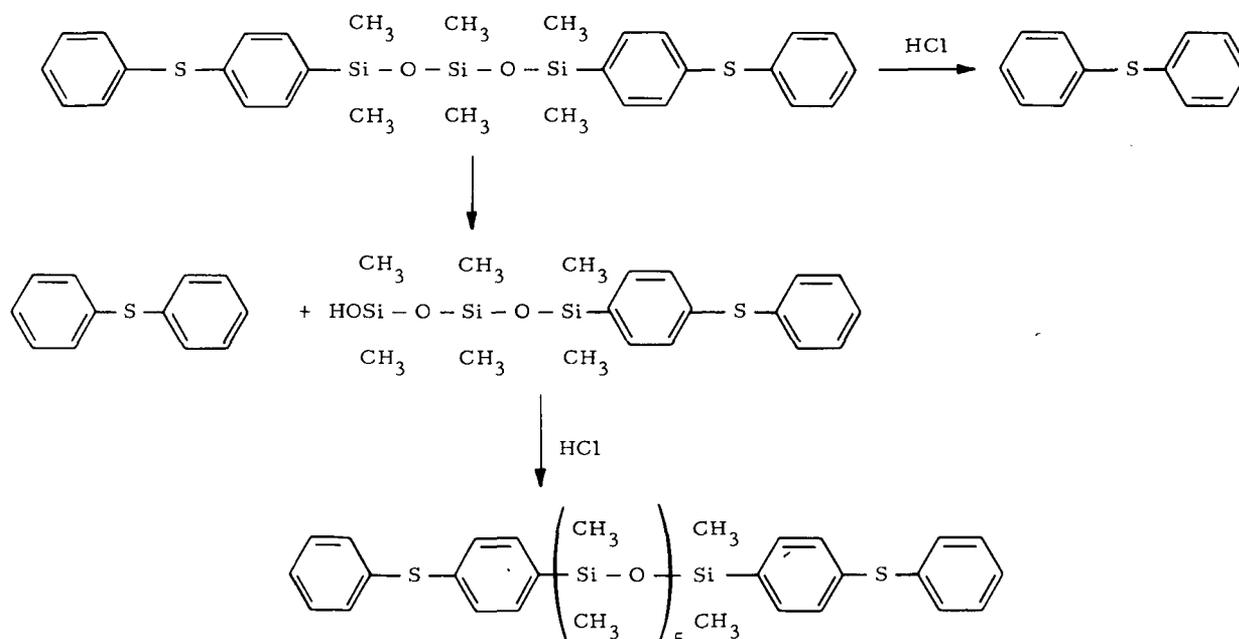
Figure 1. Modified Pour Points of  
Cohydrolysis Products

It should be noted at the same time, however, that the monochloro product (formula V, page 7, an unsymmetrical molecule) could still be expected, as a species, to have a lower pour point than HCP-1500. In our opinion the effort required to separate this monochloro fluid from the mixture was not justified by any practical benefit resulting from such separation. However, it could be synthesized by an independent method.

2. The modified pour point method is not only repeatable, but also extremely sensitive to the purity of a fluid. The case in point is the gradual increase in the pour points of HCP-1800 batches with continually improved purity (indicated by elemental analyses and N.M.R. spectroscopy). Batch No. 3 can be considered as a mixture; Batch No. 4 contained only slight traces of impurities, while Batch Numbers 5, 6 and 7 appeared to be completely pure. Note the gradual increase in pour points of the batches in question.

3. Chlorinated homologs of HCP-1500 and HCP-1800 (HCP-1600 and HCP-1900, respectively) display a large increase in pour points from those of the parent compounds.
4. The first batch of HCP-2800 (vacuum distilled to remove phenyl sulfide) has a higher pour point than that of the following batches. This may be attributed to the initially selected excessively high distillation temperature and the consequential excessive removal of lighter ends in addition to phenyl sulfide. This temperature was changed to 250°F at  $\sim 2 \times 10^{-2}$  torr. As a result, the following batches display improved low pour points, well below the requirements of this program.

It seems likely, that the low-temperature pouring characteristics of HCP-1800 (Batch No. 3), as well as that of all batches of HCP-2800 are directly related to the formation of isomeric mixtures of homologous compounds. Although, as stated earlier, the mechanisms of isomerization or other changes are not yet entirely clear, the use of these mixtures having a high proportion of meta linkages is a well-known method of pour point reduction (References 4, 5, 6). It is most likely that homologous compounds present in the lubricants would be formed by an acid catalyzed cleavage of the parent compound as shown below:



Furthermore, a hexasiloxane such as the one illustrated, even when formed in small amounts, would be expected to lower the pour point.

Several additives being considered as "lubricity agents" in the disiloxane fluids were evaluated for their effect on the pour points of HCP-1500 and HCP-C1500/1600 (9/1). The philosophy of testing rests on the premise that if the additive is able to significantly lower the pour point of the base fluid containing phenoxyphenyl substituents, this beneficial effect would probably be magnified in the case of the thioether homologs. Additionally, since the batches of HCP-1800 and HCP-2800 were needed for other evaluation tests, the phenoxyphenyl products on hand were used as base fluid mediums for further testing of blends. Furthermore, it seemed possible that certain additives might lower the melting points by virtue of mixing.

Pour point data on these mixtures are presented in Table 5.

The data in this table indicate that

1. The addition of trichlororesorcinol produces a large increase in pour point;
2. The addition of TCP (tricresyl phosphate) increased the pour point of HCP-1800 (Batch No. 3);
3. No effect is produced by either tri-p-tolyl phosphite, tri-p-tolyl thiophosphate or lead naphthenate;
4. The mixtures of HCP fluids yield pour points which are nearly arithmetical averages of those of the constituents (see Table 4).

Finally, it should be noted that HCP-4270P, a polymeric material derived from the HCP-4270 intermediate was prepared for the express purpose of increasing the viscosity of HCP fluids by blending. Since (a) this polymer was a solid at room temperature and (b) the chain ends are most likely hydroxyl terminated, blending was not performed. Discontinuation of further work was based on the premise that the pour point and low temperature viscosity of the HCP fluids could only be increased by blending with HCP-4270P. The observed pour point increase of HCP-1500 by mixing with OS-124 and any additional effect from increased hydrogen bonding due to the -OH terminal groups of HCP-4270P seem to substantiate the premise.

It should be noted that pour point testings of mixtures are of a preliminary nature only, since the effect of additives could comprise the subject of a separate, comprehensive study itself.

Generally, the modified pour point method has proved itself invaluable in fluid characterization due to its simplicity, reproducibility, rapidity and small sample aliquot requirement.

Table 5. Modified pour point data on fluid mixtures

Lubricant Mixture (by wt. )	Pour Point (°F)
HCP-1500 (Batch No. 3) <sup>(1)</sup>	-24
HCP-1500 (Batch No. 3) +5 w/o Trichlororesorcinol	-9/-12 <sup>(2)</sup>
HCP-1500 (Batch No. 3) + 3 w/o Tri-p-tolyl phosphite	-24
HCP-1500 (Batch No. 3) + 3 w/o Tri-p-tolyl thiophosphate	-23
HCP-1500 (Batch No. 3) + HCP-1800 (Batch No. 3)(1:1)	-35
HCP-1800 (Batch No. 3) <sup>(1)</sup>	-53
HCP-1800 (Batch No. 3) + 5 w/o TCP	-48
HCP-C1500/1600 (9/1) <sup>(1)</sup>	-17
HCP-C1500/1600 (9/1) + 3 w/o Lead naphthenate <sup>(3)</sup>	-17
HCP-4270 (Batch No. 2) + 5 w/o TCP <sup>(4)</sup>	-40.
<p>(1) Pour point presented for comparison</p> <p>(2) Duplicate measurements. Some crystallization observed.</p> <p>(3) Pour point of "pure" lead naphthenate = -40°F.</p> <p>(4) Product decomposition in 6 days.</p>	

## D. VISCOSITY

### 1. Description of the Apparatus and Test Method

Ordinarily, one of the first characteristics of a fluid to be examined is its viscosity-temperature relationship. Precisely for this reason viscosity was designated as a primary screening test for most of the synthesized lubricants. Viscosity baths were prepared conforming to the requirements of ASTM Method D445-53T (Test for Kinematic Viscosity).

1. The 100°F bath contains water; the heat is controlled by a Precision Scientific mercury-to-wire temperature controller and relay.
2. The 210°F bath contains silicone fluid; the heat is controlled by a mercury-to-wire temperature controller and relay.
3. The low-temperature bath (at 0°F and below) contains dry ice-cooled acetone. Cooling is controlled by addition of small, incremental quantities of crushed solid CO<sub>2</sub>.

Prior to conducting all viscosity tests, the calibrated Cannon-Fenske routine (~7 ml charge) and Cannon-Manning semi-micro viscometers (~1 ml charge) were chemically cleaned with chromic acid. A small drain stand was constructed which permitted maximum drainage of the viscometer contents and recovery of the test sample. The draining operation was performed in a laminar flow bench.

When filtration of the sample appeared necessary before the viscosity (or any other) tests, a Millipore filter holder (equipped with 0.45μ filter disks and vacuum flasks) was utilized.

### 2. Results and Discussion

The viscosities of several synthesized materials have been determined and are shown in Tables 6 and 7.

The viscosity values in Table 6 indicate the following:

1. Viscosity (just like pour point determinations) is extremely sensitive to product purity. Again, by following the viscosity history of all batches of HCP-1800, the gradual "thickening" of the fluid with increased purity is observed. This viscosity increase is graphically presented in Figure 2. The viscosities of OS-124 are also plotted, mainly to show that the ASTM slopes of the aromatic substituted siloxanes are comparable to those of the polyphenyl ethers (see also Figure 3).

Table 6. Viscosities of selected HCP fluids

Compound Designation	Kinematic Viscosity in Centistokes		
	100°F	210°F	400°F <sup>(1)</sup>
HCP-1500 (Batch No. 3)	22.62	3.97	1.1
HCP-C1500/1600 (9/1) (Batch No. 1)	29.29	4.44	1.2
HCP-C 1500/1600 (1/3) (Batch No. 2)	30.75	5.12	1.4
HCP-1600 (Batch No. 2)	3054.0	31.62	2.6
HCP-1800 (Batch No. 1)	(2)	(2)	(2)
HCP-1800 (Batch No. 2)	10.70	2.91	1.1
HCP-1800 (Batch No. 3)	12.81	3.09	1.1
HCP-1800 (Batch No. 4)	26.50	4.80	1.4
HCP-1800 (Batch No. 5)	32.56	5.29	1.4
HCP-1900 (Batch No. 1)	54.90	6.22	1.4
HCP-2800 (Blend of all batches)	20.49	4.99	1.6
(1) Extrapolated			
(2) Insufficient quantity for viscosity determinations.			

Table 7. Low-temperature viscosities of thioether fluids

Compound Designation	Kinematic Viscosity in Centistokes		
	-45°F	-35°F	0°F
HCP-1800 (Batch No. 3)	44,516	2,177.7	185.3
HCP-2800 (Blend of all batches)	22,740	8,226	599.0

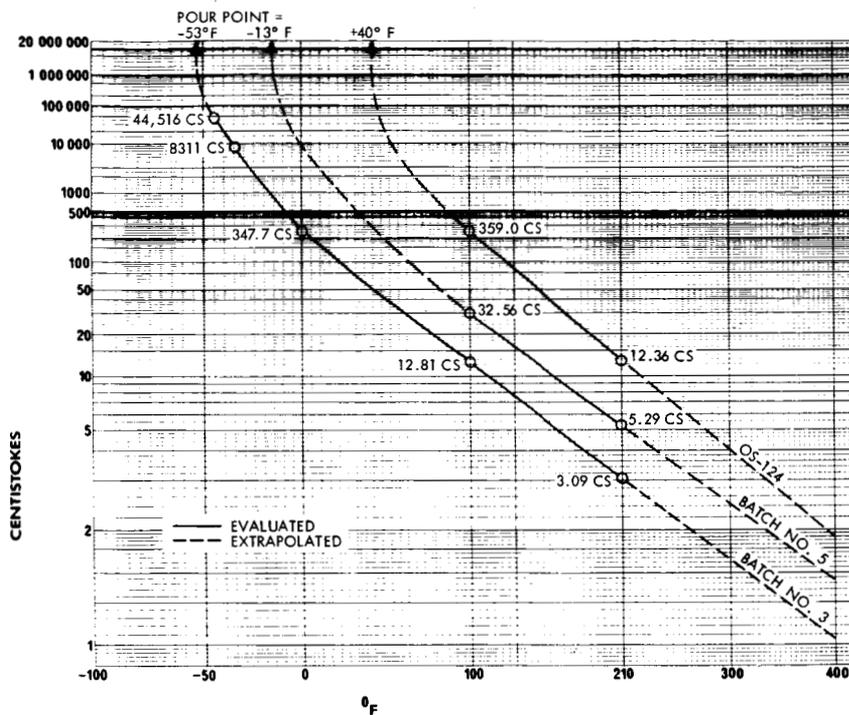
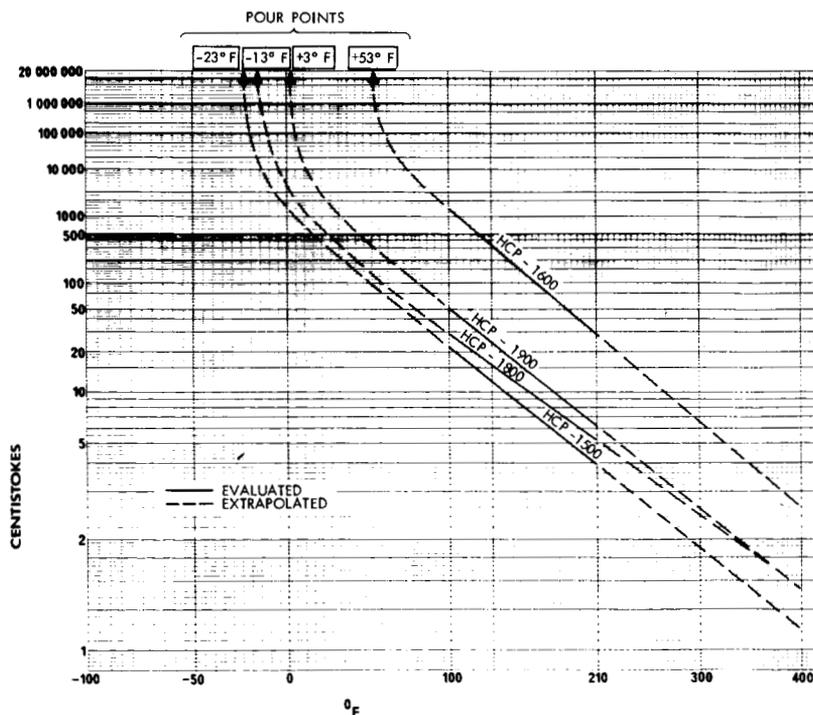


Figure 2. Effect of Purity on the Viscosity Temperature Relationship for HCP-1800 Batches

Figure 3. Effect of Chlorine Substituents on the Viscosity and Pour Point of the Chlorinated Homologs of HCP-1500, Batch No. 3 (HCP-1600, Batch No. 2) and HCP-1800, Batch No. 5 (HCP-1900, Batch No. 1)



Incidentally, it should be noted that in contrast to most aromatic compounds, the viscosity-temperature characteristics of polyphenyl ethers are very good. Chain flexibility imparted by the ether linkages is undoubtedly responsible, since the corresponding polyphenyls have rather poor viscosity-temperature properties (Reference 5). The presence of short, strong but flexible siloxane "backbones" in the HCP fluids, coupled with the ether or thioether linkages in the substituent groups seem to assure viscosity-temperature properties at least as good (if not slightly better) as those of the polyphenyl ethers.

2. The transposed data in Figure 3 graphically show that the main effects of incorporation of chlorine to produce dichlorinated homologs of HCP-1500 and 1800 are large increases in pour point and viscosity. The second observation points to the fact that the magnitude of the increase is significantly reduced on substituting sulfur for the more electronegative phenoxy group oxygen atoms. Although the effect of dichlorination is not surprising in view of the bulky nature of the chlorine atoms, the effect of the higher electronegativity of the phenoxy groups is rather large, especially since the strength of hydrogen bonding and Keesom forces is generally rather small in the case of ethers. It is likely that this effect is enhanced by a steric configuration rather different from a symmetrical planar state. Note that the true spread of viscosities between HCP-1500 and HCP-1600 is somewhat obscured by the slightly "impure" nature of these products.

If a lubricant or a hydraulic fluid is to be operable at  $-65^{\circ}\text{F}$ ,  $-40^{\circ}\text{F}$ , or  $0^{\circ}\text{F}$ , the fluid in question must possess a useful fluidity at these temperatures. For example, aircraft hydraulic fluid specifications have generally defined the useful low-temperature viscosity as 2500-3000 cs (and the high temperature viscosity as 1 cs). The data in Figure 4 (plotted with the values from Tables 6 and 7) show that the final fluid candidate, HCP-2800, is useful to as low as  $-25^{\circ}\text{F}$  and probably as high as its decomposition temperature. Low temperature use of OS-124 (data enclosed again for comparison) obviously does not even enter into consideration.

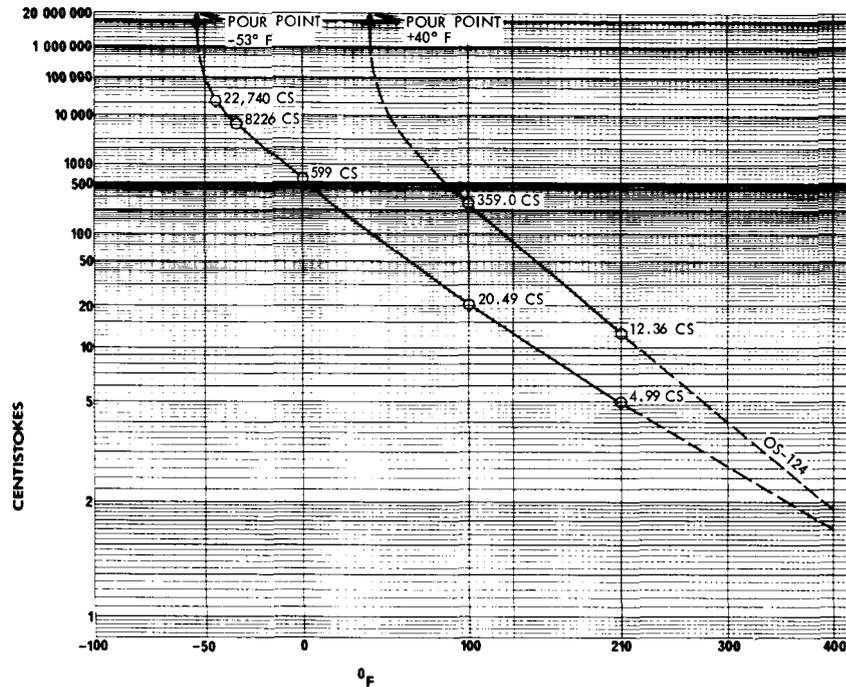


Figure 4. Viscosity-Temperature Relationship for HCP-2800 (Mixture of all Batches)

## E. VOLATILITY

The vapor pressures and evaporation rates of lubricants used in space applications are data of fundamental importance in predicting lubricant losses from critical frictional surfaces. Although most solid lubricants cause little concern due to their extremely low vapor pressures, the volatility characteristic of greases and oils is the primary criterion in their selection for space use.

Heat of vaporization data on low vapor pressure organic compounds are most suitably obtained by either the Knudsen orifice effusion or the Langmuir free-surface evaporation method. Static techniques, such as the use of the isoteniscope or the pendulum tensimeter involve heating of the low volatility test substance to rather high temperatures to obtain reliable data. In some cases, overheating may lead to decomposition. At any rate, isoteniscope vapor pressure measurements of non-uniform fluids (e. g., polymeric lubricating oils) are not permissible, since the evaporation rate and the rate of vapor pressure change of these mixtures vary continuously with progressing evaporation. Furthermore, the data obtained by static methods in the high temperature range need to be extrapolated to low temperatures by utilizing applicable vapor pressure-temperature relationships, e. g., the Clausius-Clapeyron or the Antoine equations. Extrapolation to the low temperature range involves a certain degree of inaccuracy.

In order to avoid the necessity of extrapolation, and provide for the continuous monitoring of the vaporization process, a mass sorption quartz spring microbalance was developed. The schematic of the balance is shown in Figure 5. The instrument measures precisely the evaporation rates of the candidate lubricants at various temperatures by weight loss through free-surface evaporation in ultra-high vacuum.

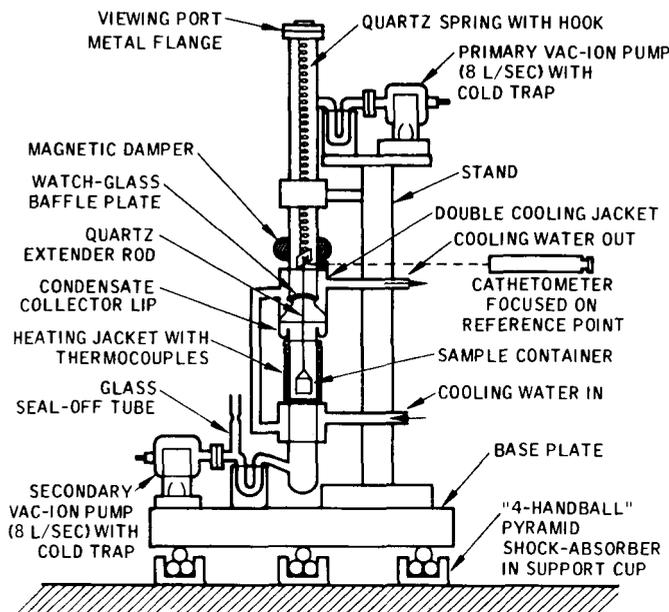


Figure 5. Schematic Diagram of the Microbalance

### 1. Description of the Apparatus and Test Method

In a vertically-positioned glass vacuum chamber equipped with a furnace zone and water-cooled condensing regions, a small quartz sample cup is suspended from a sensitive, pivot-free quartz spring. The sample container (filled with the de-gassed and helium-saturated test fluid) is carefully positioned in the middle of the furnace region while hanging on a thin quartz extender rod. The rod extends through a perforated, removable watch-glass baffle plate. The oil is heated by radiation through the vacuum envelope of the furnace zone. As the oil evaporates, the spring contracts. The movement of an appropriate reference point is measured with a cathetometer.

A permanent nichrome wire heating jacket is wound on an asbestos base at the furnace region of the balance. The heating coils are sealed in sheets of asbestos paper heavily doped with a water glass solution and further insulated with a thick asbestos cloth.

Two copper-constantan thermocouples imbedded into the middle of the furnace zone serve as integral parts of the heating jacket. One leads to a

precision millivolt potentiometer, the other to a temperature controller. The jacket is heated by applying current through a rheostat (connected to the temperature controller) capable of adjusting the jacket temperature to within 0.1°C.

The sample container, charged with ~0.5 g of the test compound (for a detailed specimen preparation procedure see Appendix IV), is carefully positioned in the middle of the furnace region while hanging on a thin quartz extender rod. The selection of the ~0.5 g initial test load provides standard positioning of the cup slightly below the middle of the heated region. The rod extends through a thin, perforated, removable watch-glass baffle plate.

The spring is permanently sealed to a horizontal stainless steel support hook which rests on the inside rim of the metal vacuum flange. This hook permits the use of a glass vacuum viewing port. Since the heating jacket is neither removable nor transparent, the viewing port assists in centering the cup by eye in the middle of the furnace zone. The assembled cup can be seen clearly through the distortion-free watch-glass baffle plate.

Quartz helices are extremely sensitive to vibration, especially when operated in high vacuum, since only the low internal friction of quartz can damp the oscillations. In the present case, the spring vibration is reduced to a negligible amplitude by a simple magnetic damper. This damper consists of a 1 in<sup>2</sup> sheet of commercially available heavy-duty aluminum foil sealed to the spring-extender rod junction. Eddy current damping is provided by a magnet positioned around the foil square on the outside of the glass vacuum chamber. Figure 6 is a close-up of the measurement region of the microbalance, showing the damper foil. The removable watch-glass baffle plate is seen behind the collector lip cooling jacket, resting on three indentations in the balance wall.

The transmission of external vibrations is prevented by shock-mounting the entire balance and pump assembly on three solid rubber ball pyramids of "four-ball" configuration (regular tetrahedron). This simple elastic mounting permits final fine positioning of the assembled test cup inside the furnace zone simply by placing balancing weights on the support plate (see Figure 5).

The spring and the extender rod are prevented from pivoting and turning by small drops of Apiezon Wax W (vapor pressure =  $1 \times 10^{-8}$  torr at 20°C). The same wax seals the damper foil to the spring and the spring to the support hook. No wax is used in the heated zone.

Rough pumping of the system to  $\sim 1 \times 10^{-3}$  torr pressure is performed with two liquid nitrogen-chilled molecular sieve sorption pumps. Ultimate vacuum of 4 to  $6 \times 10^{-8}$  torr is attained by the use of two baked, 8 liters/second, standard diode ion pumps with liquid nitrogen traps. After starting the ion pumps, the constricted glass seal-off tube connecting the sorption pumps is sealed with a blow torch, isolating the system to undergo ion pumping only. The ion pump flanges are sealed with OHFC copper gaskets, while the unbaked viewing port flange is equipped with a Viton rubber O-ring for ease of assembly.



Figure 6. Measurement Region of the Microbalance

During evaporation rate measurements current is supplied to the heating jacket through the temperature controller to obtain the lowest test (cup) temperature desired. Due to the low pressures involved in the vacuum envelope, the oil is heated essentially by radiation in the furnace zone. As the oil evaporates, the spring contracts. The movement of an appropriate reference point is measured with a precision cathetometer. No reading is taken until thermal equilibrium is reached between the heating jacket and the sample. Additional measurements are taken after specific time intervals. This procedure is repeated at each additional test temperature.

After each complete determination (consisting of duplicate evaporation rate measurements at each test temperature), the chamber pressure is carefully brought to atmospheric, and the body of the balance (containing the cold traps) is broken off the vacuum pump and thoroughly rinsed with an appropriate cleaning solvent followed with reagent grade methanol on the inside.

When the clean, dry balance chamber is re-sealed to the ion pumps in the vertical position (checked by a plumb bob) and a new seal-off tube is attached to the bottom ion pump (see Figure 5), the chamber is leak-tested to assure a hermetic system.

The liquid nitrogen balance cold traps effectively trap any volatile constituents of the sample that would otherwise contaminate the ion pumps. Pump degradation, therefore, occurs from the normally expected moisture accumulation only. The routine procedure of baking the ion pumps overnight at 200°C (while in operation on the balance) provides a vacuum of 4-6 x 10<sup>-8</sup> torr in the morning, even after five or six repeated full scale evaporation rate determinations, and increases the intervals between periodic high-temperature baking operations.

#### a. Calibration

Calibration of the quartz spring is performed by suspending weights on the spring and measuring the extension with a precision cathetometer. The extension vs. load curve is linear in the load range of interest. The spring constant is 34.78 mm/g. Since the cathetometer vernier scale may be read to the nearest 0.05 mm and accurately estimated to the nearest 0.025 mm, the accuracy of each weight loss measurement is ±7.2 x 10<sup>-4</sup> g.

The evaporation area of the sample must be known accurately, since fluids tend to creep over the cup surfaces, effectively increasing the evaporation area. Consequently, a barrier compound must be used to restrict creepage. Commercially available Braycote 806 (1H, 1H-pentadecafluorooctyl methacrylate in a 2.5 percent solution by weight in hexafluoroxylene) is an effective barrier compound which deposits an essentially transparent film with extremely low surface energy properties. The film is characterized by unusual repellancy to oils, synthetic fluids, nearly all common solvents and aqueous solutions. It is frequently used to prevent lubricant migration where the creep of oils creates problems of contamination. The barrier coating solution can be applied to the cup by full immersion or with a camel-hair brush.

By covering the entire surface area of the cup with the barrier coating the evaporation area calculation is greatly simplified, since this area remains that of a circle with a radius equal to that of the sample cup (8 mm). Microscopic examination of several classes of fluids in the coated cup indeed shows only a negligible meniscus. The evaporation area can therefore be taken as 2.01 cm<sup>2</sup> throughout the tests. Any area change due to crystallization on the sample surface is considered negligible.

Based on the measured evaporation rates, the vapor pressure of the test substance is calculated by the Langmuir equation, expressed as

$$P_{\text{torr}} = 17.14 G (T/M)^{1/2},$$

where

$G$  = evaporation rate in  $\text{g} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ ;

$T$  = absolute temperature in  $^{\circ}\text{K}$ ;

$M$  = molecular weight in g.

This equation may be used with confidence, where (a) the test substance itself is composed essentially of a pure chemical compound, and (b) neither the base compound nor the additives (if any) decompose at the test temperatures. In the cases of lubricating oils and greases consisting of mixtures of different molecular weight fractions, this equation offers, of course, only an approximation. The accuracy of this approximation depends mainly on the narrowness of the molecular weight range. Consequently, for unknown fluids, the average molecular weight is determined first.

Since during this program several mixtures were tested, and in certain cases (e. g. , the HCP-2800 batches) the presence of tetrasiloxanes (or even higher homologs) could not be discounted, the average molecular weights of the cup residues of more significant tests were also determined. By assuming a linear relationship between increasing weight percent evaporation and simultaneously increasing molecular weight, more accurate vapor pressure values were obtained. In using this method note that the low temperature vapor pressure values are invariably high, since the average molecular weight measurement by osmometry does not yield an accurate number for the weight of the smallest molecule present in the mixture. This is especially true in the case of phenyl sulfide contamination.

Since the charged sample cup of the microbalance is suspended in vacuum, heat transfer to and from the cup occurs mainly by radiation and vaporization. Under these conditions, the cup temperature is lower than that of the heating jacket.

If the cup is assumed to be suspended in a blackbody cavity whose temperature equals that of the heating jacket ( $T_j$ ), and the cup temperature is taken as  $T_c$ , utilizing the Stefan-Boltzmann Law, at thermal equilibrium, the rate of heating equals the rate of cooling:

$$A \epsilon \sigma T_j^4 = A \epsilon \sigma T_c^4 + gH$$

where

$A$  = surface area of the sample cup;

$\epsilon$  = emissivity of quartz;

$\sigma$  = the Stefan-Boltzmann constant;

$g$  = the evaporation (effusion) rate of the test substance;

$H$  = heat of vaporation for one gram of the test substance.

The cup temperature may be expressed by rewriting the above equation to

$$T_c = \left( T_j - \frac{gH}{A\epsilon\sigma} \right)^{1/4} .$$

Since all parameters on the right side of the equation are known, the theoretical cup temperatures may be calculated.

Actual thermal gradient determinations performed by placing thermocouple-instrumented dummy samples in the furnace zone have shown, however, that a rather simple physical model like the one presented above will indicate a general heat transfer mechanism only and does not yield accurate values in the temperature range of interest.

The gradient was determined experimentally by the following procedures: the sample cup, half-filled with polyphenyl ether (a mixture of five-membered ring isomers, reported  $\Delta\bar{H}_{\text{vap}} = 21.97$  kcal/mole) was suspended on a long Pyrex extender rod (no spring), so the cup hung freely in the middle of the furnace zone. A thin copper-constantan thermocouple, immersed in the oil (in effective thermal contact with the bottom of the sample cup) and firmly tied to the extender rod was welded to an electrical feed-through vacuum flange at the top of the balance.

The system was evacuated and current was supplied to the heating jacket. After each adjustment the temperatures of both the jacket and the filled sample cup were permitted to come to equilibrium. The temperature gradient was constantly monitored on a precision millivolt potentiometer.

A computer least squares analysis of ten pairs of data points ranging from jacket temperatures of 40.0 °C to 300 °C resulted in the best-fit straight line expressed as

$$y = 0.781 x - 1.26 ,$$

where

y = cup temperature (°C)

x = jacket temperature (°C)

This equation is not applicable at room temperature, since, naturally, no thermal gradient exists between the jacket and the cup.

A repeat determination was made with 99.5 percent pure n-octacosane ( $C_{28}H_{58}$ ,  $\Delta\bar{H}_{\text{vap}} = 24.14$  kcal/mole) after the following modifications were made: (a) redesign of the electrical feed-through to incorporate a Pyrex top window for exact centering of the cup in the furnace zone, and (b) the use of thicker thermocouple wires, permitting direct suspension of the now fully filled cup on the wires themselves.

Both experiments indicated that a fifteen minute period is necessary to achieve an equilibrium gradient between the jacket and the cup. Any jacket temperature may be reached in one minute by manual control (increase) of the initial heating rate.

Figure 7 represents (1) a theoretical curve, plotted according to the model presented; (2) the straight line function of the polyphenyl ether gradient determination; and (3) the data of the n-octacosane measurements. The experimental data indicate excellent repeatability, firmly establishing the high reliability of the first determination. The slightly lower values of the n-octacosane determination may be explained by considering the differences in sample mass, emissivity, heat capacity and the thermal conductivity of the wire support structure.

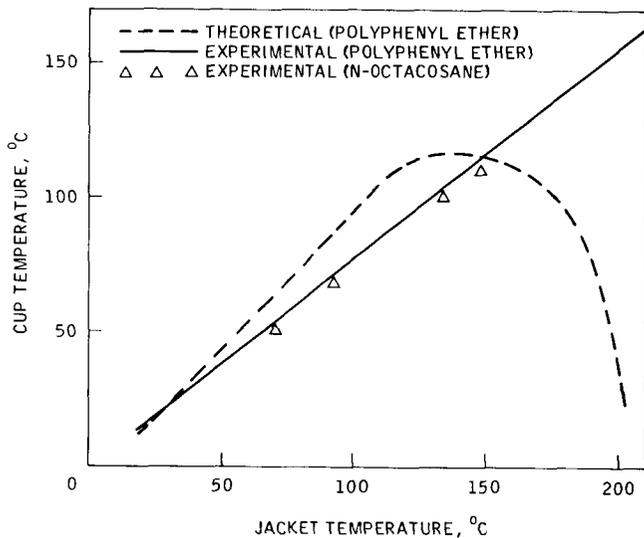


Figure 7. Furnace Zone Thermal Gradients

It is apparent that the theoretical gradient is essentially a straight line function within a certain portion of the lower temperature range. Beyond this range, with the assumption of a constant sample volume, the evaporation of the fluid significantly cools the fluid surface, causing progressively reduced cup temperatures. In the case of low-volatility fluid samples, however, surface "self-cooling" is expected to be compensated for by thermal convection within the fluid charge in the shallow cup, until the cup charge is completely depleted.

The lower slope of the experimental gradient is caused by the inaccuracies involved in the initial assumptions. The main cause of the deviation is the fact that the cup is not suspended in a perfect blackbody cavity.

#### b. Condensation

As the evaporated sample condenses in the balance chamber, the re-evaporation probability  $W$  may be expressed as

$$W = v \left( \frac{Q_{ad}}{kT} \right),$$

where

$v$  = frequency factor for an adsorbed molecule

$Q_{ad}$  = binding energy of the molecule to the substrate

$k$  = Boltzmann's constant

$T$  = absolute temperature of the adsorbed molecule.

The residence time of a molecule on a condensing surface is determined by  $Q_{ad}$  which, incidentally, is the negative of the adsorption energy. Since this residence time is inversely proportional to the substrate temperature,  $W$  closely approaches unity at liquid nitrogen temperatures. This is the reason why most of the more elaborate microbalances have liquid nitrogen baffles positioned immediately above the sample surface.

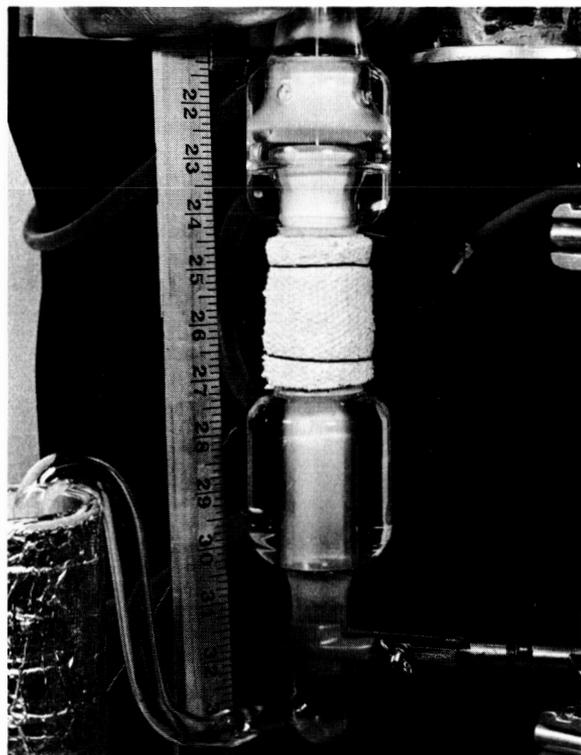
Deposition on the water-cooled glass surfaces of the present apparatus implies low-energy interaction between the substrate and the impinging molecule. Consequently, due to the small binding energy and the higher substrate temperature, the re-evaporation probability becomes significant.

On the other hand, if the impinging molecule collides not with a bare glass surface but an already formed aggregate deposit and becomes an integral part of it, this molecule will tend to re-evaporate less readily since it is now bound to the rest of the deposit by the condensation energy of the aggregate substituent.

In the case of condensing liquids it must be noted that during the initial phase of condensate nucleation only very small droplets are formed. Since the vapor pressure of liquids with convex surfaces (e. g. , droplets) is greater than that of liquids with plane surfaces, re-evaporation during the initial phase of condensation is, more likely than after coalescing of these droplets takes place.

During this high temperature calibration with n-octacosane, the entire test charge was evaporated from the cup. Subsequent cathetometer measurements of the spring assembly showed that only 1.3 percent of the initial sample weight deposited on these critical surfaces. The major portion of this condensate was found on the extender rod below the baffle plate.

Apparently the baffle plate and the water-cooled condensing regions are extremely effective in trapping the effused molecules. In Figures 6 and 8 the white test substance (n-octacosane) serves as a color tracer and clearly indicates the distribution of the trapped condensate.



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Figure 8. Distribution of Condensate (n-Octacosane) in the Microbalance

Since in actual testing only one third to one half of the initial sample charge is evaporated, pro-rated condensation or spring constant correction factors are unnecessary. The significance of these factors would fall within the experimental errors imposed by the accuracy of each cathetometer reading. The net effect of the above interactions was found by calibrating the vacuum microbalance with pure compounds of low volatility and known vapor pressure. The 99.5% pure calibration compounds\* selected were

1. n-heptadecane,  $C_{17}H_{36}$  (mol. wt = 240.48, melting point  $23^{\circ}C$ , heat of vaporization  $\Delta\bar{H}_{vap} = 15.61$  kcal/mole, see Reference 7)
2. n-octacosane,  $C_{28}H_{58}$  (mol. wt = 394.77, melting point  $61^{\circ}C$ , heat of vaporization  $\Delta\bar{H}_{vap} = 24.14$  kcal/mole, see Reference 7)

The calibration data are presented in Table 8. The Antoine equation for n-heptadecane (Reference 8) is

$$\log_{10} p_{\text{torr}} = 7.0115 - \frac{1847.82}{145.52 + t(^{\circ}C)}$$

\*Obtained from Lachat Chemicals, Inc., Chicago, Illinois.

The Clausius-Clapeyron equation for n-octacosane (Reference 7) is expressed in the following form:

$$\log_{10} P_{\text{torr}} = (-0.2185) \frac{24,144.2}{T(^{\circ}\text{K})} + 10.575460$$

The measured values in Table 8 are in good agreement with the calculated values, especially in view of the fact that both equations were derived from measurements at considerably higher temperatures and vapor pressures than those of the present work. These equations are extrapolated over five orders of magnitude in the case of n-heptadecane (Reference 9) and over three orders of magnitude with n-octacosane (Reference 7).

This good agreement is graphically presented in Figure 9, where the respective vapor pressure equations as well as the Hughes data are shown. This graph represents the average vapor pressure values versus  $1000/^{\circ}\text{K}$  plotted on semilog paper.

## 2. Results and Discussion

The preliminary measurements performed during the first year of this program indicated that disubstituted disiloxanes display low enough vapor pressures to qualify as aerospace functional fluids (see Reference 1).

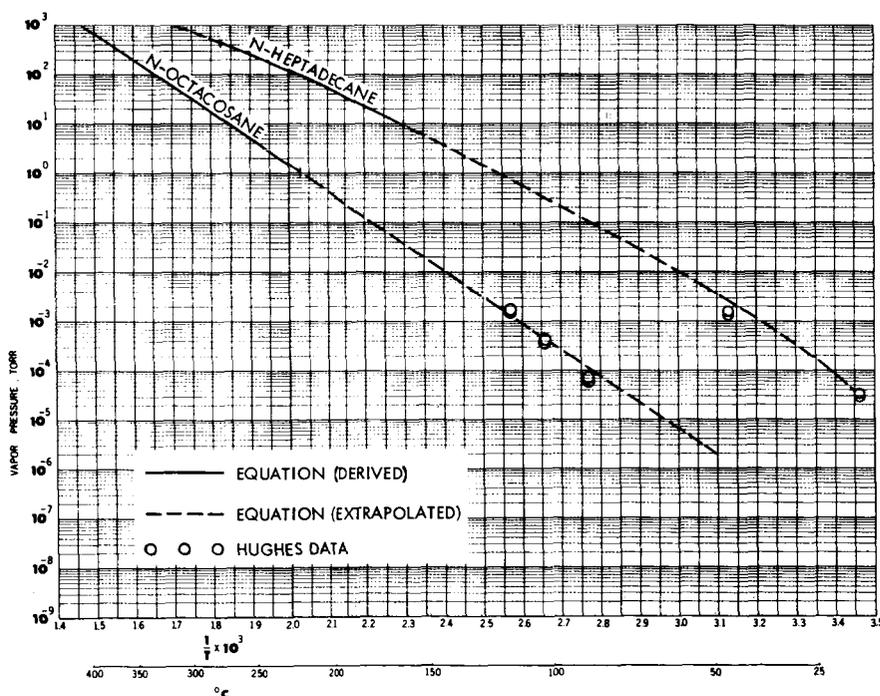


Figure 9. Vapor Pressures of Calibration Compounds

Table 8. Vapor pressures of pure calibration compounds

Compound	Temp. (°C)	Evaporation Time (sec)	Weight Loss (mg)	Vapor Pressure (torr)	
				Observed	Calculated <sup>(1)</sup>
n-heptadecane	16.5	3600	15.84	$4.10 \times 10^{-5}$	$4.00 \times 10^{-5}$
n-heptadecane	16.5	3600	12.96	$3.40 \times 10^{-5}$	$4.00 \times 10^{-5}$
n-heptadecane	47.2	300	43.20	$1.42 \times 10^{-3}$	$2.65 \times 10^{-3}$
n-heptadecane	47.2	300	41.76	$1.37 \times 10^{-3}$	$2.65 \times 10^{-3}$
n-octacosane	87.6	1800	15.12	$6.85 \times 10^{-5}$	$8.91 \times 10^{-5}$
n-octacosane	87.6	1200	8.64	$5.88 \times 10^{-5}$	$8.91 \times 10^{-5}$
n-octacosane	103.4	300	15.12	$4.20 \times 10^{-4}$	$3.66 \times 10^{-4}$
n-octacosane	103.4	300	14.40	$4.00 \times 10^{-4}$	$3.66 \times 10^{-4}$
n-octacosane	116.4	180	33.12	$1.56 \times 10^{-3}$	$1.08 \times 10^{-3}$
n-octacosane	116.4	180	36.00	$1.69 \times 10^{-3}$	$1.08 \times 10^{-3}$

(1) Per the applicable equation, given in text.

The second year's effort, with respect to vapor pressure measurements, was concentrated on evaluating fluids with low pour point and good lubricity, e. g. , the HCP-1800 batches and the final candidate fluid, HCP-2800.

Elemental analyses (see Table 2) of HCP-1800, Batch No. 1 are fairly consistent with theoretical values; the average molecular weight is, however, somewhat high. N.M.R. spectroscopy also indicated impurity. Batch No. 2 is obviously not the same composition. Batch No. 3 values are very close to the theoretical; N.M.R. spectroscopy, however, indicated an "isomeric" mixture, as well as some phenyl sulfide contamination. Batches 4, 5, 6 and 7 were pure as indicated by both elemental analyses and spectroscopy. It should be noted that Batch No. 4 still contained very slight traces of (a) some impurity and (b) phenyl sulfide, which impurity effectively lowered the pour point of the pure product (see Table 4).

Vapor pressure and evaporation rate measurements were performed with all of the above batches, mainly to (a) determine the effect of "isomerization" on the volatility of HCP-1800, (b) determine the effect of trace quantities of the relatively high volatility phenyl sulfide, especially in the low temperature range, and (c) observe the effect of closer molecular weight control on the calculations, e. g. , taking the average molecular weight of the cup residue in account. While the calculations for the first three batches were done using the average molecular weight determinations of the original fluid only (as obtained by vapor pressure osmometry, see Table 2) the values

for Batch No. 4, as well as for the composite batches of HCP-2800 (the final fluid) were more accurately calculated by establishing the previously discussed spread of molecular weight values between the original fluid and the cup residue.

The data on the first two batches of HCP-1800 are presented in Table 9; on Batch No. 3 and 4 in Table 10.

Table 9. Vapor pressure and evaporation rates of HCP-1800, Batch No. 1\* and No. 2\*\*

Batch No.	Cup Temp. (°C)	Evaporation Time (sec)	Weight Loss (mg)	Evaporation Rate (g · cm <sup>-2</sup> · sec <sup>-1</sup> )	Vapor Pressure (torr)
1	22.4	56,100	32.40	$2.87 \times 10^{-7}$	$3.68 \times 10^{-6}$
	67.9	900	7.92	$4.38 \times 10^{-6}$	$6.02 \times 10^{-5}$
	67.9	900	5.76	$3.18 \times 10^{-6}$	$4.38 \times 10^{-5}$
	84.6	600	6.48	$5.37 \times 10^{-6}$	$7.57 \times 10^{-5}$
	84.6	600	5.76	$4.78 \times 10^{-6}$	$6.73 \times 10^{-5}$
	100.5	300	8.64	$4.78 \times 10^{-5}$	$2.06 \times 10^{-4}$
	100.5	300	7.20	$1.19 \times 10^{-5}$	$1.72 \times 10^{-4}$
2	20.3	54,000	112.32	$1.04 \times 10^{-6}$	$1.36 \times 10^{-5}$
	68.0	900	12.96	$7.16 \times 10^{-6}$	$1.01 \times 10^{-4}$
	68.0	900	10.08	$5.57 \times 10^{-6}$	$7.87 \times 10^{-5}$
	83.6	600	11.52	$9.55 \times 10^{-6}$	$1.38 \times 10^{-4}$
	83.6	600	11.52	$9.55 \times 10^{-6}$	$1.38 \times 10^{-4}$
	99.5	300	11.52	$1.91 \times 10^{-5}$	$2.82 \times 10^{-4}$
	99.5	300	10.08	$1.67 \times 10^{-5}$	$2.47 \times 10^{-4}$
*Average mol. wt. of fluid = 530 **Average mol. wt. of fluid = 333					

Table 10. Vapor pressure and evaporation rates of HCP-1800, Batch No. 3\* and No. 4.\*\*

Batch No.	Cup Temp. (°C)	Evaporation Time (sec)	Weight Loss (mg)	Evaporation Rate (g · cm <sup>-2</sup> · sec <sup>-1</sup> )	Vapor Pressure (torr)
3	21.4	50,400	73.44	$7.25 \times 10^{-7}$	$9.62 \times 10^{-6}$
	68.1	1,800	10.08	$2.78 \times 10^{-6}$	$3.99 \times 10^{-5}$
	68.1	1,800	6.48	$1.79 \times 10^{-6}$	$2.57 \times 10^{-5}$
	85.3	1,800	7.20	$1.99 \times 10^{-6}$	$2.91 \times 10^{-5}$
	85.3	2,700	4.32	$7.96 \times 10^{-7}$	$1.17 \times 10^{-5}$
	101.9	900	3.60	$1.99 \times 10^{-6}$	$2.98 \times 10^{-5}$
	101.9	900	2.88	$1.59 \times 10^{-6}$	$2.39 \times 10^{-5}$
	142.0	300	18.72	$3.10 \times 10^{-5}$	$4.89 \times 10^{-4}$
	142.0	300	20.88	$3.46 \times 10^{-5}$	$5.46 \times 10^{-4}$
4	22.6	55,800	7.20	$6.42 \times 10^{-8}$	$8.43 \times 10^{-7}$
	68.4	1,800	2.88	$7.96 \times 10^{-7}$	$1.14 \times 10^{-5}$
	68.4	1,800	2.16	$5.97 \times 10^{-7}$	$8.54 \times 10^{-6}$
	102.2	1,800	5.04	$1.39 \times 10^{-6}$	$2.09 \times 10^{-5}$
	102.2	1,800	4.32	$1.19 \times 10^{-6}$	$1.79 \times 10^{-5}$
	125.3	900	7.20	$3.98 \times 10^{-6}$	$6.06 \times 10^{-5}$
	125.3	900	7.92	$4.38 \times 10^{-6}$	$6.65 \times 10^{-5}$
	141.8	300	12.96	$2.15 \times 10^{-5}$	$3.35 \times 10^{-4}$
	141.8	300	14.40	$2.39 \times 10^{-5}$	$3.71 \times 10^{-4}$

\* Average molecular weight of fluid = 491

\*\* Average molecular weight of fluid = 488; cup residue = 530

The average vapor pressure values at each test temperature of the subject batches are plotted vs.  $1000/^\circ\text{K}$  on semilog paper in Figure 10. Examination of the data indicates that

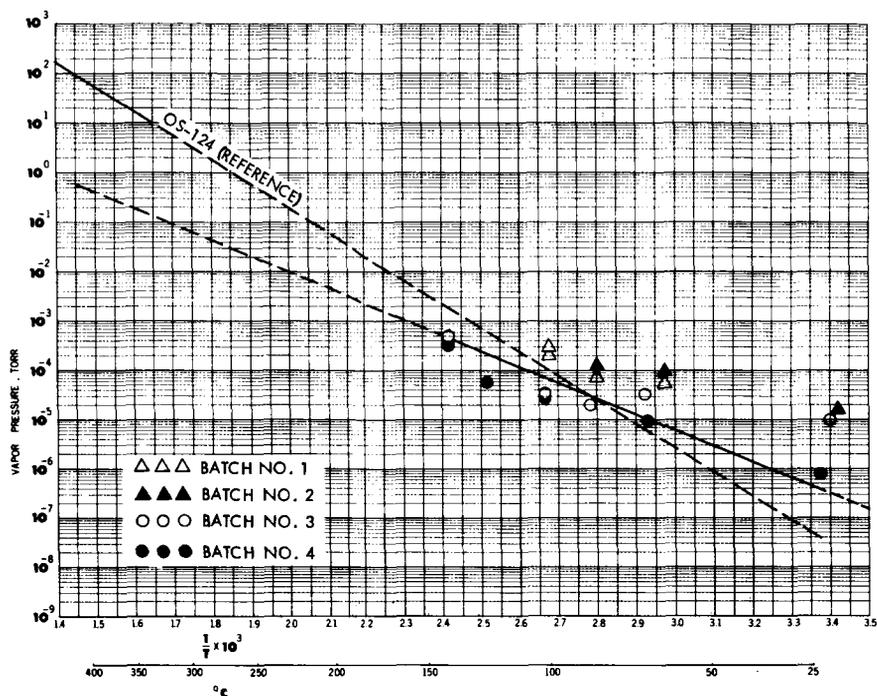


Figure 10. Vapor Pressure of Various Batches of HCP-1800

1. Increased efficiency in synthetic and purification techniques resulted in ever-decreasing vapor pressures in the lower temperature range. This is a clear indication of reduction in phenyl sulfide (and other possible low molecular weight material) contamination. Note that I.R. and N.M.R. studies of the cold trap residue of the first three batches conclusively indicated considerable amounts of phenyl sulfide. Only an insignificant amount was found in the case of Batch No. 4.
2. Since the first two batches were rather impure as compared to the following ones, the final vapor pressure slope (drawn by eye) is purposely biased by the data of the last two batches. The most impure Batch No. 2 is included, mostly to show that the vapor pressure values are not only useful in indicating the differences in molecular structure, but their proximity points out the fact that efficient purification of the final product is feasible only in terms of phenyl sulfide removal.
3. The vapor pressure differences between Batch No. 3 and 4 (the "isomeric" mixture and the structurally correct product, respectively) are more pronounced in the low than in the higher

temperature range. In fact, above  $\sim 180^{\circ}\text{F}$ , the values of both batches are quite close. The low temperature range spread may be attributed to phenyl sulfide, as well as preferential evaporation of any lower boiling isomer.

4. Generally, the volatility of HCP-1800 is as low, or lower than, most aerospace fluids (see OS-124 vapor pressure curve included for comparison). Note that the values above  $\sim 150^{\circ}\text{C}$  ( $\sim 300^{\circ}\text{F}$ ) should be considered as extrapolated approximations only.

The volatility of HCP-2800 (mixture of Batch No. 3 and 4) is given in Table 11 and is indicative of that of the final blend of all batches; in Figure 11 the average vapor pressure values are plotted. The fact that the slope is parallel with, and somewhat lower than that of HCP-1800 is consistent with expectations in view of the homologous nature of HCP-2800. Note that no phenyl sulfide could be detected in the cold traps after the vapor pressure determinations.

Table 11. Vapor pressure and evaporation rates of HCP-2800, Batch No. 3 and 4 Combined

Cup Temp. ( $^{\circ}\text{C}$ )	Evaporation Time (sec)	Weight Loss (mg)	Evaporation Rate ( $\text{g}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ )	Vapor Pressure (torr)
67.6	1800	5.04	$1.39 \times 10^{-6}$	$1.81 \times 10^{-5}$
67.6	1800	5.04	$1.39 \times 10^{-6}$	$1.81 \times 10^{-5}$
102.5	900	10.08	$5.57 \times 10^{-6}$	$7.54 \times 10^{-5}$
102.5	900	7.92	$4.38 \times 10^{-6}$	$5.91 \times 10^{-5}$
117.1	900	10.80	$5.97 \times 10^{-6}$	$8.14 \times 10^{-5}$
117.1	900	9.36	$5.17 \times 10^{-6}$	$7.03 \times 10^{-5}$
133.2	600	12.96	$1.08 \times 10^{-5}$	$1.48 \times 10^{-4}$
133.2	600	11.52	$9.55 \times 10^{-6}$	$1.31 \times 10^{-4}$
149.3	300	12.96	$2.15 \times 10^{-5}$	$2.94 \times 10^{-4}$
149.3	300	12.24	$2.03 \times 10^{-5}$	$2.77 \times 10^{-4}$
165.9	300	22.32	$3.70 \times 10^{-5}$	$4.99 \times 10^{-4}$
165.9	300	25.92	$4.30 \times 10^{-5}$	$5.74 \times 10^{-4}$
Average molecular weight of fluid = 587; cup residue = 729				

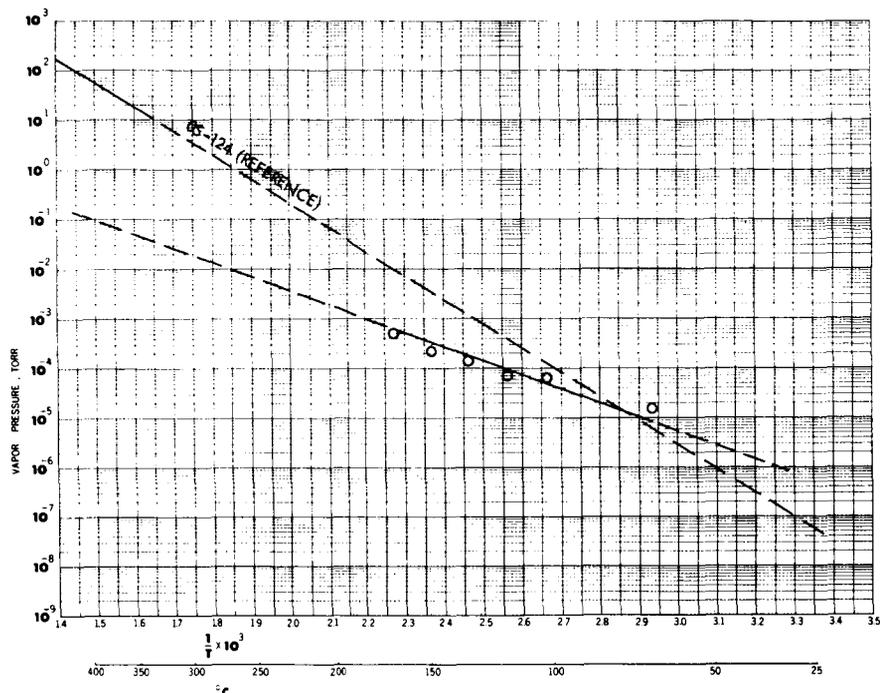


Figure 11. Vapor Pressure of Mixed Blends of HCP-2800

## F. LUBRICITY

### 1. Description of the Apparatus and Test Method

During the first year of this program the Shell 4-Ball Tester was utilized in screening the initial fluids for lubricity. The main advantage of this apparatus is its widely accepted use, and the ready availability of comparative data. The applicability of the 4-Ball Tester to the present program was, however, soon questioned, since (a) at least 8.5 ml of a sample is required for each test (the used product is obviously non-recoverable unless extensive purification techniques are developed); (b) the procedure per Federal Test Method Standard No. 791a, Method 6514.1 is not exactly ideal to determine the boundary lubricating qualities of fluids at low operating velocities comparable to valve closing and opening speeds (test conditions: 1200 rpm, 10 kg load, 2 hours testing at 400°F), and (c) the cost of each test is considerable.

Since most of the syntheses of the present effort yielded only very small quantities of the end product, it was decided that it would be valuable to develop a wear test procedure which would utilize only a very small amount of a fluid lubricant, but still give some reliable indication of its lubricity. In order to have enough material available for both the radiation stability test and a retain sample, a means of evaluating lubricity was developed which would require no more than ~1.5 milliliter of fluid.

The LFW-1 test machine was considered because of the well-established repeatability of several test procedures (References 10, 11, 12, 13). The machine itself has been adequately described elsewhere (Reference 14). The general operating principle of the LFW-1 is illustrated in Figure 12. Oils are ordinarily evaluated in a rectangular aluminum trough (requiring approximately 200 ml of fluid) which fits snug against the face of the machine, so that the lower part of the test ring just dips into the oil. In the present case, it was decided to use wick feeding out of a very small cylinder, the wick to be in direct contact with the ring. A small device was constructed to fit on the face of the LFW-1 tester, utilizing the existing threaded holes for the oil reservoir (trough). The device and wick, with its loading spring, are shown in Figure 13. The wing nut is used to clamp the wick holder after adjusting it in position. Precision-grade test rings and rectangular blocks were used. Both were machined from oil-hardened steel ( $R_c$  58-62).

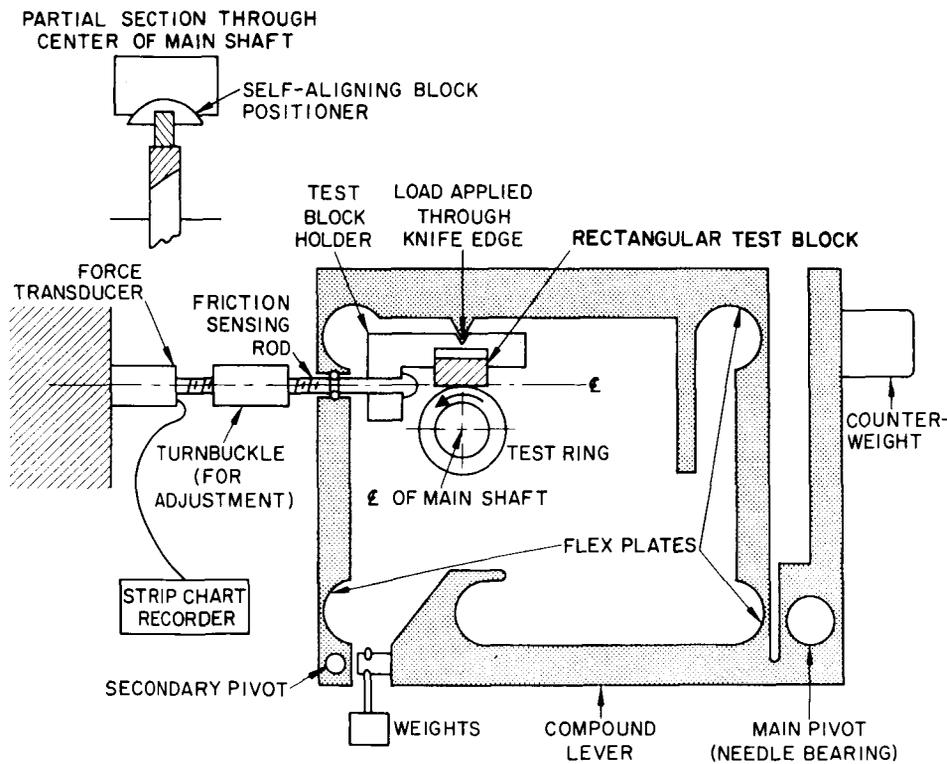


Figure 12. LFW-1 Tester, General Operating Principle

In brief, a small piece of round felt is placed in a tube, charged with the lubricant, and spring loaded against the pre-lubricated test ring. In the unloaded condition, the ring is rotated for 10 cycles to further distribute the

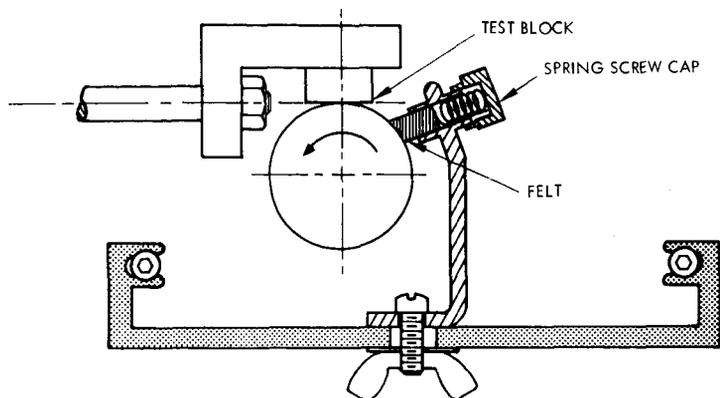


Figure 13. LFW-1 Wick Feeding Device

lubricating oil. The ring is then rotated at 40 rpm\* while being step-loaded in one-pound increments applied to the bale rod at one-minute intervals. The load which causes the onset of loud, continuous, high-pitched screaming noise (indicating breakdown in lubrication) is considered excessive and the test is terminated. One pound less than this critical load is designated as the "O.K. load".

This first determination is utilized to indicate the load-carrying ability of the fluid and designated as a trial run only. The initial phase of the full-scale wear test is identical to that of the trial run with respect to the loading sequence. The total applied load is, however, reduced to one pound below the critical trial run failure load. On completion of the loading sequence the test is continued at 40 rpm to 5000 cycles, or to failure. The total applied load of the 5000 cycle test, however, does not exceed 8 pounds under any circumstances, regardless of any higher O.K. loads obtained. The small volume LFW-1 test procedure is a repeatable method utilizing the precision-grade, hardened steel rings and rectangular blocks. The failure criteria and detailed testing procedure are attached as Appendix V. Because of the wide variance in the performance of both the lubricants being synthesized and the commercial materials being used for comparison, a rating system has been devised, shown in Table 12.

## 2. Results and Discussion

To provide a frame of reference with respect to the general performance of the HCP fluids compared to several better known lubricants, the O.K. loads and ratings of selected HCP fluids are compared to those of various commercial lubricants in Table 13.

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\*A few tests were conducted at 20 and 30 rpm, but the drive motor could not maintain constant speed under these conditions.

Table 12. LFW-1 lubricant ratings chart

Rating Number	Maximum Load on Bale Rod (pounds)	Cycles Completed (at 40 rpm)	Step-Loading	Quantity of Debris
1a	8*	5000**	No	Light
1b	8	5000	No	Heavy
2	8	5000	Yes	No Requirement
3	7	5000	Yes	No Requirement
4	6	5000	Yes	No Requirement
5	5	5000	Yes	No Requirement
6	4	5000	Yes	No Requirement
7	3	5000	Yes	No Requirement
8	2	5000	Yes	No Requirement
9	1	5000	—	No Requirement
10	1	<5000	—	No Requirement

\*Highest load used  
 \*\*Maximum duration. Test stopped at this point.

Table 13. LFW-1 lubricant ratings

Lubricant	Viscosity at 77°F (cs)	O.K. Load (lbs)	Rating Number
DC-200	32	1	9
HCP 1500 (Batch No. 3)	40	1	9
HCP-C1500/1600 (3/1) Batch No. 2	32	1	9
HCP-C1500/1600 (1/3) Batch No. 2	54	2	8
HCP-1600	6500	3	—*
Mineral (white) oil	172	8	1b
HD Motor Oil SAE 30	200	11	1a
FS-1265	300	13	1a
OS-124	800	21**	1b
HCP-1800 (Batch No. 1)	~30***	>19****	2
HCP-1800 (Batch No. 3)	20	17	3
HCP-1800 (Batch No. 6)	60	21**	2
HCP-1900 (Batch No. 1)	100	>19****	2
HCP-2800 (Final mixture of all batches)	32	21**	2

\*Too viscous for 5000 cycle run.  
 \*\*Limit of the test machine.  
 \*\*\*Estimated, see Table 6.  
 \*\*\*\*Test terminated because of high  $F_K$ . No failure per criteria in Appendix V.

It should be noted that the load-carrying capability of the fluid is dependent on (a) its viscosity at the operating temperatures, (b) its chemical composition, stability and boundary lubrication capability by surface reactions (if any) and (c) the thickness of the elasto-hydrodynamic film, which is in turn a function of not only the viscosity but the rotational speed as well. The slow 40 rpm rotational mode of the mini-volume test standardizes the speed factor. The interaction of fluid viscosity and lubricity is, however, rather complex and difficult to fully interpret (i.e., a better lubricant runs cooler than a poor one; the viscosity and the EHD film thickness at any particular test temperature, therefore, becomes a function of lubricity). Nevertheless, the method proves itself useful in screening lubricants by (a) additional determination of the 5000 cycle wear test, (b) observation of the wear debris formed and (c) notation of possible gel formation. Although the ratings chart (see Table 12) specifies no requirement in terms of gel formation, wear scar width or scar condition, the observation of these additional parameters helps in determining total performance.

The following conclusions and observations may be drawn from the data in Table 13:

1. The test method provides a suitable means of rating lubricants, one which compares well with standard wear tests. Its use permits separation of lubricants generally considered "fair" to "poor" from those considered "good" or "excellent". Note, for example, that FS-1265 (300) gives excellent antiwear performance on both the Falex Tester and the Shell 4-Ball Tester, while the results with DC-200 are rather marginal (Reference 1).
2. The sensitivity of the new test is indicated by the separation of the two cohydrolysis products: C1500/1600 (1/3) and C1500/1600 (3/1). The second material contains considerably more chlorine, and has a higher viscosity; it would, therefore, be expected to provide better antiwear than the first.
3. The load-carrying abilities of HCP-1800 and HCP-2800 may be attributed in large part to their chemical composition, since room temperature viscosities of the various batches are roughly equivalent to those of HCP-1500 and the C1500/1600 cohydrolysis products. Replacement of the ether linkage (HCP-1500) with a thio linkage (HCP-1800 and HCP-2800) has apparently improved the low-temperature and lubricating characteristics of this material family simultaneously. The possible shortcomings of the sulfur compounds may lie in characteristically unpleasant odor caused by trace quantities of phenyl sulfide (the pure compounds have no discernible odor) and the fact that they tend to gel during the friction test. Incidentally, a tendency to thicken and gel was observed in DC-200 silicone fluids as well. Gelation of silicones is a well-known phenomenon (Reference 15) and is considered a major drawback in their use under boundary conditions.

4. The friction and wear characteristics of HCP-1900 far surpass those of the non-chlorinated homolog. Note that the O.K. load determination of HCP-1900 was terminated after 19 pounds of bale rod load simply because the magnitude of the sensed friction force reached the limit of the force transducer. No high-pitched scream or severe scraping could be noticed. In addition, while gelation and black discolorization of the HCP-1800 and HP-2800 batches were repeatedly observed during the 5000 cycle friction testing, and formation of copious wear debris was noted (average high-pressure block wear scar width = 0.07 inch), HCP-1900 retained its color and fluidity during comparable tests with no manifestation of gelation.

The amount of wear debris formed with HCP-1900 was negligible (average high-pressure block wear scar width = 0.04 inch). Apparently the incorporation of chlorine atoms imparts sufficient fluid stability and provides the necessary surface active agent for improved boundary lubrication. It is unfortunate that the pour point of HCP-1900 is +3°F; nevertheless, this fluid is by far the best lubricant synthesized to date, actually surpassing the lubricity of HCP-2800, which exhibited some gelation and debris-forming tendencies. Since the quantity and type of wear debris do not enter into rating consideration, caution must be exercised in interpreting the O.K. load value and rating number without some due consideration of debris formation. For example, the heavy duty SAE 30 oil, as well as FS-1265, are known high-performance lubricants. Nevertheless, the O.K. loads of the HCP fluids are higher, in spite of the fact that their rating numbers are lower. Moreover, the gelation and debris generation tendencies of nearly all HCP fluids were significantly worse than those of the commercial lubricants.

This phenomenon may be interpreted only in terms of surface reactions under boundary conditions. The HCP fluids are poorer lubricants than either the motor oil or the fluorosilicone fluid; nevertheless, under high loads, the failure criteria (as set forth in Appendix V) are not reached due possibly to surface reactions of sulfur products with the steel substrate. It is likely that this boundary layer wears away rather rapidly (thus forming copious amounts of debris as compared to those formed with the commercial lubricants at lower loads), but immediately reforms, just to wear further away. Neither the additives in the SAE 30 oil, nor the fluorosilicone itself are able to demonstrate this capability.

Since HCP-1900 apparently provides both sulfur and chlorine at the frictional interfaces without the formation of significant quantities of debris, the boundary lubrication qualities of this fluid surpass those of the subject commercially available lubricants.

Several sets of strip charts showing the initial portion of the loading sequence friction force are presented in Figures 14, 15 and 16. Presentation of these figures is designed (a) to show the repeatability and sensitivity

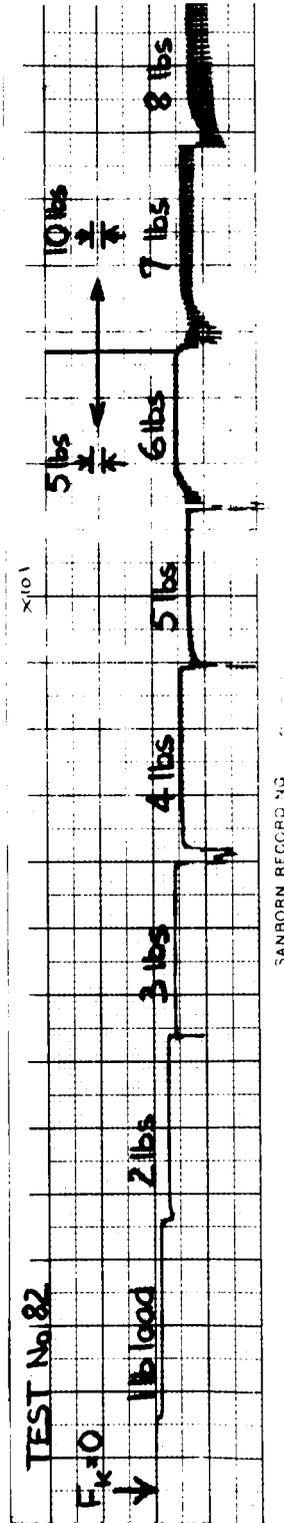
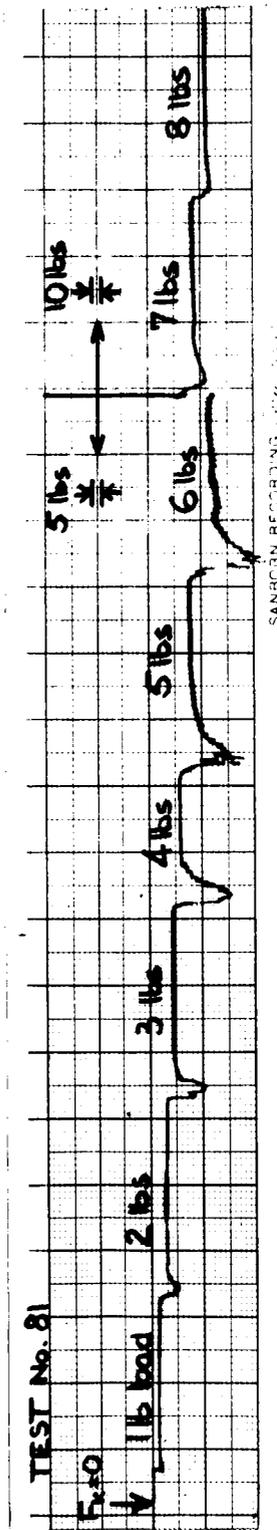
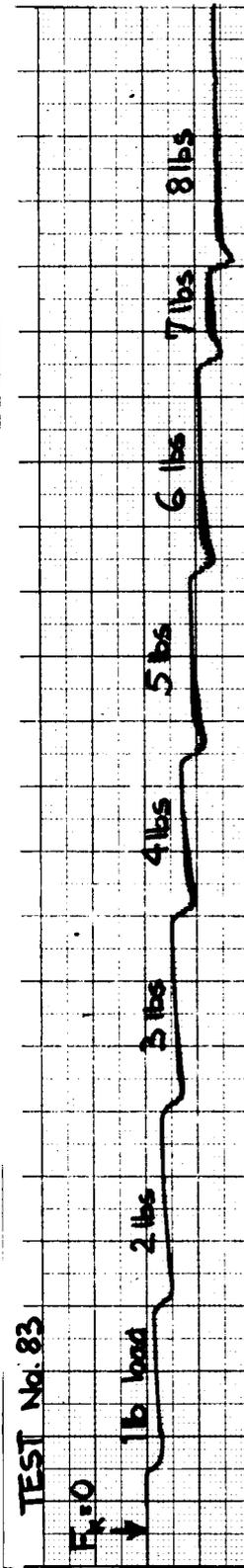
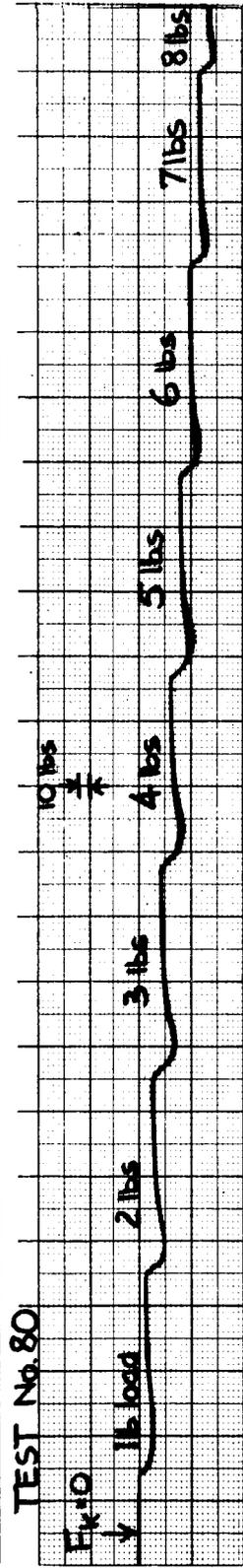
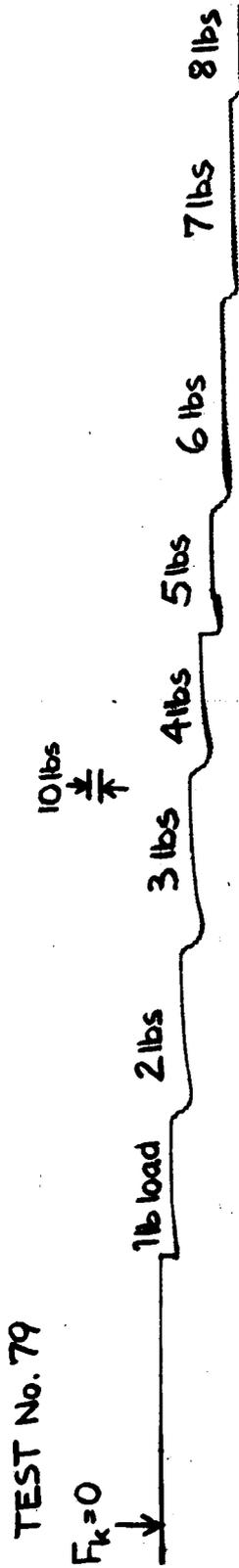
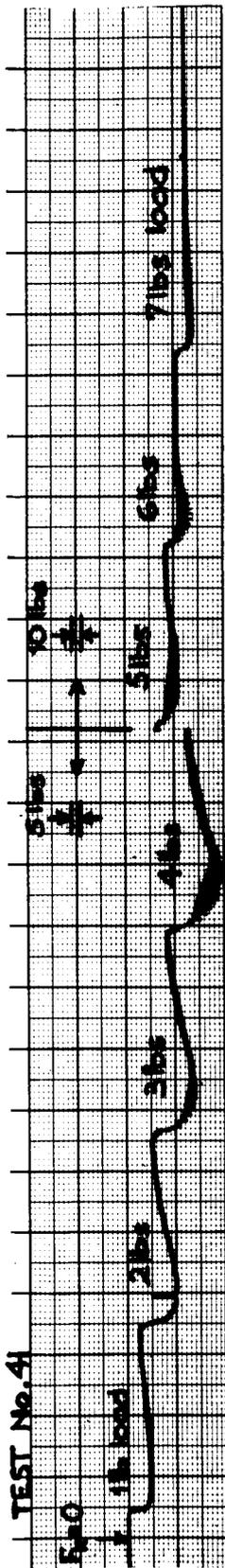


Figure 14. Friction Traces of (a) Non-irradiated, and (b) Irradiated OS-124.  
 (LFW-1 Tests, Step-loading to Obtain O.K. Load, 40 rpm Rotation)



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Figure 15. Friction Traces of (a) Non-irradiated HCP-2800, Batch No. 1, (b) Irradiated HCP-2800, Batch No. 1, and (c) Non-irradiated HCP-2800 Final Mixture. (LFW-1 Tests, Step-loading to Obtain O.K. Loads, 40 rpm Rotation.)



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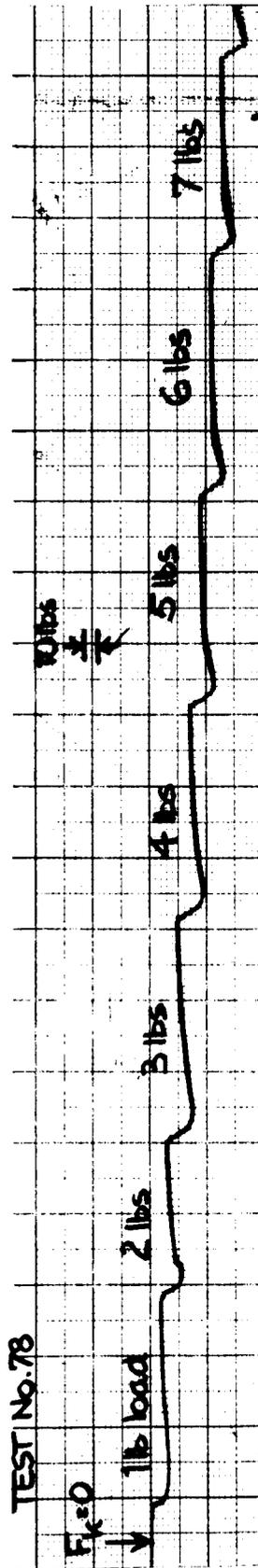
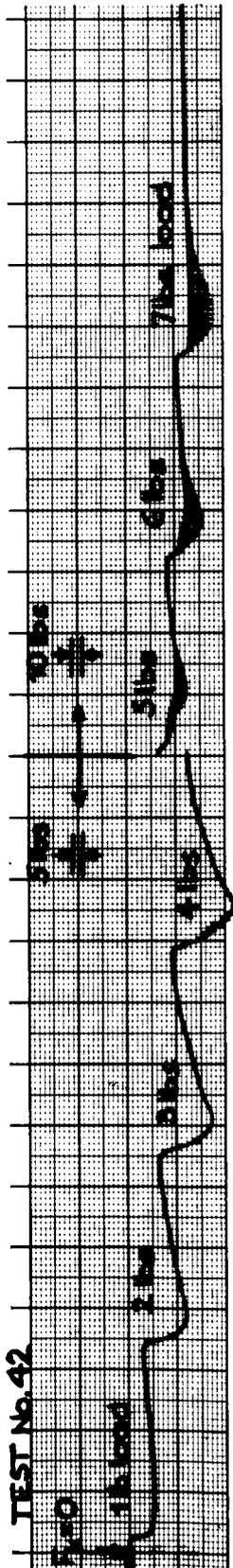


Figure 16. Friction Traces of (a and b) HCP-1800, Batch No. 1; (c) HCP-1800 Batch No. 6. (LFW-1 Tests, 5000 Cycle Test Step-loading, 40 rpm Rotation.)

of the new method; and (b) to indicate the effect of irradiation on HCP-2800 compared to that on OS-124. Note that in some cases the length of the friction traces at any given load vary from test to test due to the malfunctioning of the chart drive mechanism; normally step-loading occurs in one minute intervals at 40 rpm.

Figure 14 shows the friction traces obtained with non-irradiated and irradiated (to  $10^{10}$  ergs/g(C)) OS-124. Actually, there is little difference between the lubricities. There is, perhaps, a slightly greater amount of surface damage indicated in the case of the irradiated product. It is, however, obvious that polyphenyl ether has poor boundary lubrication capabilities, as indicated by the sharp increase in friction on repeated loadings.

The improved boundary lubricating capacity of HCP-2800 is demonstrated in Figure 15, where the original and the irradiated HCP-2800, Batch No. 1, as well as the original HCP-2800 final batch mixture test charts are presented. Although some surface damage is indicated after 4 pounds of load in each case, it seems that neither irradiation, nor variation in batches appears to change the lubrication characteristics of these fluids. Some variation between these batches (in the original condition) was expected, since Batch No. 1 was irradiated in a phenyl sulfide-contaminated condition, while the final mixture contains only slight traces of this product. The friction traces, nevertheless, indicate negligible differences. The wear-in characteristics are significantly better than those of the polyphenyl ether.

Figure 16 is intended not only to show the repeatability of the test within a given batch, but to demonstrate the effect of purity and the consequential increase in viscosity (and, therefore, lubricity) of HCP-1800. The charts of test Numbers 41 and 42 are duplicate runs of the 7 lb step-loading portion of the 5000 cycle test of HCP-1800, Batch No. 1 (viscosity estimated to be 30 cs at 77°F, see Table 13), while the chart of Test No. 78 represents the 8 lb step-loading portion of the 5000 cycle test of HCP-1800, Batch No. 6 (viscosity measured at 60 cs at 77°F, also see Table 13). Taking the attenuation of the friction readings in account (observe the friction force at, and after 5 pounds of load in each case), the reduced friction and degree of surface damage is apparent in the case of HCP-1800, Batch No. 6.

A portion of this testing sequence was focused on the evaluation of selective additives dissolved in HCP-1500, Batch No. 3 and HCP-C1500/1600 (9/1), Batch No. 1. These fluids appeared to be ideal base fluids, since their lubricity rating numbers are only 9 and 8, respectively (see the modified rating chart enclosed in Table 12); any improvement on blending would be more pronounced in these cases than if HCP-1800 or HCP-2800 were utilized.

Note that the LFW-1 "mini-volume" determination of additive acceptance consists of a single O.K. load determination. If this test failed to uncover a significant improvement, or if the pour point of the base fluid was raised to an unacceptably high value on blending, further consideration or evaluation of the unsuccessful additive terminated.

Data on the preliminary additive mixtures are enclosed in Table 14. The data show that the addition of trichlororesorcinol to HCP-1500 (Batch No. 3) resulted in a threefold improvement in the O.K. load of the base fluid. The sizable increase in its melting point (see Table 5), however, negates the beneficial effect of the additive. Neither tri-p-tolyl phosphite, tri-p-tolyl thiophosphate or TCP increased lubricity. Triphenylstibine and lead naphthenate appear to show some promise. Note, however, that in 1970 the addition of 5 percent TCP to HCP-1500 resulted in a smaller wear scar in Shell 4-Ball Wear Tests conducted at 400°F (Reference 1).

Table 14. LFW-1 lubricant tests on additive blends

Lubricant	Maximum O.K. Load in Step Loading Procedure
HCP-1500 (Batch No. 3) - no additive	1 lb
HCP-1500 (Batch No. 3) +5% (by weight) Trichlororesorcinol	3 lbs
HCP-1500 (Batch No. 3) +5% (by weight) Triphenylstibine	2 lbs
HCP-1500 (Batch No. 3) +3% (by weight) Tri-p-tolyl phosphite	1 lb
HCP-1500 (Batch No. 3) +3% (by weight) Tri-p-tolyl thiophosphate	1 lb
HCP-1500 (Batch No. 3) +5% (by weight) TCP	1 lb
HCP-C1500/1600 (9/1) - no additive	2 lbs
HCP-C1500/1600 (9/1) +3% (by weight) Lead naphthenate	3 lbs

The special fixture and test method which have been devised for the LFW-1 Tester made possible the evaluation of very small quantities of lubricating oils. The method has the advantages of simplicity, small volume required, ease of test monitoring, and sensitivity to both viscosity and boundary lubricating qualities. Based on a limited number of tests the repeatability appears to be good.

In agreement with the Project Manager, further lubricity evaluation (e. g., thermal vacuum bearing tests and bearing tests in humidity) will be performed in the Project Manager's facility.

## G. RADIATION STABILITY

On exposure of organic materials to radiant energy of sufficient magnitude, various chemical changes take place in the process of energy dissipation. These changes include excitation, ionization and bond rupture, followed possibly by other processes, e. g., splitting of the ionized molecule to another ionic fragment and a free radical. The actual changes that take place in a particular material depend on the chemical structure of the material and the type and energy of the irradiation, as shown in Table 15, where the data are taken from Reference 16.

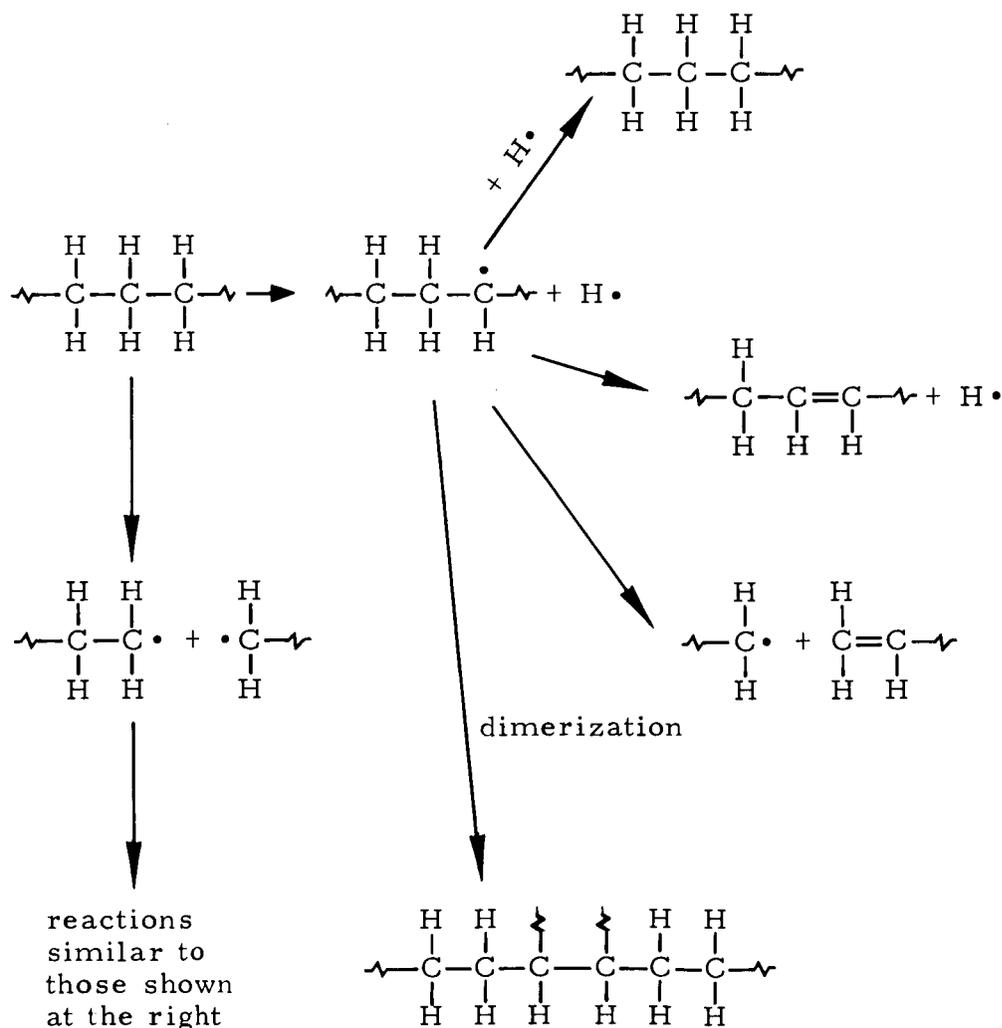
In the case of organic compounds, carbon-carbon and carbon-hydrogen bonds are broken, as well as those between carbon and other atoms present. These changes are then followed by other reactions. When carbon-hydrogen

Table 15. Effect of radiation on materials

Material	Radiation Dosage Required for Threshold Damage (ergs/gm (C))*
Polyphenyl ethers	$1 \times 10^{11}$
Mineral oils	$5 \times 10^{10}$
Dimethyl silicones	$1 \times 10^8$
Methyl phenyl silicones	$1 \times 10^{10}$
Chlorinated silicones	$5 \times 10^9$
Dibasic acid esters	$5 \times 10^{10}$
Silicate and disiloxane esters	$1 \times 10^{10}$
Phenolic (filled)	$3 \times 10^{10}$
Polyester	$9 \times 10^9$
Polytetrafluoroethylene	$2 \times 10^6$
<p>*Ergs per gram (carbon) refers to the energy absorbed by the carbon-walled, CO<sub>2</sub>-filled ion chamber selected as the standard. It is indirectly a measure of the field and not a measure of the energy absorbed by the sample.</p> <p>The above table is for static irradiation in air.</p>	

bonds are broken, the fragments produced may lose more hydrogen atoms or split further into smaller fragments. They may also react with other hydrogen atoms to regenerate the original molecule, or with other free radicals present to produce molecules with a higher molecular weight. When carbon-carbon bonds are broken,  $\beta$ -elimination of hydrogen atoms, coupling, and disproportionation occur.

Aromatic hydrocarbons are quite stable to radiation, and much higher dosages are required to cause the changes shown. The extra stability is attributed to the resonating structure of the benzene ring, which allows considerable absorption of excitation energy without breaking bonds. Incorporation of aromatic rings in a compound will make it more stable by providing a "sink" to absorb the excitation energy.



Aromatic ethers are about as stable to radiation as the corresponding aromatic hydrocarbons. They both form some higher molecular weight material and hydrogen gas.

Aliphatic esters are rather unstable to radiation: rupture of the ester bonds takes place along with the breaking of the carbon-carbon and carbon-hydrogen bonds. Again, incorporation of aromatic rings increases the radiation stability of the whole molecule.

The radiation resistance of polymeric silicone oils is notoriously poor, because dimethylsiloxane compounds generally undergo breaking of carbon-hydrogen bonds in the methyl groups; this results in coupling (cross-linking) and hydrogen evolution. When the methyl groups are replaced by phenyl groups, however, larger doses of radiation are required to cause comparable amounts of degradation.

A fluorocarbon polymer such as poly(tetrafluoroethylene) is readily degraded by radiation. The polymer chain is broken (carbon-carbon bond rupture), as well as carbon-fluorine bonds, resulting in low molecular weight fragments with olefinic bonds. Irradiation of fluorocarbon ethers, such as poly(hexafluoropropylene ether), causes depolymerization and formation of volatile products by the same mechanisms, but the presence of the ether groups makes these more stable than the straight fluorocarbons.

The damage done to organic lubricants by radiant energy affects virtually all the physical properties that are generally used to characterize these materials: viscosity, volatility, pour point, acidity, thermal stability, and many others. In turn, these downgrade the primary capability of the material to lubricate. Thus viscosity can either increase or decrease (sometimes both, in mixtures). The increases due to crosslinking and polymerization are associated with elevated pour points and reduced volatility. The decreases, caused by bond fracture, are generally accompanied by significant increases in volatility, which severely limit the high temperature usefulness, even when viscosity changes are small.

Increases in acidity result from the radiation-induced formation of free radicals in the presence of oxygen. This can rapidly use up any inherent or built-in corrosion protection in the lubricant, and hastens the degradation at high temperatures.

Increasing the range and effectiveness of radiation-resistant lubricants by incorporating additives does not appear to be a fruitful approach. They operate with greatest effectiveness in fluids which have inherently poor radiation stability, and even in these cases do not improve the compounds to the point of equality with polyphenyls, polyphenyl ethers, etc. Certain free radical scavengers (e. g., iodobenzene) are very effective in diesters, but they are consumed during radiation, and form insoluble compounds. In addition, some antirads destroy the effects of certain antioxidants, even without radiation. It is of interest that aromatic oxidation inhibitors (antioxidants) undergo only slight damage under direct radiation attack but are rapidly consumed in oil solution by reaction with free radicals.

The common corrosion inhibitors are generally not radiation-resistant, for example, long-chain fatty acids and esters. Metal and non-metal salts of aromatic petroleum sulfonates offer some resistance, however.

This applies to alkylated naphthalene derivatives, and may be extended to salts of alkylphenyl sulfides. In this connection, Hughes devoted all of the effort to tailoring radiation-resistant, stable molecules that would withstand the required dosages, rather than trying to salvage fluid properties by additives of questionable effectiveness.

## 1. Description of the Apparatus and Test Method

Irradiation of all samples was conducted in the Hughes 7000 Curie Cobalt-60 source. The time of exposure was calculated to give a dosage of  $10^{10}$  ergs/gram (carbon).

In 1970, each lubricant was irradiated in both a deaerated state, under vacuum ( $\sim 10^{-6}$  torr), and under normal atmospheric conditions (without deaeration). During the current effort, the lubricants were irradiated in the degassed condition, under vacuum only, because (a) the first round of testing indicated a negligibly small effect of oxygen on the degree of fluid degradation with disubstituted siloxanes (see Reference 1); (b) a space lubricant, in spite of the presence of labyrinth seals, would soon undergo degassing after launch and (c) lesser number of samples permit more thorough evaluation within the allotted time and funding.

Special irradiation containers were designed and built entirely of glass. The "atmospheric" containers were stoppered with vented ground glass joints. The vacuum vials were fabricated from 1.2 in. dia. x 5 in. long test tubes with male ground glass joints. A pre-blown constriction ( $\sim 1/4$  in. dia.) 3 inches from the bottom of the tube formed a bulb. Each container was able to hold  $\sim 30$  ml of fluid. The volumes of irradiated lubricants ranged from 0.5 to 20 ml. The details of degassing and sample preparation under vacuum are given in Appendix VI.

## 2. Results and Discussion

During the first round of irradiation studies HCP-1500 Batch No. 1 and 2 were the only experimental fluids exposed to radiation. Viscosity and pour point changes, compared to OS-124, are given in Table 16 for the reader's convenience. To show the dramatic change in the flowing properties of the polysiloxane DC-200, the appearances of the polyphenyl ether and the silicone fluid after irradiation are shown in Figure 17. Complete gelation of the silicone, originally 10 centistokes is immediately apparent.

Pour point and viscosity changes in the more significant products of the second year's effort (the thioether fluids) are also indicated in Table 16. The results therein show that

1. All thioether fluids tend to thicken somewhat on irradiation but to a lesser degree than OS-124. The effect of gamma radiation on HCP-1500 is indeterminate, since in one case some scission (because there were some volatiles present) and in the other some crosslinking are indicated.

Table 16. Pour point and viscosity changes observed on irradiated fluids

Lubricant Designation	Pour Point (°F)		Viscosity in Centistokes			
	Non-Irradiated	Irradiated (Vacuum)	Temp.	Non-Irradiated	Irradiated (Vacuum)	% Change
DC-200 (10 cs)	-85 <sup>(1)</sup>	(2)	100°F 210°F	9.2 <sup>(1)</sup> 4.2 <sup>(1)</sup>	(2) (2)	∞ ∞
OS-124	+40	+45	100°F 210°F	359.0 12.36	387.1 12.66	+7.3 +2.4
HCP-1500 Batch No. 1 (clear)	-35	-25	100°F 210°F	31.32 5.61	29.90 5.44	-4.5 -3.0
HCP-1500 Batch No. 2 (dark)	-10	-15	100°F 210°F	52.70 6.63	56.83 6.82	+7.3 +2.8
HCP-1800 (Batch No. 3)	-53	-51	100°F 210°F	12.81 3.09	13.45 3.40	+4.8 +9.1
HCP-1800 (Batch No. 6)	-15	-15	100°F 210°F	32.56 5.29	34.18 5.36	+4.7 +1.3
HCP-1900 (Batch No. 1)	+3	+2	100°F 210°F	54.90 6.22	69.55 7.24	+6.7 +1.4
HCP-2800 (Batch No. 1)	-65	-61	100°F 210°F	10.89 3.09	11.19 3.15	+2.7 +2.1
(1) Vendor data. (2) Completely gelled.						

2. The greatest degree of viscosity change among the HCP fluids occurred with HCP-1900, the chlorinated thioether homolog. This phenomenon is consistent with past findings on reduced radiation stability of chlorinated silicones (see Table 15). In addition, on opening the radiation vial, the biting odor of hydrochloric acid was unmistakable, suggesting the sites of scission and crosslinking.
3. HCP-2800 suffered the least change among all the Hughes fluids. It should be noted, however, that this first batch of the trisiloxane homolog was irradiated in a phenyl sulfide-contaminated condition ( 8-10 w/o content) due to unavailability of the vacuum-distilled

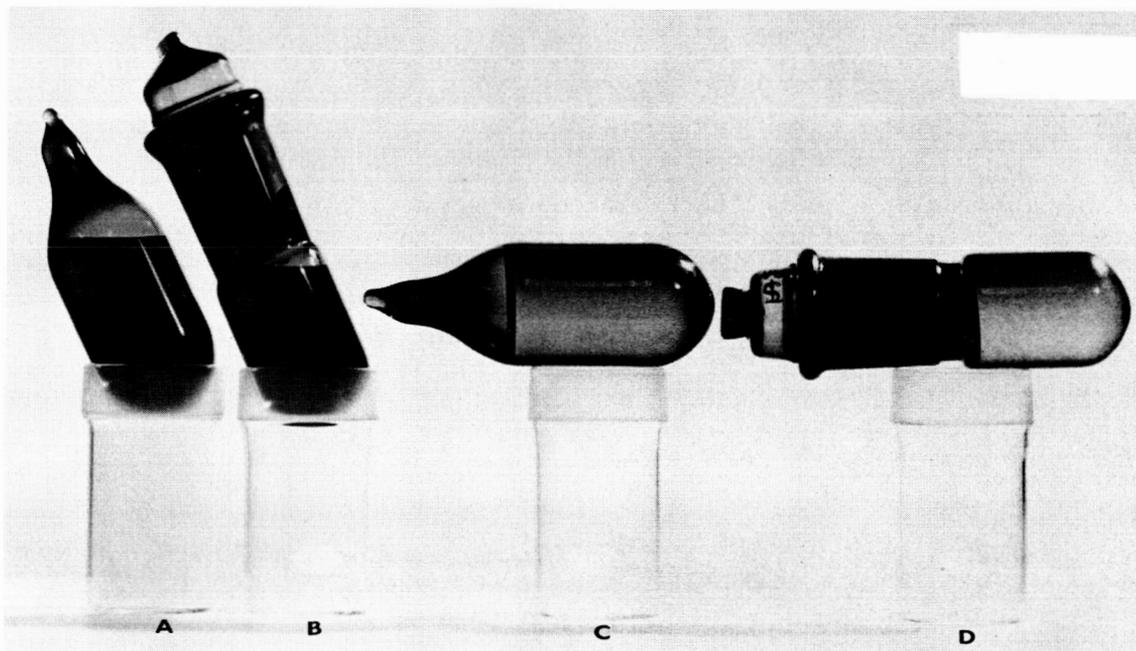


Figure 17. Appearance of Baseline Fluids in their Irradiation Containers After Irradiation ( $\sim 10^{10}$  ergs/gm C)

- a. OS-124, vacuum sealed vial
- b. OS-124, atmospheric vial
- c. DC-200, grade 500, vacuum sealed vial
- d. DC-200, grade 500, atmospheric vial

sample at the scheduled irradiation start (note the anomalously low pour point). Since phenyl sulfide is the primary scission product, as indicated by N. M. R. spectroscopy (see discussion in the appropriate section), additional amounts of phenyl sulfide would have no detrimental influence on the radiation effects imparted to the basic HCP-2800 molecule. (If there is any effect, the stable structure of the contaminant suggests additional shielding against further decomposition.) 0.5 ml of the final HCP-2800 was, nevertheless, irradiated and examined spectroscopically (see Appendix I, Figures I-16 and I-17) for evidence of decomposition. There were no discernible differences between the spectra of the various batches, with possible exceptions in the sizes of the respective aromatic proton peak areas and slight variations in methylic multiplet splitting.

4. In each case, the pour point was effected to a significantly lesser degree than the viscosity.
5. The degradation of the polydimethylsiloxane fluid was catastrophic.

Densities and the refractive indices of the fluids before and after irradiation were closely monitored as well. The data are presented in Table 17. Density measurements were performed with glass pycnometers in accordance with FTMS 791, Method 402.2, while the  $n_D$  values were determined by the

Table 17. Density and refractive index changes on irradiation

Lubricant Designation	Density at 25°C (g/cm <sup>3</sup> )		n <sub>D</sub>			
	Non-Irradiated	Irradiated (Vacuum)	Non-Irradiated	Temp (°C)	Irradiated (Vacuum)	Temp (°C)
OS-124	1.1914	1.1941	1.6325	20	1.6327	20
HCP-1500 (Batch No. 1)	----(1)	1.1016	1.5634	22	1.5605	21
HCP-1500 (Batch No. 2)	1.1084	1.1080	1.5632	22	1.5605	21
HCP-1800 (Batch No. 3)	----(1)	----(1)	1.5957	21	1.5948	21
HCP-1800 (Batch No. 6)	1.1098	1.1158	1.6083	21	1.6090	21
HCP-1900 (Batch No. 1)	1.1874	1.1902	1.6100	21	1.6131	21
HCP-2800 (Batch No. 1)	1.1076	1.1093	1.5992	21	1.5991	21
(1) Not measured.						

use of a Zeiss Model No. 323185 refractometer. The respective changes are obviously negligible.

Since measurement of gas evolution could not be performed with the existing, all-glass irradiation containers, chemical degradation of the products is indicated by (a) spectroscopy (see the appropriate section) and (b) elemental analyses of the fluids, not only in the prepared but also in the irradiated condition. Admittedly, the detailed mechanisms of radiation degradation are not known, nor is the stoichiometry of the degradation reactions pinpointed. Nevertheless, the small changes in elemental analyses and in the molecular weights may be attributed to fluid stability, as shown by the data in Table 18. This table contains the elemental analyses and average molecular weights of the thioether fluids before and after irradiation.

The negligible differences in elemental analyses and molecular weights, supported by I. R. and N. M. R. spectroscopy, are indications of only slight degrees of chemical degradation of the HCP fluids. In particular, additional performance data, including pour point, viscosity and lubricity, substantiate the fact that the non-chlorinated thioether siloxanes (HCP-1800 and HCP-2800) are excellent radiation-resistant lubricants.

Table 18. Effect of irradiation on the elemental analyses and average molecular weights of HCP fluids<sup>(1)</sup>

Compound Designation		C%	H%	Si%	S%	Cl%	Mol. Wt.
HCP-1800 (Batch No. 3)	non-irradiated	67.08	5.73	11.44	12.80	-	491
	irradiated	66.92	6.02	10.77	12.54	-	497
HCP-1800 (Batch No. 6)	non-irradiated	66.92	6.00	11.45	12.57	-	517
	irradiated	65.82	5.51	11.66	12.52	-	518
HCP-1900 (Batch No. 1)	non-irradiated	58.88	5.23	10.02	10.91	12.35	562
	irradiated	58.80	4.84	10.53	11.47	12.71	578
HCP-2800 (Batch No. 1)	non-irradiated	64.91	5.69	12.03	13.17	-	384
	irradiated	67.09	5.98	11.24	13.02	-	483

(1) For theoretical values of pure compounds see Table 2.

#### H. THERMAL AND OXIDATION STABILITY

The initial decomposition temperature is reached when thermal fragmentation of the molecule causes a measurable change in vapor pressure and evaporation rate, and can serve as a guide to the upper temperature performance limit of a potential lubricant.

The oxidation resistance of inhibited and most uninhibited organic materials decreases rapidly as the temperature is raised. If sufficient oxygen is present, the oxidation rate of inhibited oils about doubles for each 10°C (18°F) rise in temperature. It is, however, known that the stability of polyphenyls, polyphenyl ethers and aromatic compounds in general is less temperature dependent (Reference 5).

Moreover, it is recognized that the flammability of fluids is intimately associated with oxidation processes and may be associated with thermal decomposition.

##### 1. Description of the Apparatus and the Test Method

The thermal and oxidation stability of selected batches of HCP-1800 and the final HCP-2800 mixture were evaluated by (a) differential thermal analyses (DTA) as well as (b) thermogravimetric analyses (TGA) in pure argon and oxygen.

The analyses were performed on a du Pont 900 thermal analyzer with the DTA and TGA attachments. During DTA the samples (~10 mg) were weighed into the sample cup and purged with the test gas for several minutes before closing and sealing for the analyses. The sample cups were also continuously purged with the respective gasses while the analyses were being run. Aluminum oxide was used in the reference cup.

For the TGA the interior of the furnace was continuously purged with the test gas during the entire run.

The heating rate for all analyses was 10°C/minute.

## 2. Results and Discussion

The stability of the thioether fluids was first indicated by the DTA of HCP-1800, Batch No. 3 in argon and oxygen. The respective thermograms are presented superimposed in Figure 18. The results confirm the expectation of good thermal and oxidation stability of thioether siloxanes: this batch appears to be stable in pure oxygen up to ~300°C (572°F). Complete interpretation of the curves without additional thermogravimetric data was, however, difficult.

In order to substantiate the original findings, samples of pure HCP-1800 (from the mixture of Batch No. 5, 6 and 7) and the final mixture

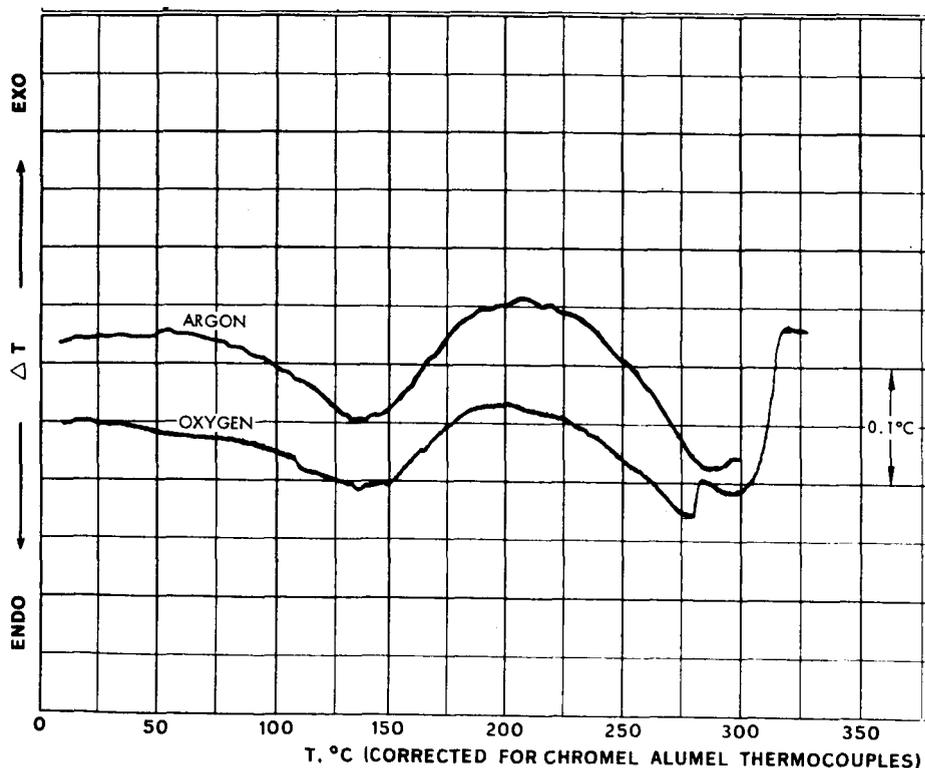


Figure 18. Differential Thermal Analyses of HCP-1800 (Batch No. 3) in Various Environments

of HCP-2800 were subjected to both DTA and TGA in argon and oxygen. The thermograms of these tests are shown in Figures 19 through 26. The data indicate little difference in fluid decomposition behavior in the subject test gases, conclusively showing stability up to at least 250°C in all cases. The more definitive TGA slope of HCP-1800 may be attributed to the product's purity, while the slower evaporation of HCP-2800, as well as its low initial weight loss temperature, may be attributed to the trace amounts of phenyl sulfide and other trace quantities of lower molecular weight components. Its slightly reduced thermal stability due to the presence of the somewhat less stable trisiloxane linkage cannot be discounted.

## I. ADDITIVE ACCEPTANCE

Polysiloxane oils are notorious for poor additive acceptance. It is a consensus among research chemists that in the case of inert fluids (e. g., polysiloxanes or fluorinated polyethers) additive synthesis must begin with an intermediate of the final fluid to insure solubility.

A portion of the current effort was devoted to determining the solubility of various additives in the HCP fluids. Initial work (see Reference 1) already indicated that these experimental fluids have unusually good additive acceptance, due most likely to the introduction of aromatic groups in the molecule.

### 1. Description of the Apparatus and the Test Method

Small-drop solubility tests were performed on spot plates to determine the feasibility of using additives to improve the lubricity of the low-pour point base fluids synthesized in this program. The following simple procedure was used:

1. One drop of the experimental base fluid was placed in a well of a white spot plate. The plate was positioned under a microscope adjusted to a suitable magnification.
2. A droplet of a liquid additive or a few crystallites of a solid additive were deposited at the edge of the fluid drop. After observing the characteristics of the boundary layer, the mixture was thoroughly stirred at room temperature. Rapid disappearance of schlieren (in the case of oil), or ready dissolution of the crystallites indicated good solubility.
3. Any sample that indicated moderate or poor solubility at room temperature was gently stirred and heated over a soft Bunsen flame. The warm mixture was observed under the microscope for solubility.
4. The mixture was permitted to cool to room temperature and kept under constant observation to note any re-precipitation or any other form of additive separation.

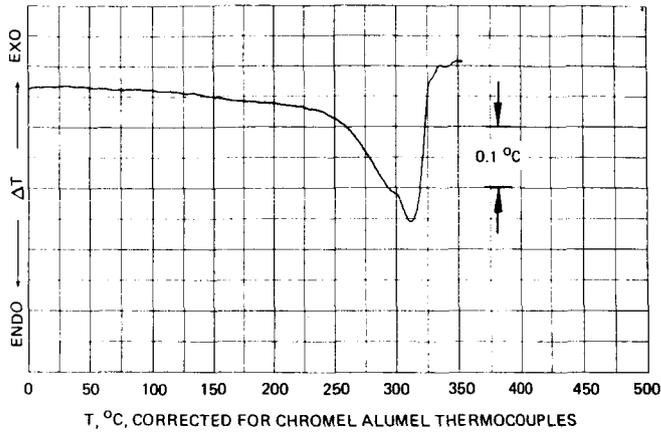


Figure 19. DTA Thermogram of Pure HCP-1800 in Argon

Figure 2-. DTA Thermogram of Pure HCP-1800 in Oxygen

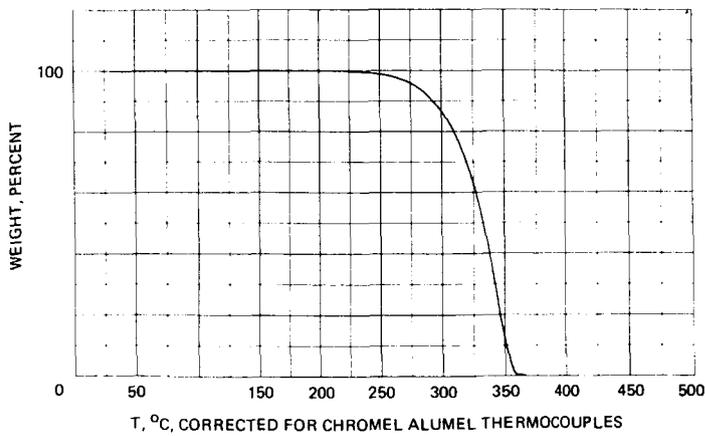
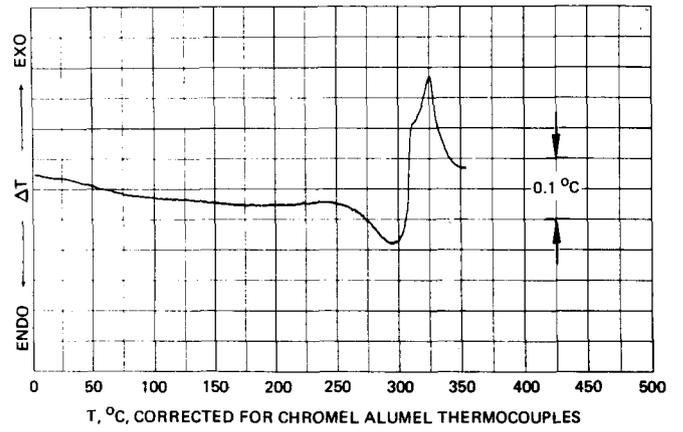


Figure 21. TGA Thermogram of Pure HCP-1800 in Argon

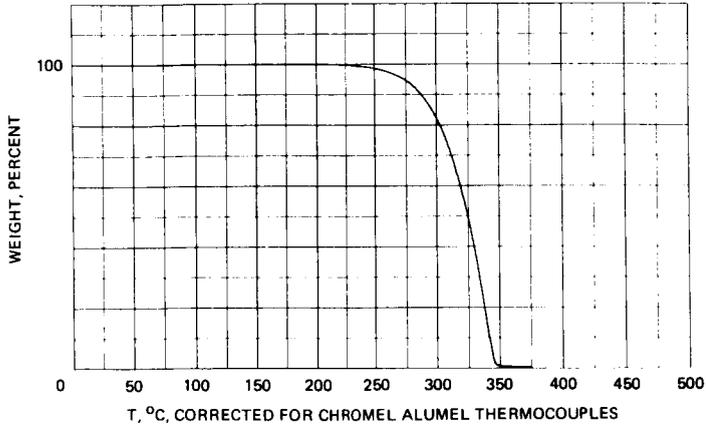


Figure 22. TGA Thermogram of Pure HCP-1800 in Oxygen

Figure 23. DTA Thermogram of HCP-2800 in Argon

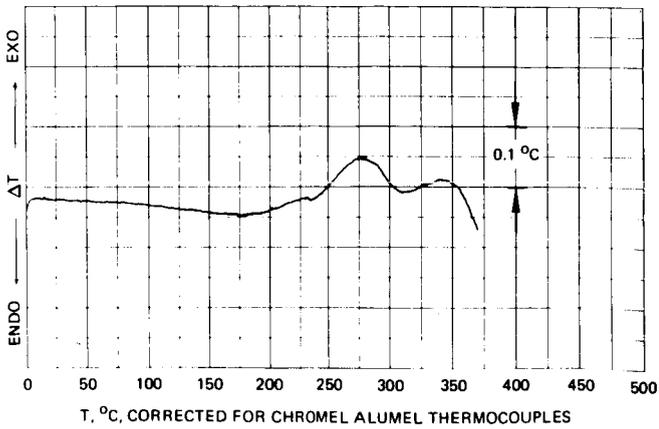
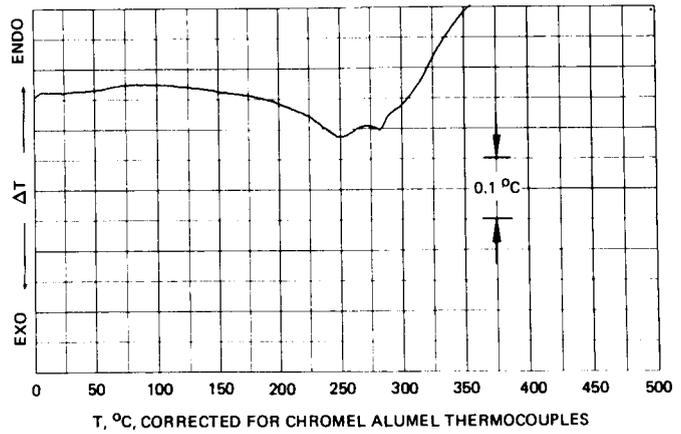


Figure 24. DTA Thermogram of HCP-2800 in Oxygen

Figure 25. TGA Thermogram of HCP-2800 in Argon

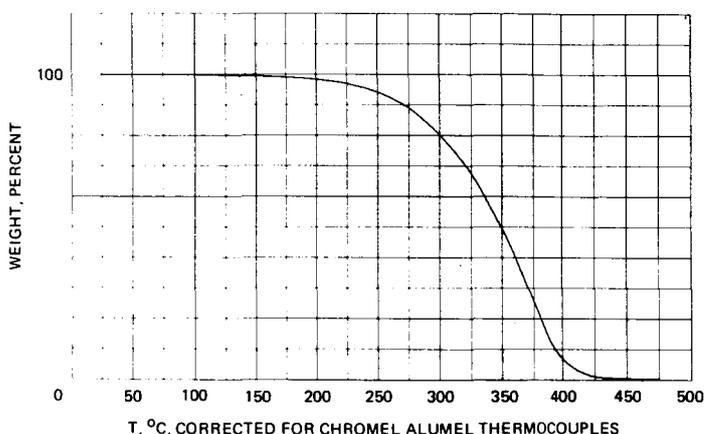
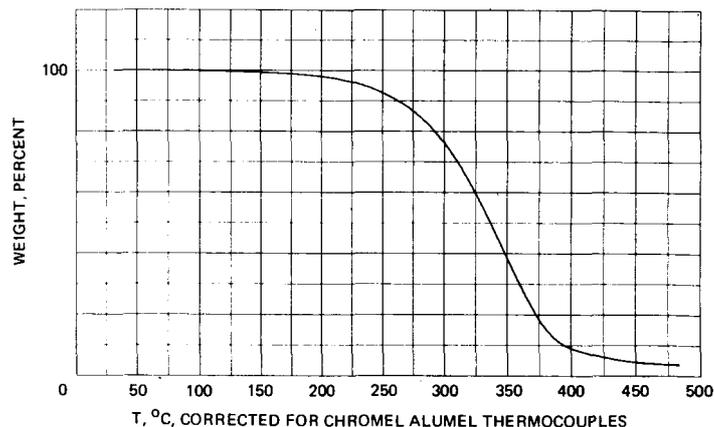


Figure 26. TGA Thermogram of HCP-2800 in Oxygen

Note, again, that additive acceptance tests were performed mostly by dissolving selected additives in HCP-1500 and HCP-C1500/1600 (see section 4.F) and, occasionally, in other HCP fluids.

## 2. Results and Discussion

The solubility data are compiled in Table 19.

The results presented in Table 19 continually indicate the excellent additive acceptance of the disubstituted disiloxane fluid families under investigation. It should be noted that none of the commercial or synthesized additives examined herein were soluble in polysiloxane oils (DC-200) at room temperature, even after prior heating. As might be expected, the experimental base fluids are miscible with the polyphenyl ether OS-124.

The second batch of HCP-4270 did not, however, continue to show the kind of satisfactory acceptance the first batch did with TCP, phenyl sulfide and triphenylphosphine (Reference 1). Although this anomalous behavior cannot be definitely explained at this time, it should be noted that elemental

Table 19. Additive acceptance of HCP fluids

Base Fluid	Additive	Miscibility at Room Temperature	Observation
HCP-1500 (Batch No. 3)	Trichlororesorcinol (solid) <sup>(1)</sup>	Good	Rapid disappearance of swirl marks (schlieren).
HCP-1500 (Batch No. 3)	Tri-p-tolyl phosphite (liquid)	Good	Rapid disappearance of schlieren.
HCP-1500 (Batch No. 3)	Tri-p-tolyl thiophosphate (solid)	Good	Rapid disappearance of schlieren.
HCP-1500 (Batch No. 3)	Tricresyl phosphate (liquid)	Good	Rapid disappearance of schlieren.
HCP-1500 (Batch No. 3)	Phenyl sulfide (liquid)	Good	Rapid disappearance of schlieren.
HCP-1500 (Batch No. 3)	Triphenylphosphine (solid)	Moderate	Good miscibility on heating. No separation on cooling.
HCP-1500 (Batch No. 3)	Molybdenum dialkyl dithiocarbamate (solid, Molyvan A)	Moderate	Good miscibility on heating. No separation on cooling.
HCP-1500 (Batch No. 3)	Antimony dithiocarbamate (solid)	Moderate	Good miscibility on heating. No separation on cooling.
HCP-1500 (Batch No. 3)	Cadmium dithiocarbamate (solid)	Moderate to Poor	Good miscibility on heating. Separation on cooling.
HCP-1500 (Batch No. 3)	OS-124 (liquid)	Good	Cloudy mixture. Does not clear up on heating. Rapid disappearance of schlieren.
C1500/1600 (3/1)	Triphenylstibine (solid)	Good	Rapid disappearance of schlieren.
C1500/1600 (3/1)	Tricresyl phosphate (liquid)	Good	Rapid disappearance of schlieren.
C1500/1600 (3/1)	Lead naphthenate (liquid)	Good	Rapid disappearance of schlieren.

(1) Physical state at room temperature.

Table 19. Additive acceptance of HCP fluids (continued)

Base Fluid	Additive	Miscibility at Room Temperature	Observation
HCP-C1500/1600 (9/1)	Lead naphthenate	Good	Rapid disappearance of schlieren.
HCP-1800 (Batch No. 2)	Triphenylstibine (solid)	Good	Rapid disappearance of schlieren.
HCP-1800 (Batch No. 2)	Tricresyl phosphate (liquid)	Good	Rapid disappearance of schlieren.
HCP-1800 (Batch No. 2)	Lead naphthenate (liquid)	Good	Rapid disappearance of schlieren.
HCP-1800 (Batch No. 3)	OS 24 (liquid)	Good	Rapid disappearance of schlieren.
HCP-1800 (Batch No. 3)	Tri-p-tolyl phosphite (liquid)	Good	Rapid disappearance of schlieren.
HCP-1800 (Batch No. 3)	Tri-p-tolyl thiophosphate (solid)	Good	Rapid disappearance of schlieren.
HCP-4270 (Batch No. 2)	Triphenylstibine (solid)	Moderate	Either partial solubility, or formation of few thin, needle-like crystallites.
HCP-4270 (Batch No. 2)	Tricresyl phosphate (liquid)	Good	Fluid darkening and some precipitate formation in tightly capped vials in ~10 days.
HCP-4270 (Batch No. 2)	Lead naphthenate (liquid)	Poor	Immediate formation of precipitate on mixing.

analysis and average molecular weight measurements of the second batch of HCP-4270 indicated significant deviations from the theoretical structure (see Table 2). Another possible explanation may be the insolubility of some of the lead naphthenate isomers in the fluid. Results of additive mixing effects on the pour point and lubricity of selected HCP fluids are discussed in previous sections (see sections 4. C and 4. F, respectively).

Attempts were also made to improve the radiation resistance of commercially available liquid space lubricants by blending them with selected members of HCP fluids, e. g., HCP-1800 or HCP-1900, since literature data indicate that polynuclear aromatics, in concentrations of ~20 volume percent,

can provide protection for silicone oils at radiation dosages up to  $10^{11}$  ergs/gm(C) (Reference 17). This protection apparently extends to the reduction of frictional gelation as well (Reference 15).

Drop solubility tests, normally used to determine the additive acceptance of the products, uncovered that neither HCP-1800 nor HCP-1900 are sufficiently soluble in (a) F-50 (chlorophenylmethylpolysiloxane), (b) FS-1265 (300cs), (c) DC-200 (500cs), and (d) Krytox 143AC (perfluoro-alkyl polyether) to permit the preparation of the blends (~20 percent by volume of the Hughes fluids) for irradiation. The radiation protection concept, therefore, is not usable for these commercially available fluids.

## J. ESTIMATED PROPERTIES

### 1. Bulk Modulus

The properties of the HCP fluids suggest likely candidacy as hydraulic fluids in spacecraft hydraulic servomechanisms. Since bulk modulus (reciprocal of compressibility) is one of the prime properties of any hydraulic fluid (because efficient power transfer requires a high bulk modulus, low compressibility liquid), the isothermal secant bulk modulus of HCP-1800 and HCP-2800 were estimated by a method set forth in Reference 18. According to this method, the isothermal secant bulk modulus for non-halogenated methyl and phenyl siloxane fluids at any temperature and pressure can be determined from the standard state density, i. e., density at atmospheric pressure and a temperature of 25°C (77°F). The authors claim that due to the erratic nature of most bulk modulus measurements, results calculated by this method are likely to be more accurate than experimentally measured values.

The calculated moduli for the subject HCP fluids are compared with those obtained on some prime space shuttle hydraulic fluid candidates, e. g., silicone oils and C-ethers (Reference 6), in Table 20. (Note that C-ethers are modified polyphenyl ethers.)

The data confirm the attainment of the original goal of the present synthesis program - combining the properties of silicones with those of aromatic ethers. The theoretically sound values of bulk moduli of the subject HCP fluids are nearly arithmetic averages of experimental values on the silicone fluid and C-ether. The high compressibility of silicone fluids is significantly lowered by the introduction of low-compressibility aromatic groups.

### 2. Surface Tension

Although no conclusive correlation can be established between wettability (surface tension) and the lubricity of a fluid, many technologists prefer high surface tension space lubricants. High surface tension is normally associated with reduced surface migration and consequently reduced

Table 20. Bulk moduli of HCP fluids and selected commercial lubricants

Lubricant Designation	Isothermal Secant Bulk Modulus at 4000 psi (psi)	
	100°F	350°F
MIL-H-5606	212,000	106,000
Silicone oil	195,000	100,000
C-ether	340,000	235,000
HCP-1800	260,000	144,000
HCP-2800	250,000	132,000

vaporization of the surface migrated fluid (Reference 6). Furthermore, in the case of hydraulic fluids, a relatively high surface tension is desirable in order to minimize leakage through seals.

The surface tension of HCP fluids was calculated from bond parachor values (Reference 19) using the well-known relationship (Reference 20) in the form of

$$\gamma = \left( \frac{P\rho}{M} \right)^4$$

where

- $\gamma$  = surface tension in dynes/cm;
- P = bond parachor;
- $\rho$  = standard density in g/cm<sup>3</sup>;
- M = molecular weight in g.

The results are tabulated in Table 21, along with comparative values obtained with the commercial fluids included in Table 20.

Table 21. Surface tension of HCP fluids and selected commercial lubricants

Lubricant Designation	Surface Tension (dynes/cm) at 75°F (24°C)
MIL-H-5606	30*
Silicone oil	27*
C-ether	50*
HCP-1800	40
HCP-2800	35
*Data from Reference 6.	

Again, note the difference between the values for the silicone and the C-ether, and the median position of the HCP fluid values.

#### K. GREASE COMPOUNDING

Compounding of the grease was deferred until screening of the synthesized fluids was complete. Although there may be some radiation resistance provided by whatever thickener is used, there was no purpose in experimentation of this kind without utilizing the optimum fluid, HCP-2800.

Five outstanding thickeners were available; ammeline, silica, indanthrene blue, copper phthalocyanine, and sodium N-octadecylterephthalamate. Greater effectiveness (with the latter salt) has been obtained by mixing it with other aromatic salts, such as sodium benzoate, but the use of these materials must be weighed against the known effects of neutrons (in the ultimate application) on metallic ions. An exception would be the copper in copper phthalocyanine, since this element is a subgroup metal, and shares not only covalent linkages with the bonding nitrogen electrons, but coordinate linkages with the non-bonding nitrogen electrons. Hence the copper is complexed, and the molecule is extremely stable.

Various forms of silica have been found satisfactory as grease thickeners. Shell Oil greases APL 700 and APL 701 are based on naphthene- and aromatic-rich petroleum oils, thickened with silica. These materials, and the silica/alkylbenzene greases are probably limited to about 225°F, but this does not rule silica out as a thickener. Of course, soaps of fatty acids are by comparison rapidly degraded by radiation, mostly by softening. Moreover, exposure to neutrons will cause lithium and sodium soaps to become radioactive (Reference 16).

The final choice rested on a silica (Cabosil) filler to produce an NLGI Grade 2 experimental grease sample from ~15 ml of HCP-2800 (Batch No. 1).

By agreement with the Project Manager, compounding of the grease was performed by Bray Oil Co., Los Angeles, under the technical supervision of Dr. Ulrich B. Bray.

As a point of reference before attempting to compound the sample of HCP-2800, a grease was prepared from dimethylsilicone fluid (General Electric SF96, 50 cs.) using 7.29 weight percent Cabosil H-5 alone. This grease had a penetration of 253 and was stable to heat, degassing to 0.5 torr, and working.

A grease was then made (14.8 g) consisting of 95.23% HCP-2800 oil and 4.77% Cabosil H-5. This grease was too soft to run a penetration test. Cabosil H-5 was added in increments to obtain the following results:

5.74% Cabosil H-5	335 penetration
6.32% Cabosil H-5	318 penetration
6.84% Cabosil H-5	280 penetration

A vacuum was pulled on the 6.84% Cabosil H-5 grease to 0.5 torr and the grease then had a penetration of 327. In a couple of days, the grease had degelled to a liquid.

To determine the effects of phenyl groups on a grease gelled with Cabosil H-5, a grease was made using methylphenylsilicone fluid (Dow Corning DC510, 50 cs.) and Cabosil H-5. At 6.8% Cabosil H-5, a penetration of 280 was obtained and the grease was stable to heating and vacuum.

At this point, it was decided that the grease with the HCP-2800 needed a gel stabilizer, Ucon LB-3000. This was added till the HCP-2800 contained 1.02% Ucon LB-3000. Then increments of Cabosil H-5 were added to give a grease containing 8.86% Cabosil H-5, 0.99% Ucon LB-3000 and the balance HCP-2800. This grease had a penetration of 362 after vacuum degassing. This grease is thermally unstable, thinning on heating and thickening upon cooling.

To a 2 g sample of the above grease was added 3.71% of Baragel 24, an organically modified bentonite clay grease thickener. By adding one drop of water and one drop of methanol with working and later heating and degassing to 0.5 torr, a grease was obtained of approximately 280 penetration (sample too small to test), but the grease is still thermally unstable.

To the remaining grease without Baragel 24, Cabosil H-5 was added in increments to obtain a penetration of 280 at 77°F. The final product, 3L-27-2, has 11.68% Cabosil H-5 and 0.94% Ucon LB-300, with the balance HCP-2800. It is still not a very stable gel, in that penetration changes noticeably with temperature. The final grease was filtered into three ml. syringes marked 3L-27-2. Two of these syringes have been forwarded to the Project Manager.

It appears that inorganic thickeners like Cabosil or Bentonite clays do not form stable gel structures with HCP-2800. Addition of synergistic agents can not remedy this phenomenon. The most likely cause of low gel stability is inherent in the nonpolymeric nature of the thioether fluid.

Since the experimental grease does not have sufficient thermal stability, the above data serves only as a guide for future work. The next likely filler candidate for investigation should be copper phtalocyanine.

## 5. CONCLUSIONS

A two year synthesis and evaluation study was terminated by the synthesis of an outstanding radiation resistant lubricant candidate which is extremely promising with respect to a wide temperature range, good lubricity, oxidation resistance, low vapor pressure and excellent additive acceptance.

This fluid, designated as HCP-2800, which is 1,5-bis[3-(phenylthio)phenyl]-1,1,3,3,5,5-hexamethyltrisiloxane displays the following physical properties:

Pour point	=	-53°F
Viscosity, kinematic		
-45°F	=	22,740 cs.
-35°F	=	8,226 cs.
0°F	=	599 cs.
100°F	=	20.49 cs.
210°F	=	4.99 cs.
400°F (extrapolated)	=	1.6 cs.
Vapor pressure		
100°F	=	$1 \times 10^{-6}$ torr
350°F	=	$1 \times 10^{-3}$ torr
Thermal and Oxidation Stability	=	to 500°F
Bulk moduli (isothermal secant)		
100°F	=	250,000 psi.
350°F	=	132,000 psi.
Surface tension at 75°F	=	35 dynes/cm
LFW-1 lubricant ratings	=	2 (OS-124 = 1b)

200 grams of the lubricant have been forward to the Project Manager for further evaluation.

Most of the physical properties as well as lubricity of the HCP fluids have been determined by specially designed test methods that enabled the evaluation of micro-quantities of lubricants. These new, repeatable methods correlate well with established test procedures and successfully bridge the gap between the capabilities of the research chemist and the requirements of the evaluating technologist.

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## APPENDIX I.

This appendix consists of infrared and nuclear magnetic resonance spectra presented in Figures I-1 through I-7.

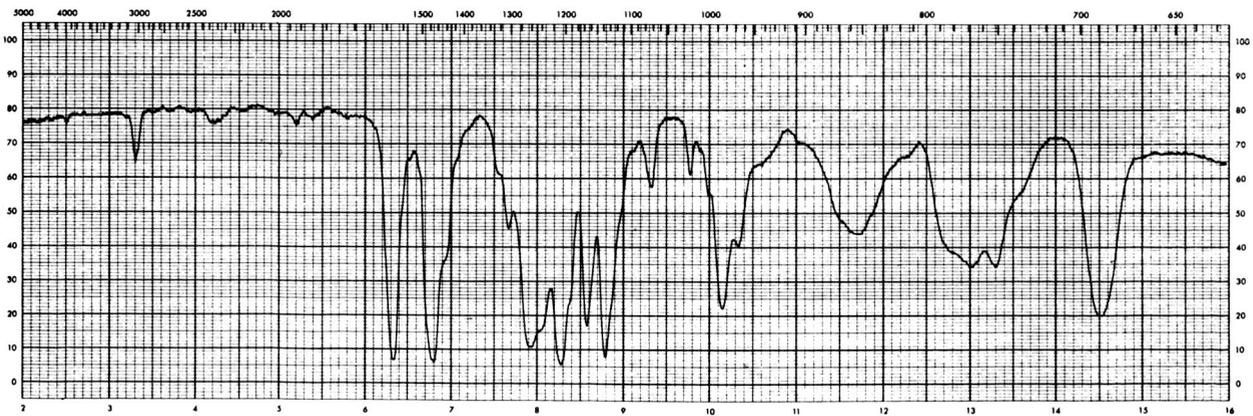
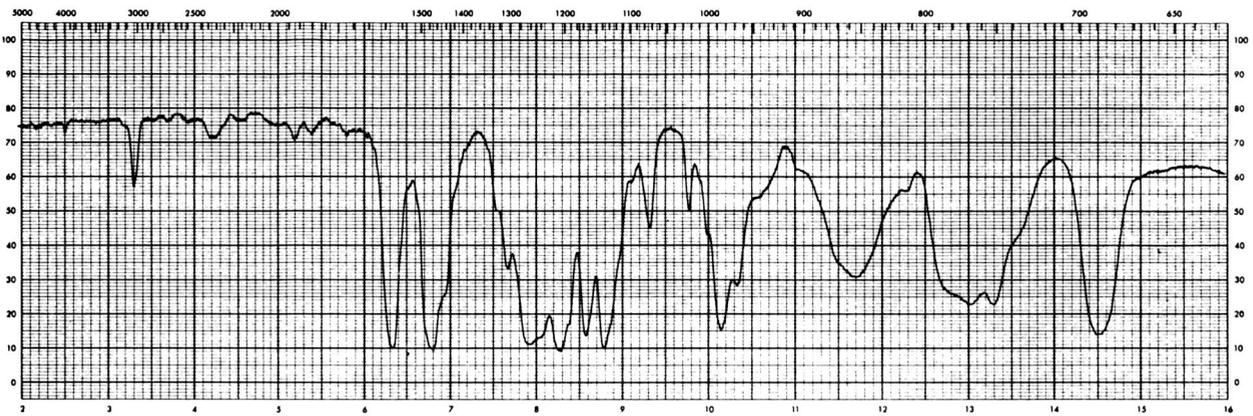
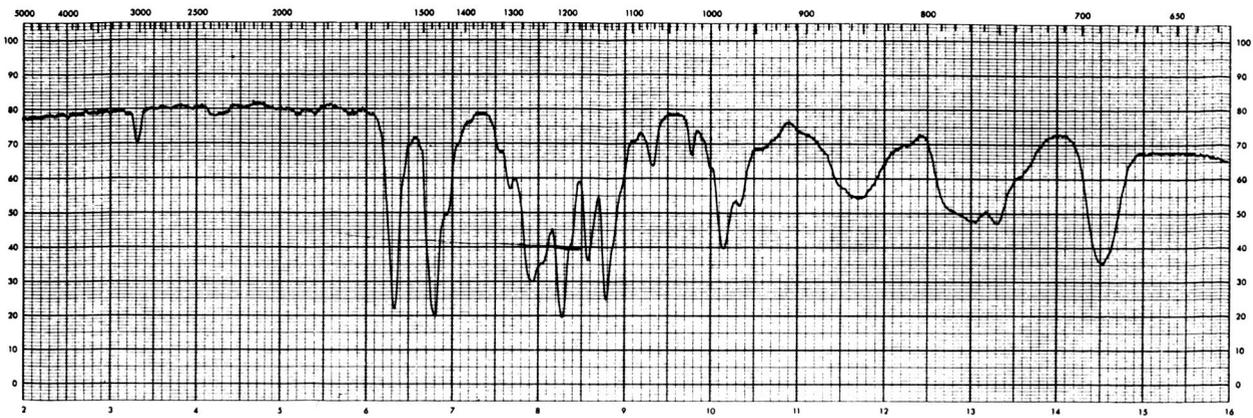


Figure I-1. I. R. Spectra of OS-124 (a) Non-Irradiated, (b) Irradiated In Air and (c) Irradiated In Vacuum, Obtained Between Salt Crystals

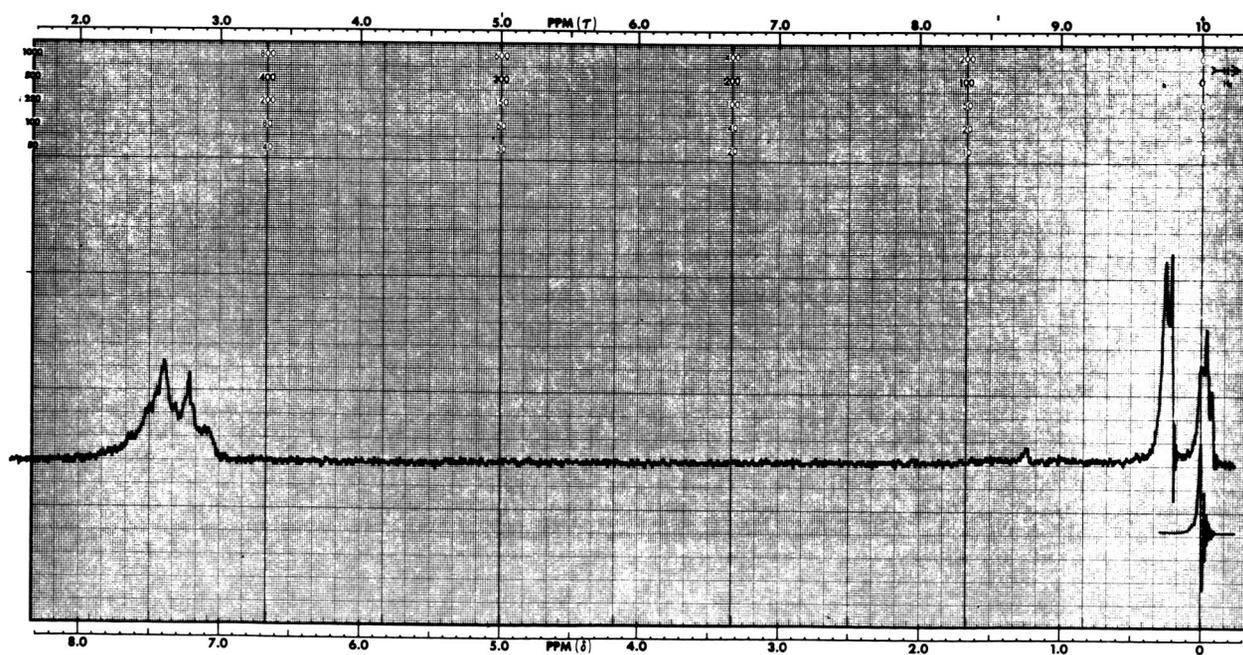
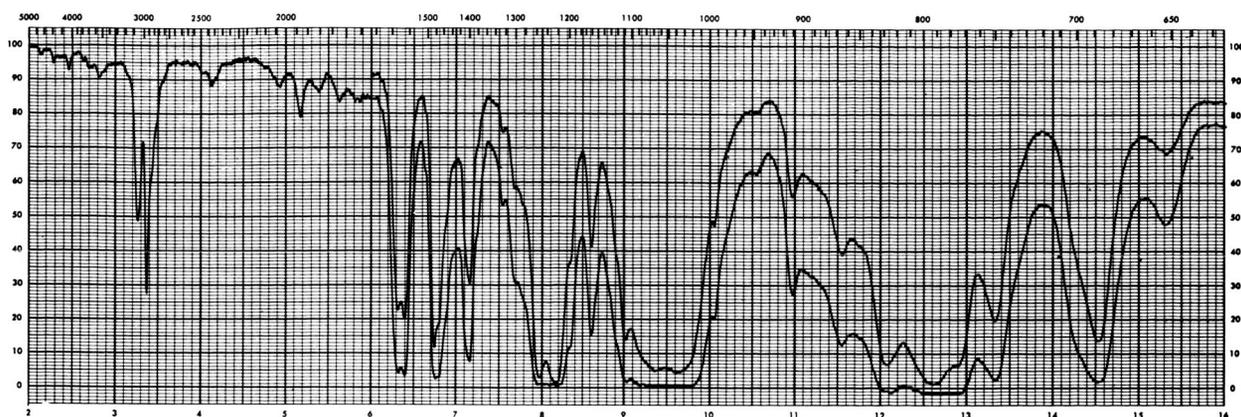


Figure I-2. IR and NMR Spectra of Non-Irradiated HCP-1500  
 Batch No. 1. IR Between Salt Crystals. NMR Parameters:  
 R. F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep  
 Width = 500 Hz; Spectrum Amplitude = 25

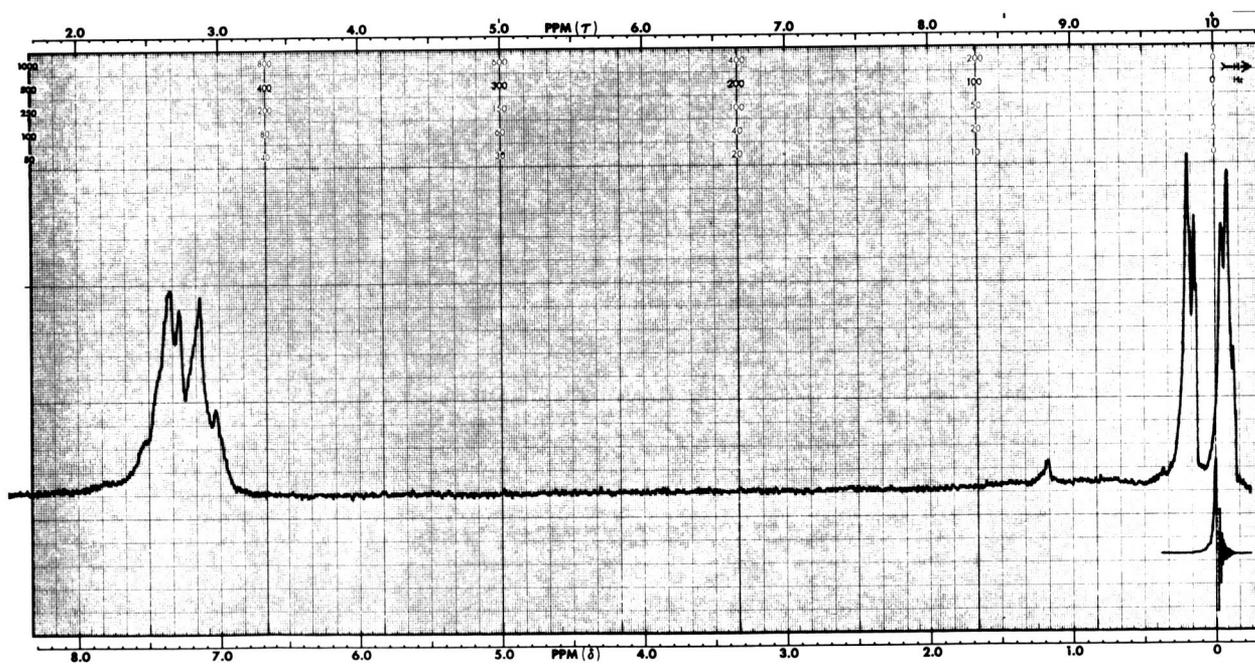
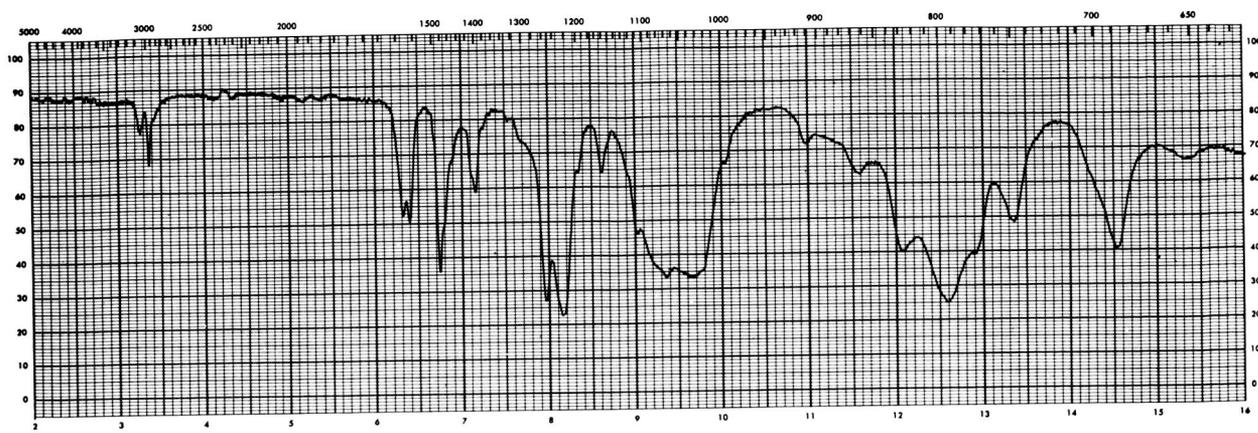


Figure I-3. IR and NMR Spectra of HCP-1500, Batch No. 1,  
 Irradiated in Air. IR Between Salt Crystals. NMR  
 Parameters: R.F. Field = 0.10 mG; Sweep  
 Time = 500 Sec.; Sweep Width = 500 Hz;  
 Spectrum Amplitude = 20

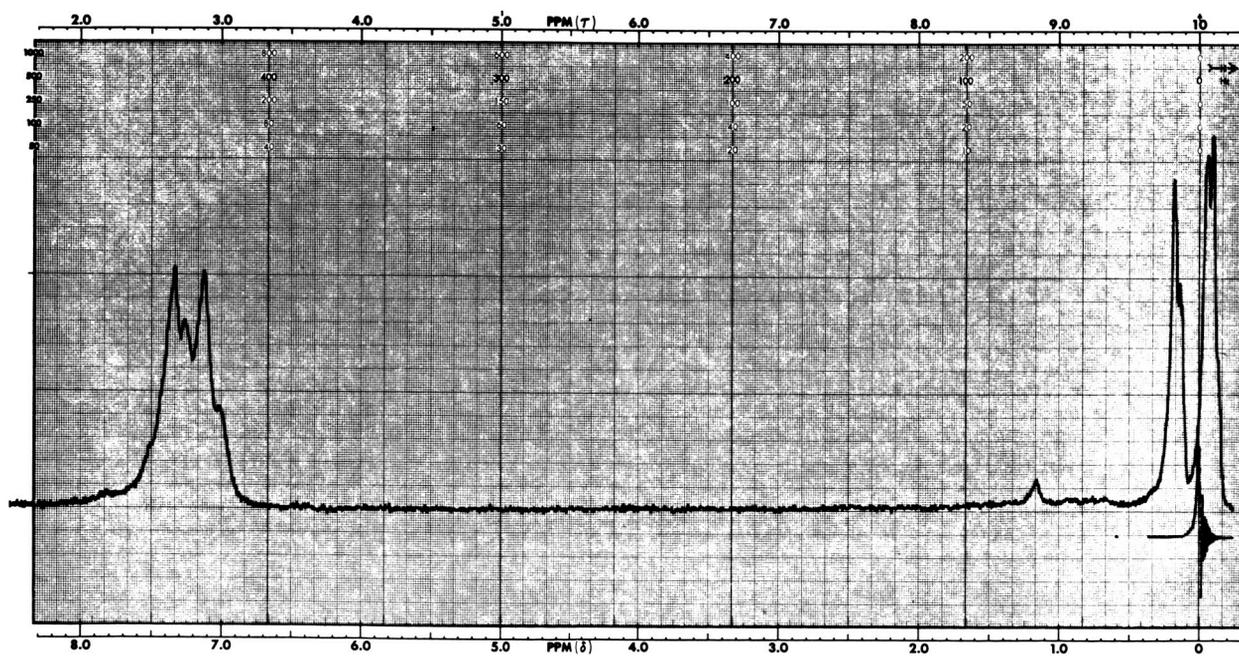
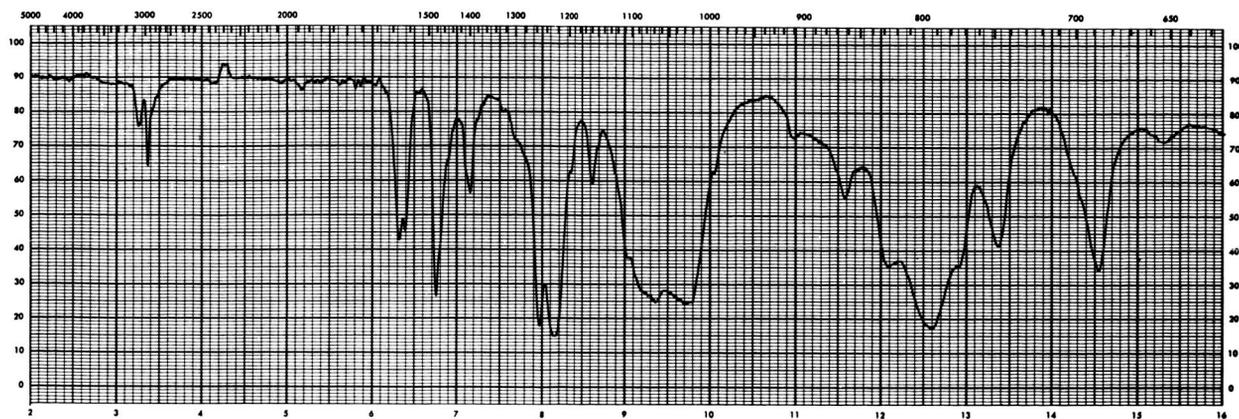


Figure I-4. IR and NMR Spectra of HCP-1500 Batch No. 1,  
 Irradiated in Vacuum. IR Between Salt Crystals;  
 NMR Parameters: R.F. Field = 0.10 mG;  
 Sweep Time = 500 Sec.; Sweep Width =  
 500 Hz; Spectrum Amplitude = 20

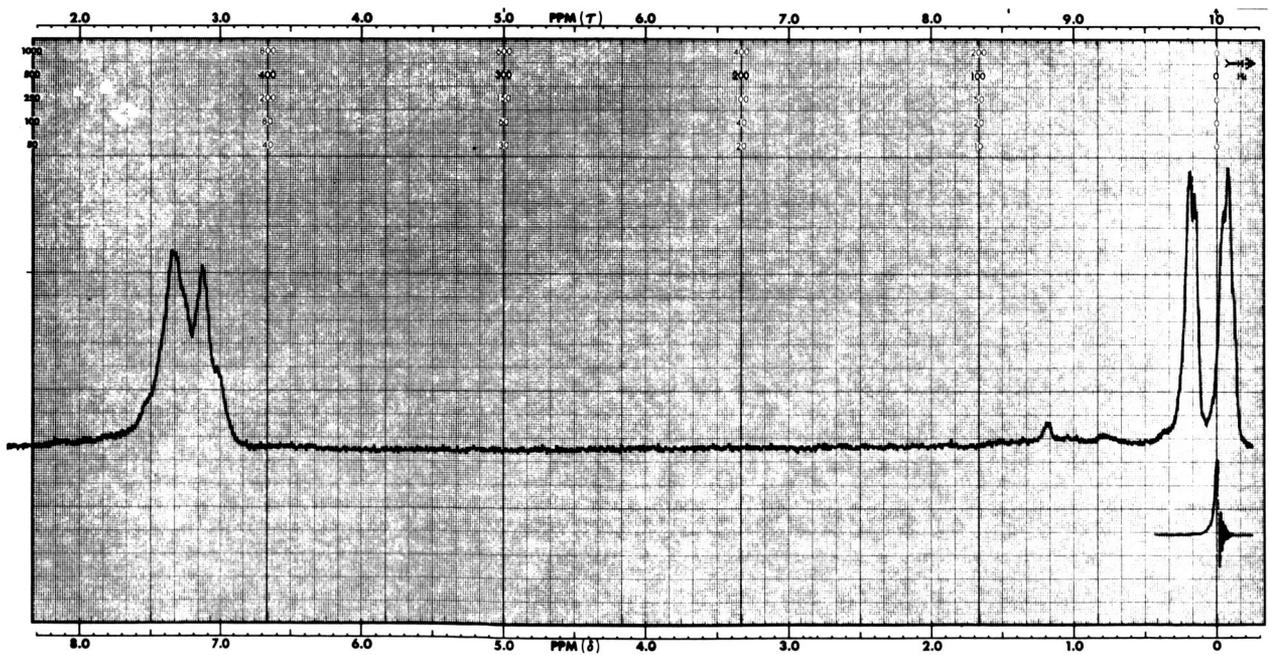
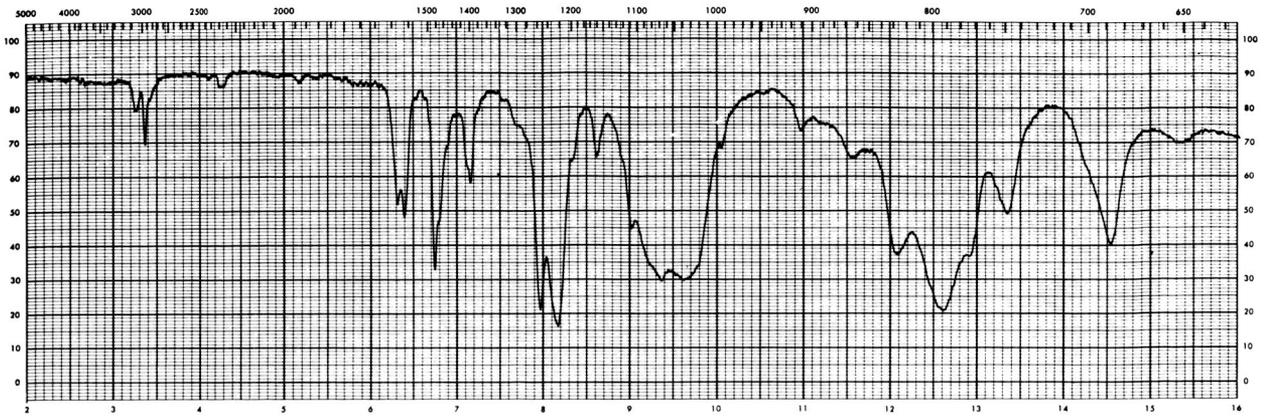


Figure I-5. IR and NMR Spectra of Non-Irradiated HCP-1500  
 Batch No. 2. IR Between Salt Crystals. NMR Parameters:  
 R. F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep  
 Width = 500 Hz; Spectrum Amplitude = 12.5

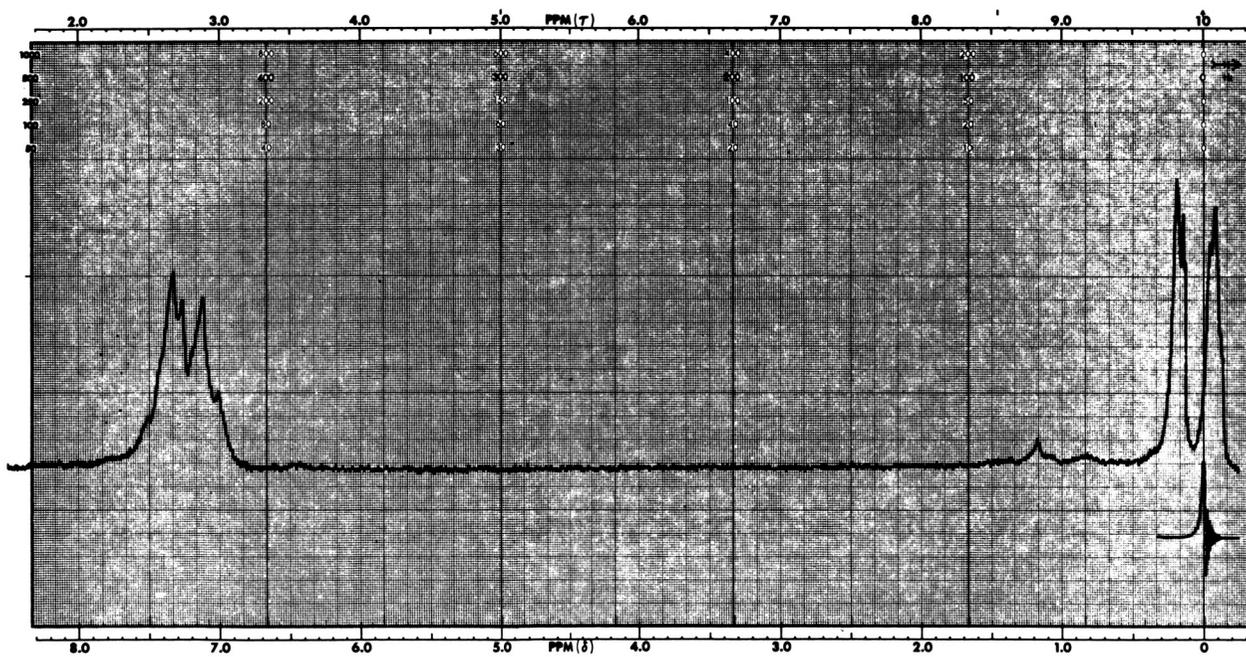
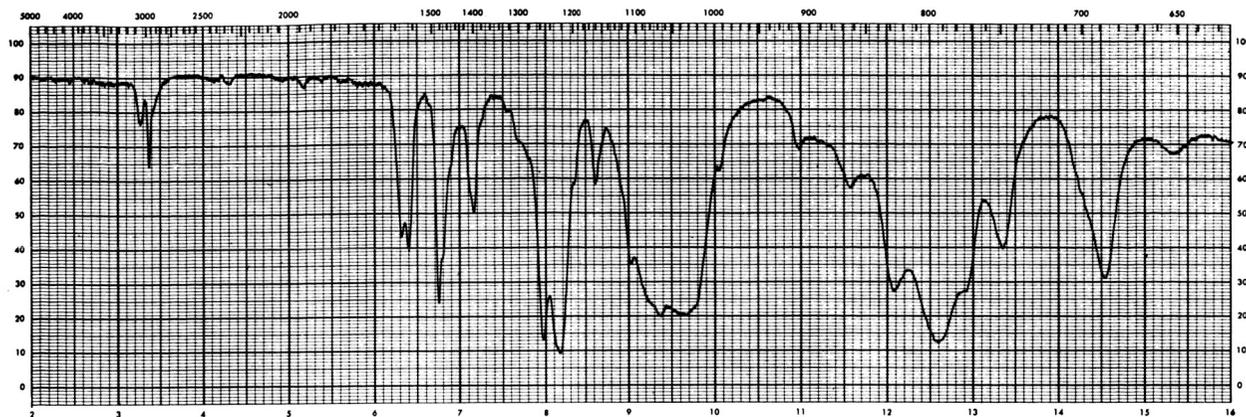


Figure I-6. IR and NMR Spectra of Atmospheric Irradiated HCP-1500, Batch No. 2, Irradiated in Air. IR Between Salt Crystals. NMR Parameters: R.F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 20

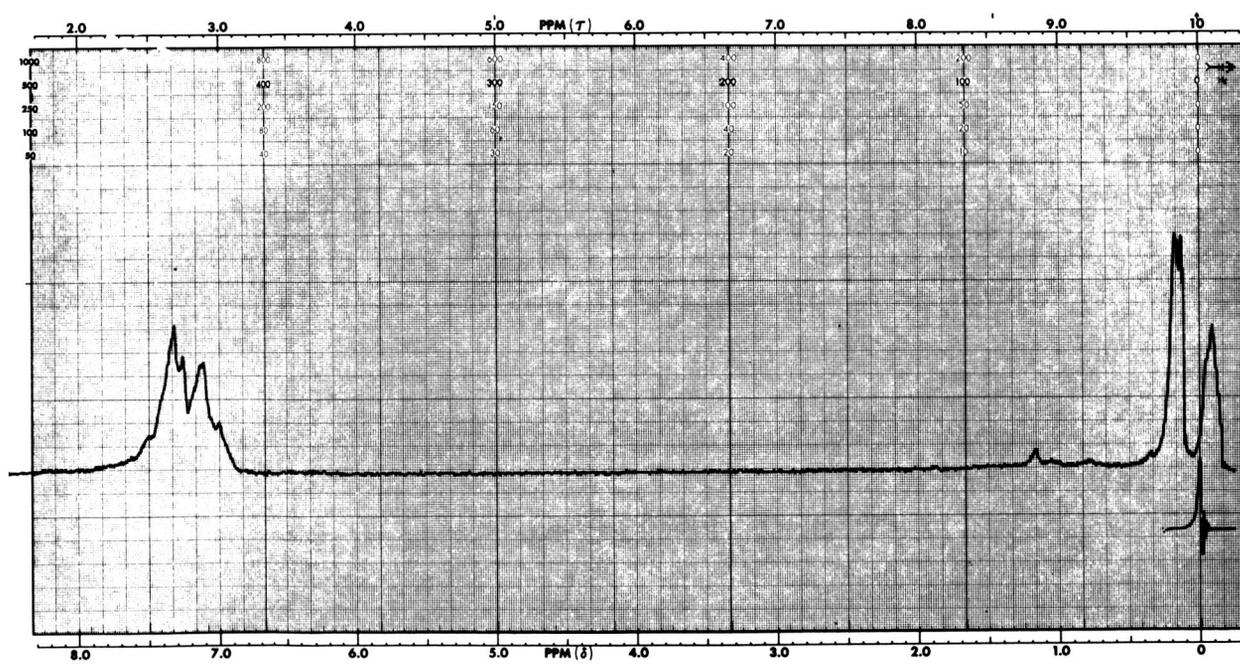
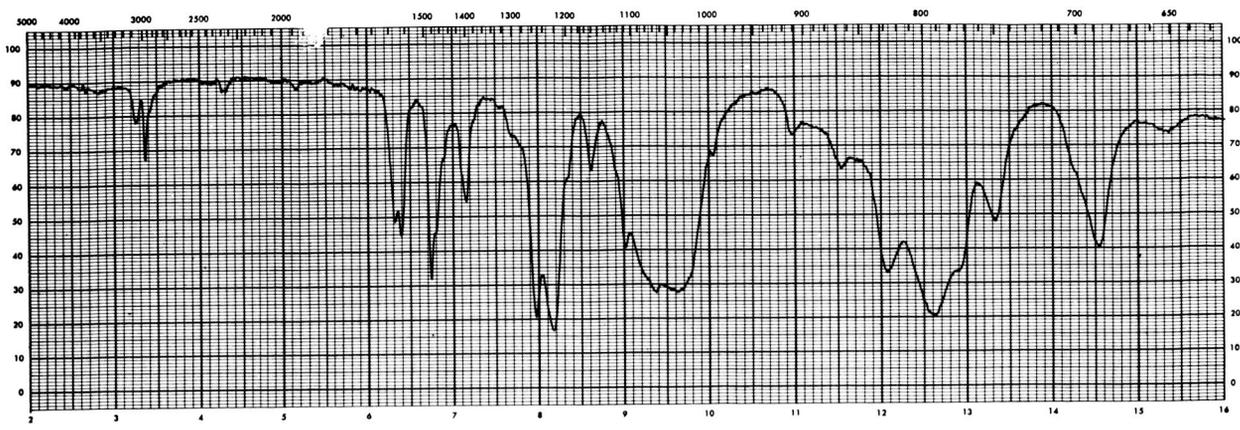


Figure I-7. IR and NMR Spectra of HCP-1500, Batch No. 2, Irradiated in Vacuum. IR Between Salt Crystals. NMR Parameters: R.F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 20

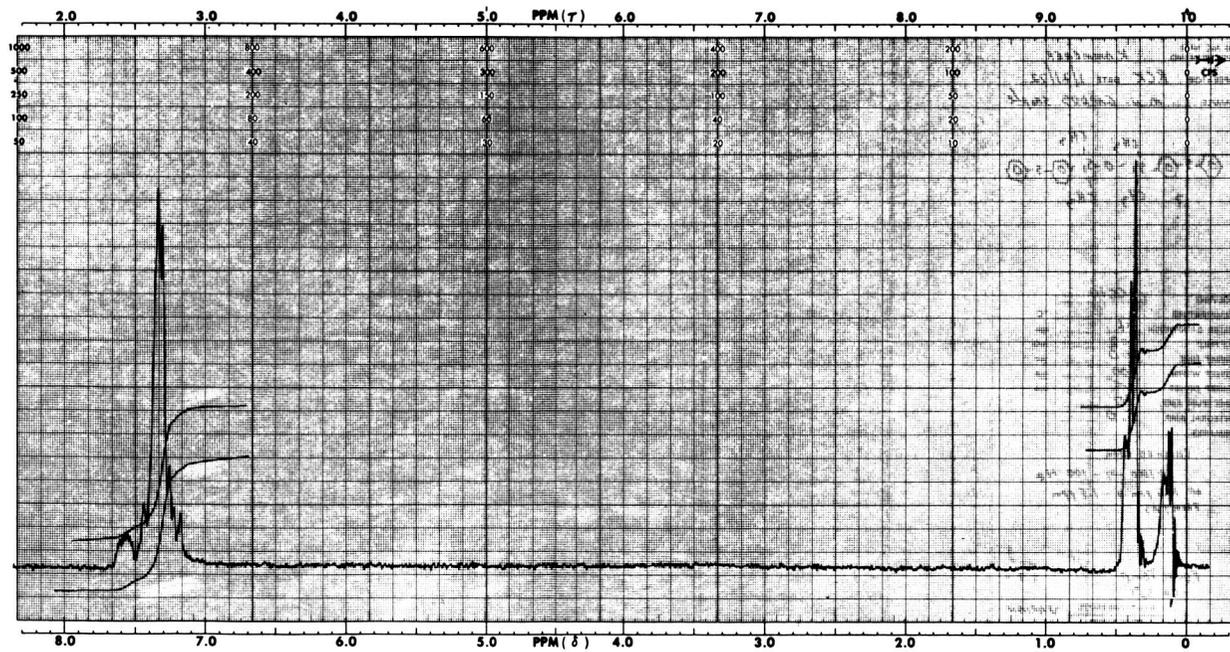
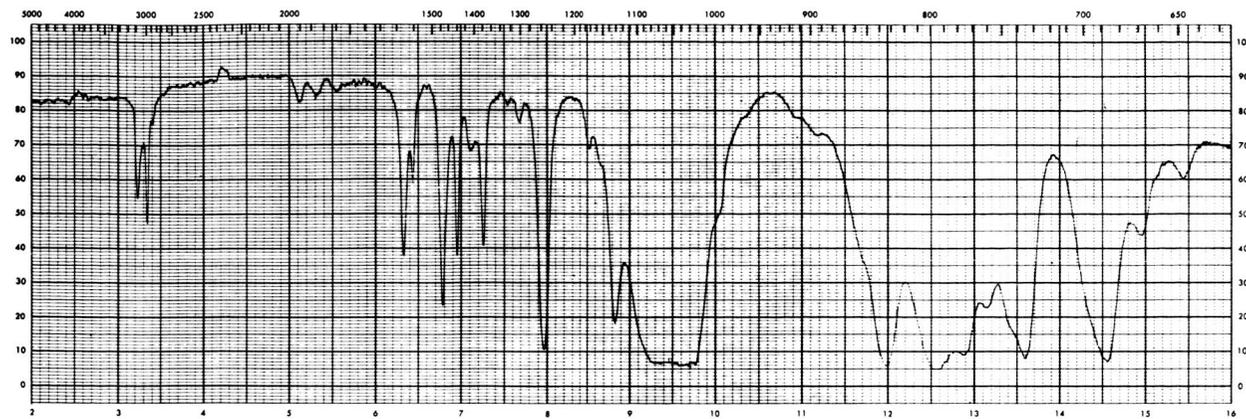


Figure I-8. IR and NMR Spectra of Non-Irradiated HCP-1800, Batch No. 3. IR Between Salt Crystals. NMR Parameters: R.F. Field = 0.02 mG; Sweep Time = 250 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 10

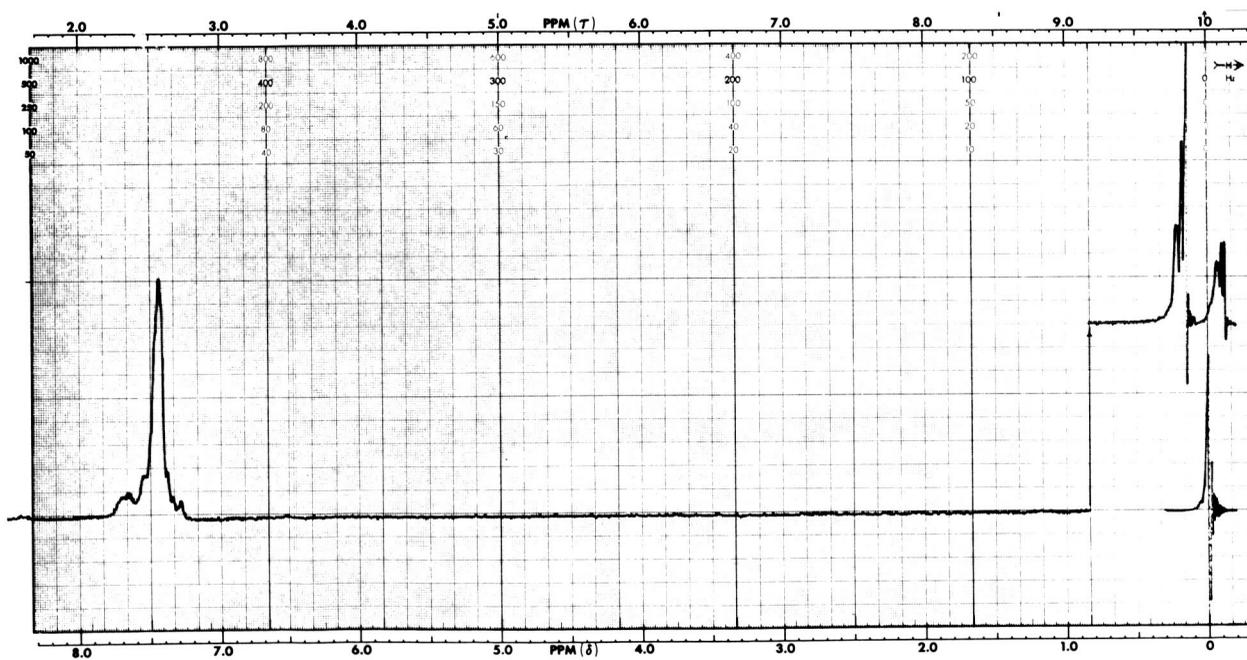
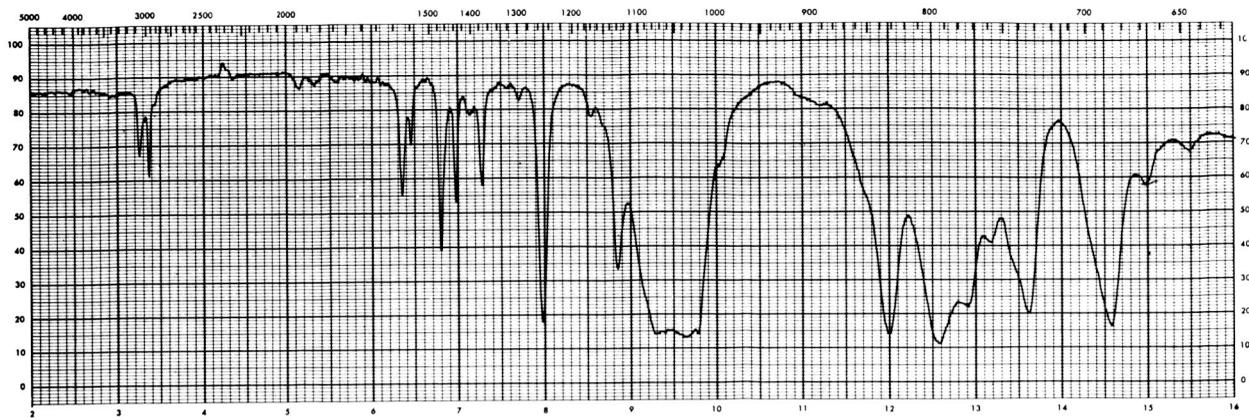


Figure I-9. IR and NMR Spectra of HCP-1800, Batch No. 3, Irradiated in Vacuum. IR Between Salt Crystals. NMR Parameters: R. F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 10

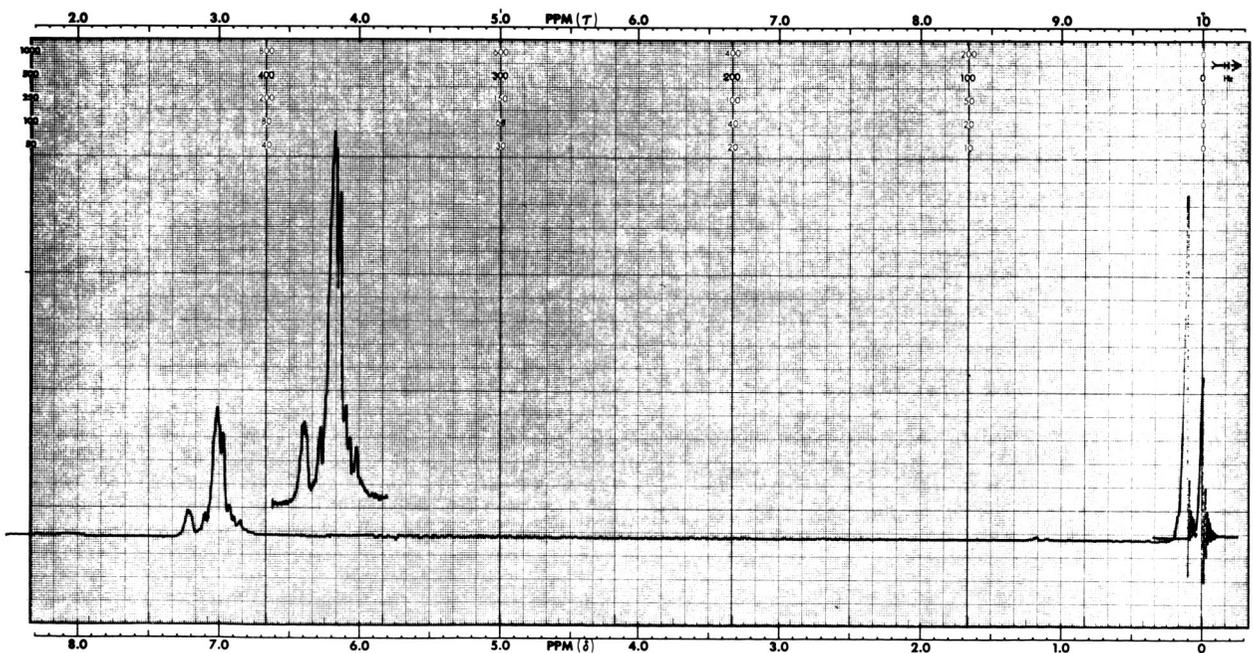
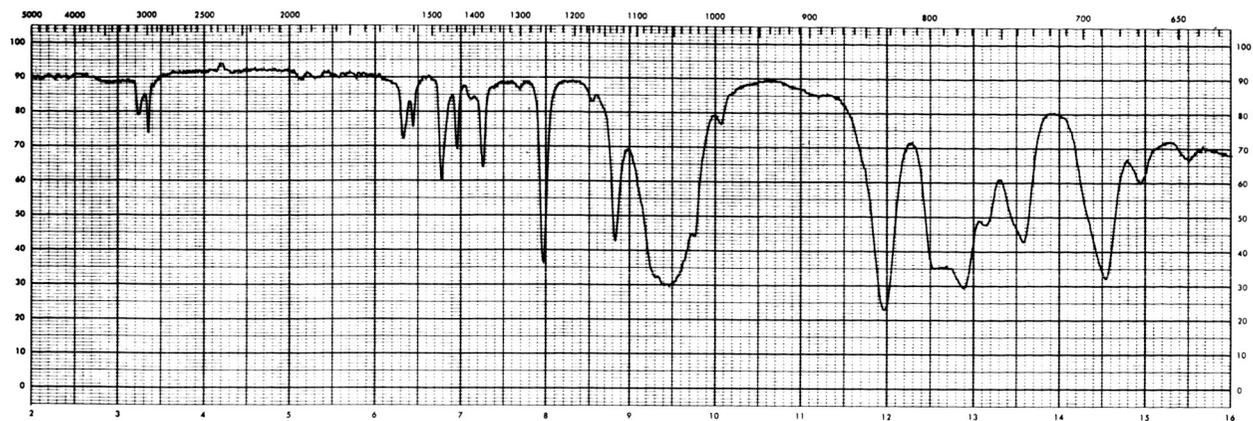


Figure I-10. IR and NMR Spectra of Non-Irradiated HCP-1800, Batch No. 6. IR Between Salt Crystals. NMR Parameters: R. F. Field = 0.10 mG; Sweep Time = 250 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 5

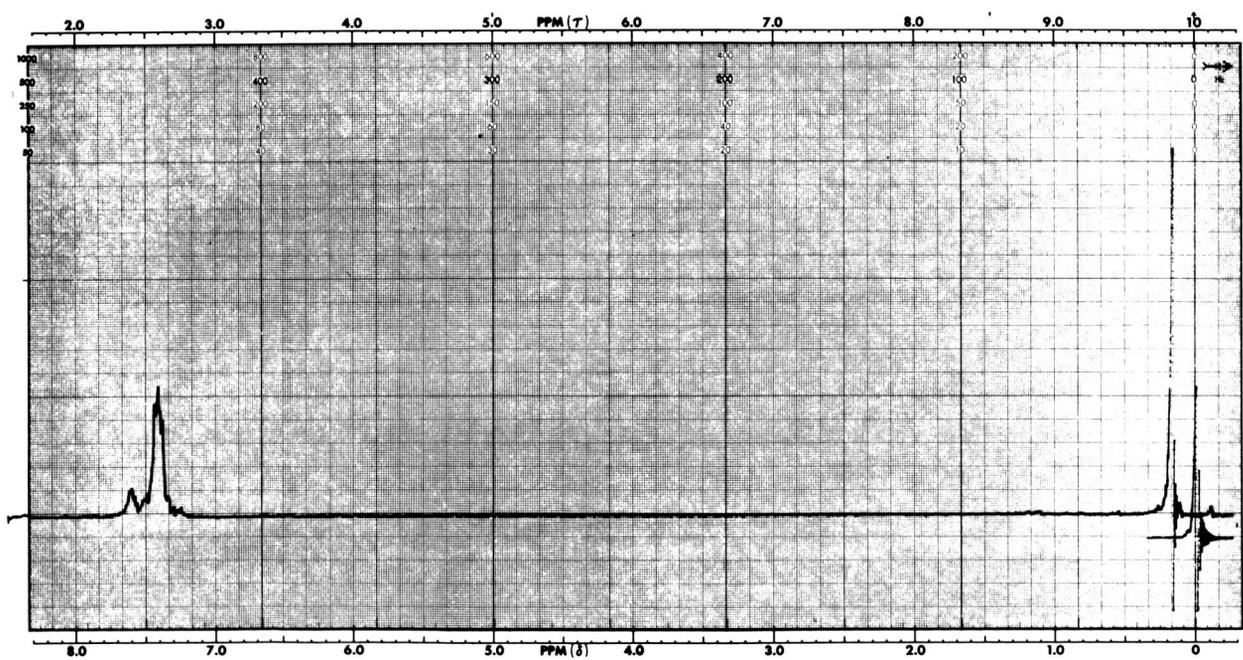
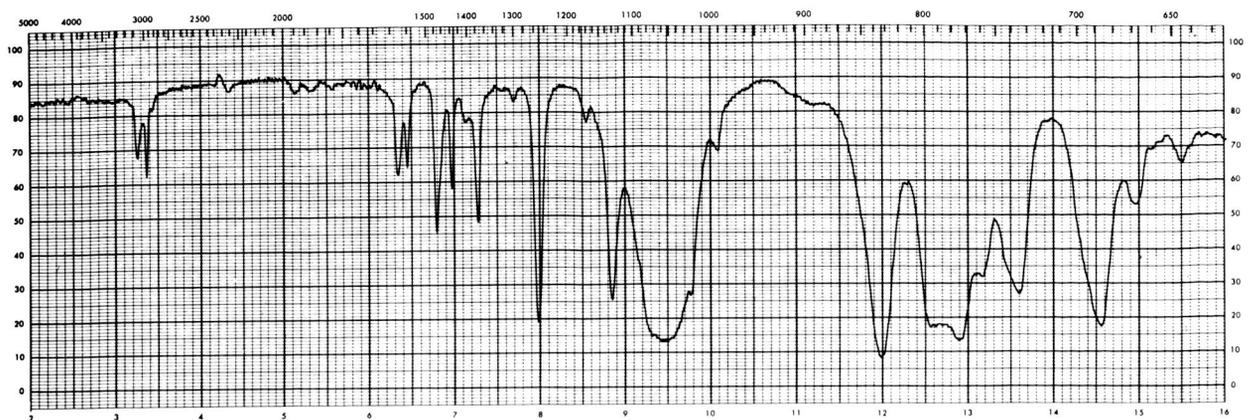


Figure I-11. IR and NMR Spectra of Vacuum Irradiated HCP-1800, Batch No. 6, Irradiated in Vacuum. IR Between Salt Crystals.  
 NMR Parameters: R.F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 6.3

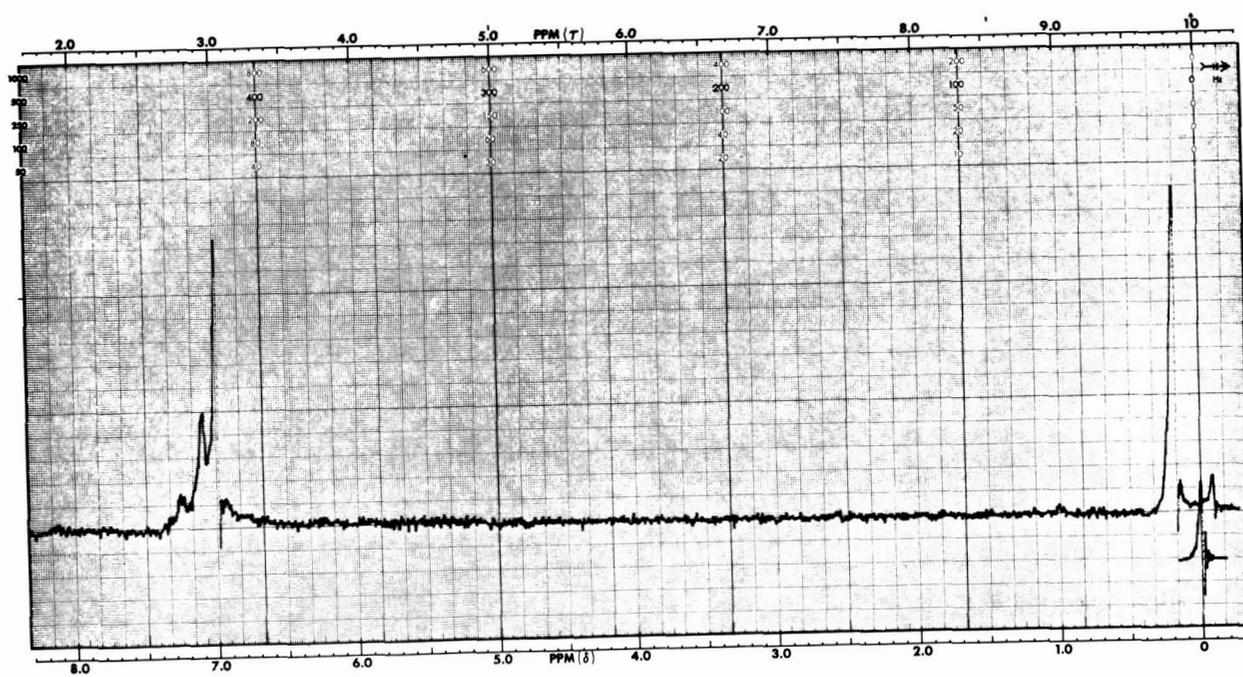
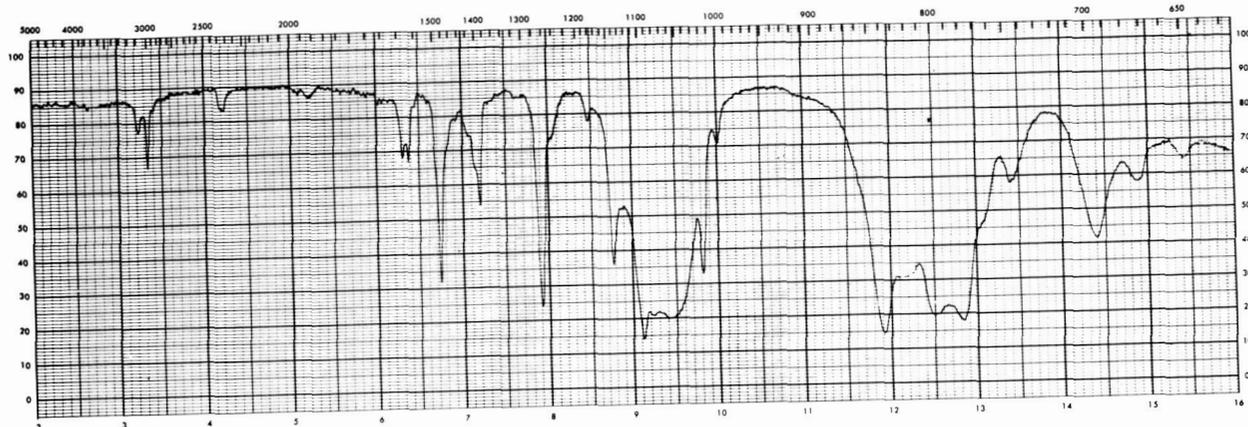


Figure I-12. IR and NMR Spectra of Non-Irradiated HCP-1900, Batch No. 1. IR Between Salt Crystals. NMR Parameters: R. F. Field = 0.06 mG; Sweep Time = 250 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 16

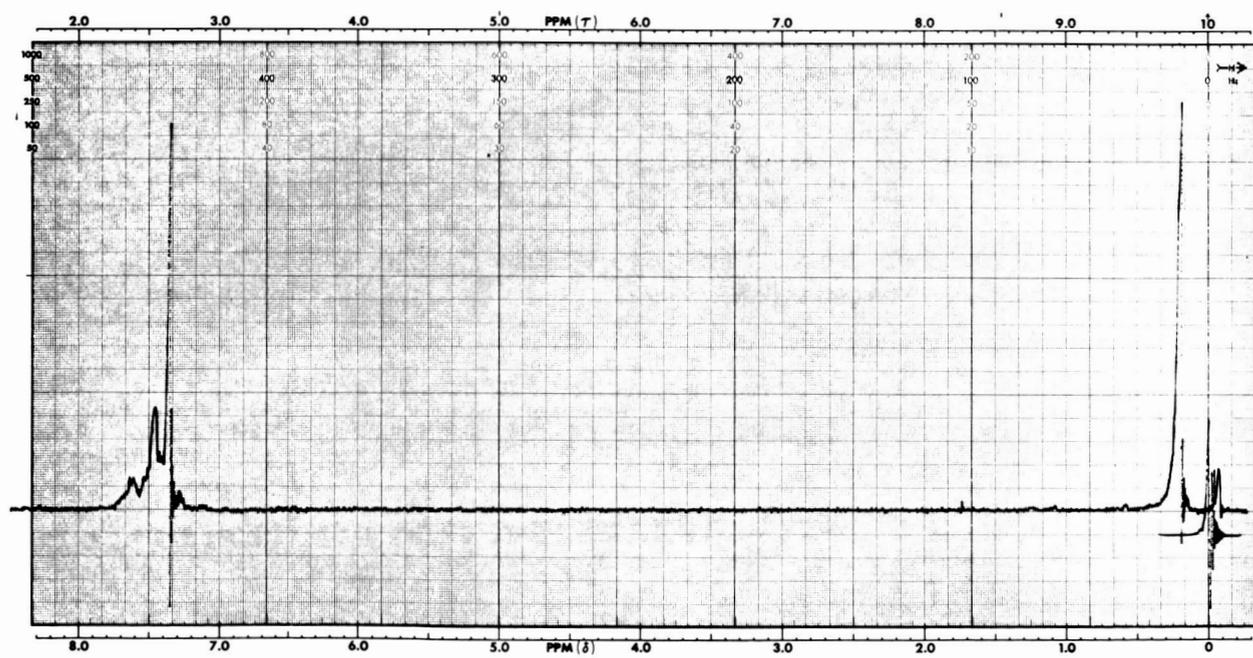
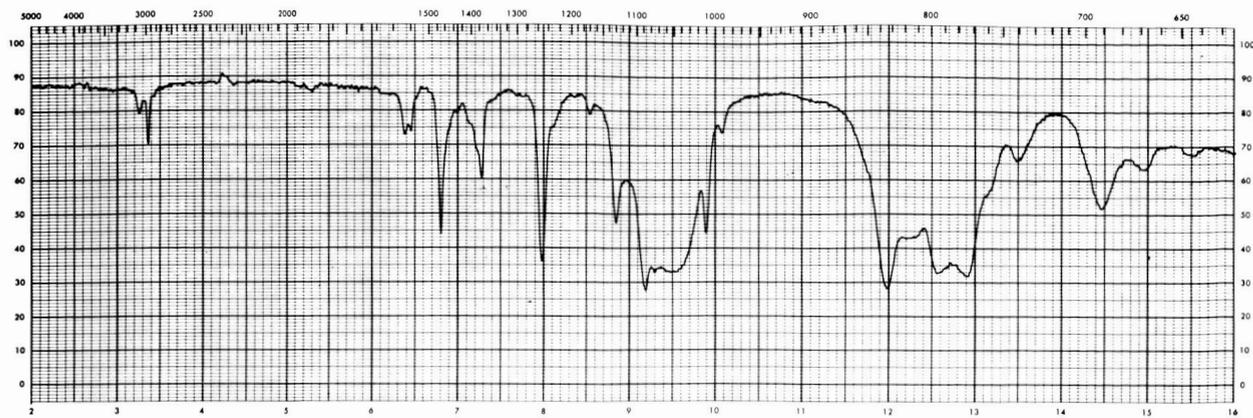


Figure I-13. IR and NMR Spectra of HCP-1900, Batch No. 1, Irradiated in Vacuum. IR Between Salt Crystals. NMR Parameters: R.F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep Width = 50 Hz; Spectrum Amplitude = 12.5

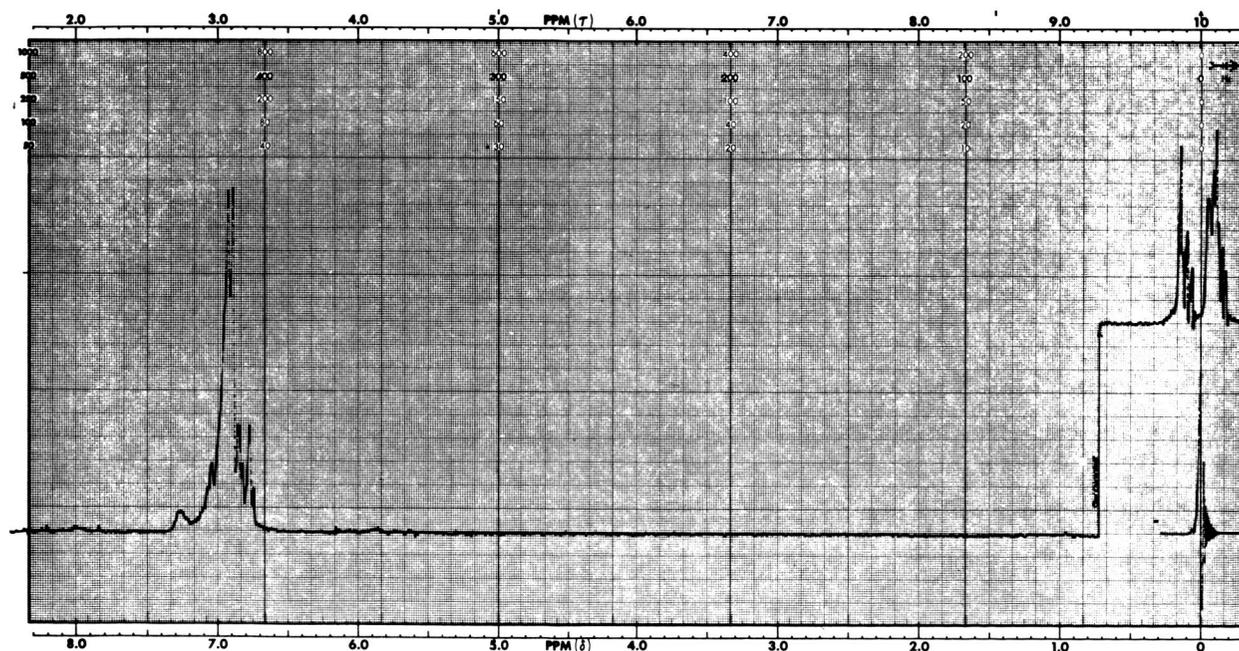
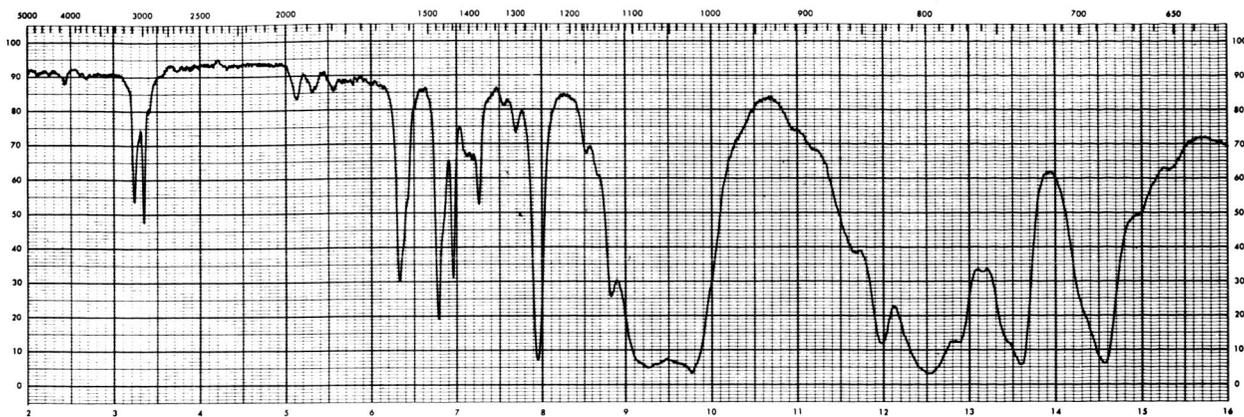


Figure I-14. IR and NMR Spectra of Non-Irradiated HCP-2800, Batch No. 1. IR Between Salt Crystals. NMR Parameters: R. F. Field = 0.10 mG; Sweep Time = 250 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 8.0

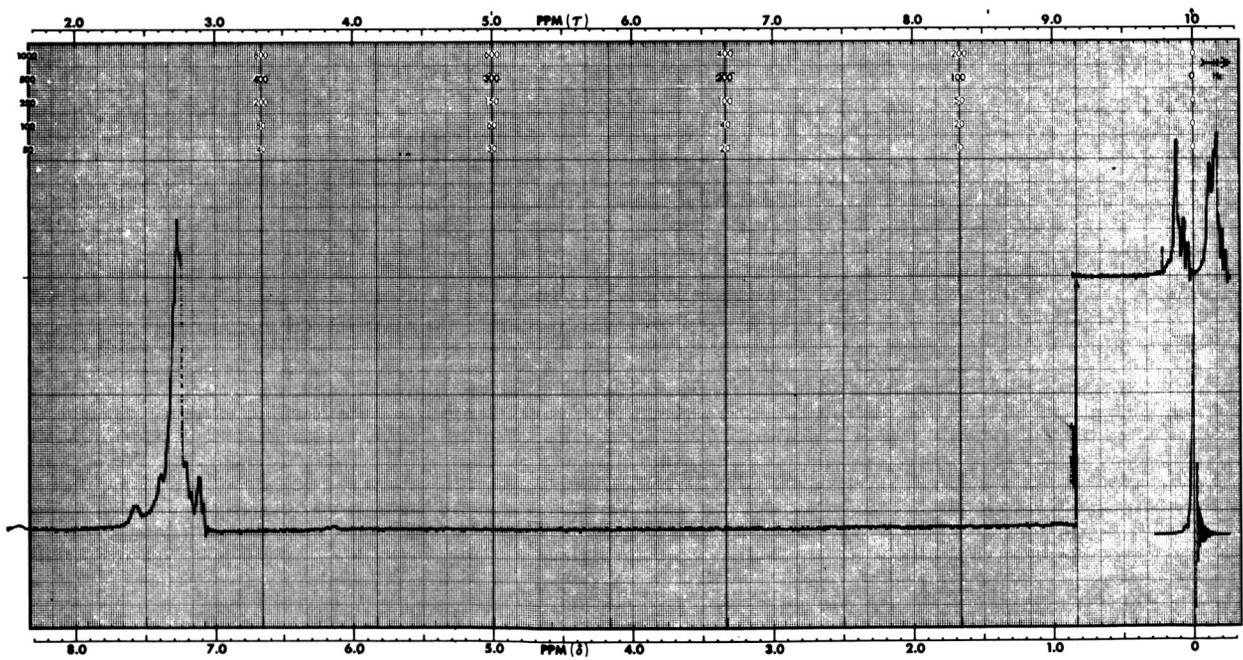
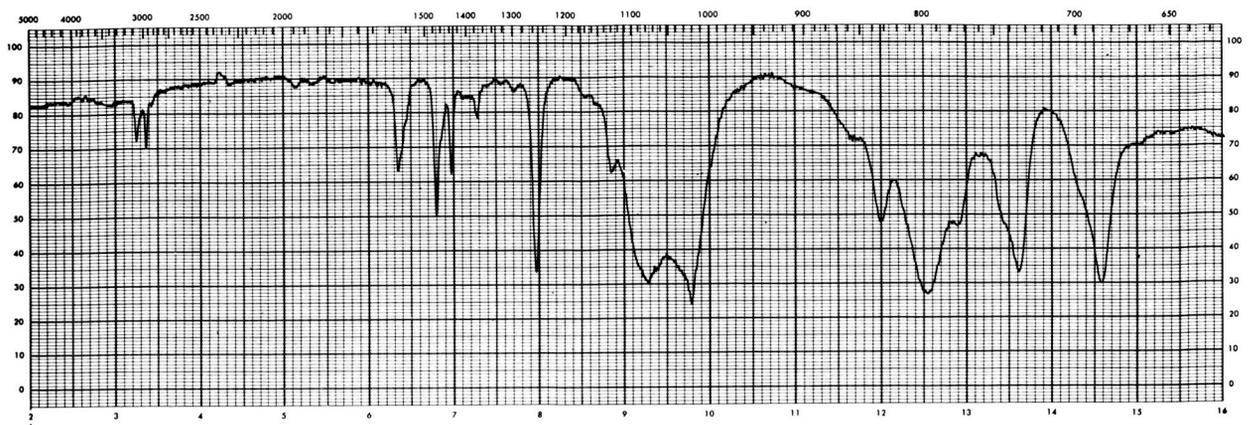


Figure I-15. IR and NMR Spectra of HCP-2800, Batch No. 1,  
 Irradiated in Vacuum. IR Between Salt Crystals. NMR  
 Parameters: R.F. Field = 0,10 mG; Sweep Time  
 = 500 Sec.; Sweep Width = 500 Hz; Spectrum  
 Amplitude = 10

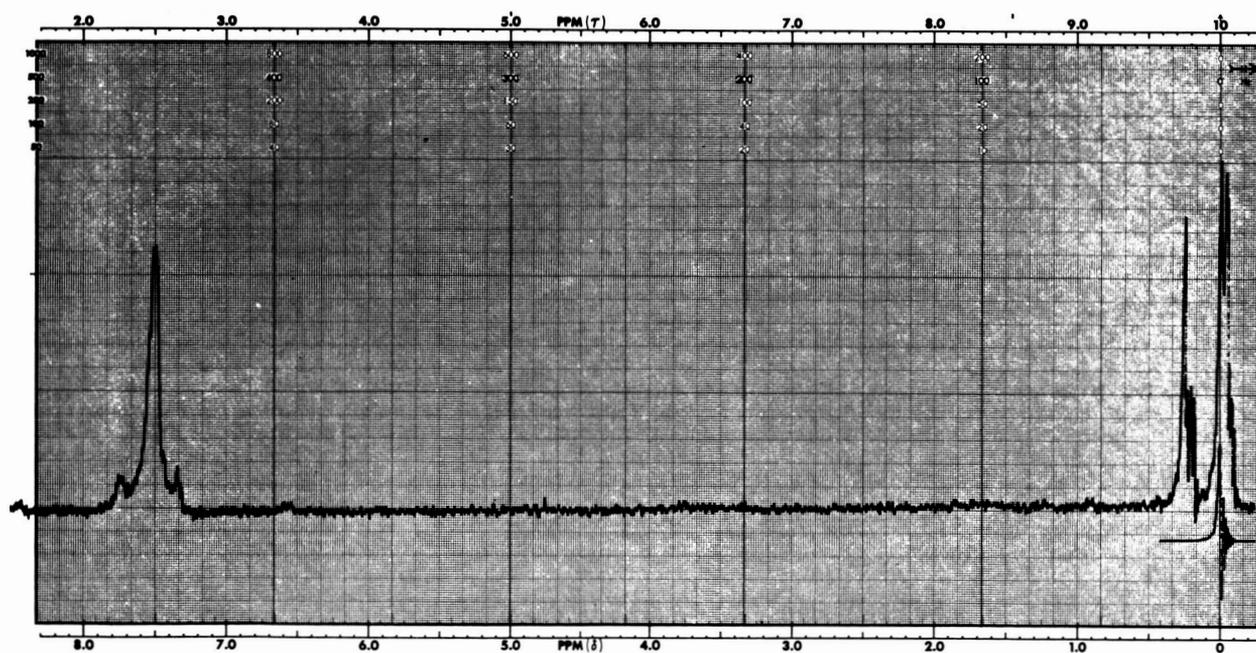
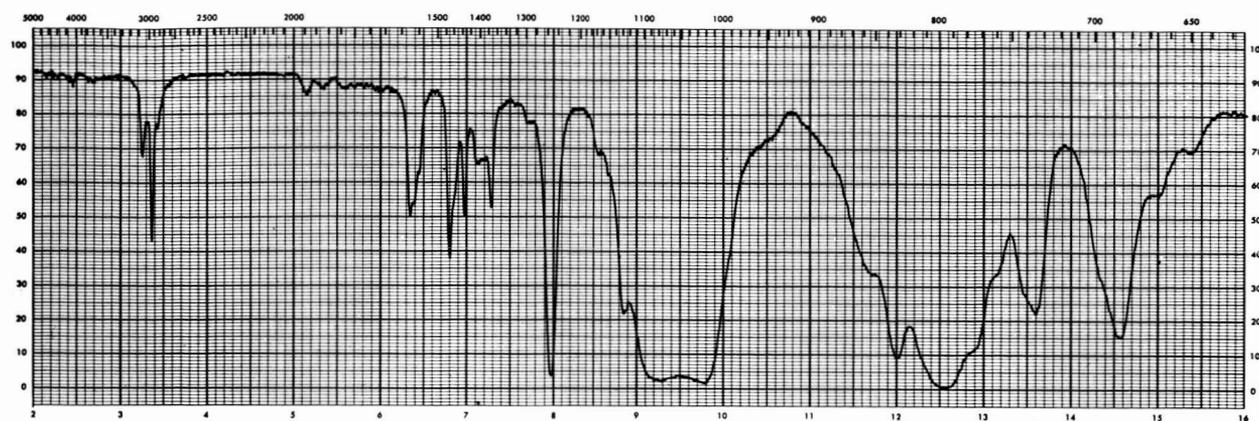


Figure I-16. IR and NMR Spectra of Non-Irradiated HCP-2800 Final Blend. IR Between Salt Crystals. NMR Parameters: R. F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 32

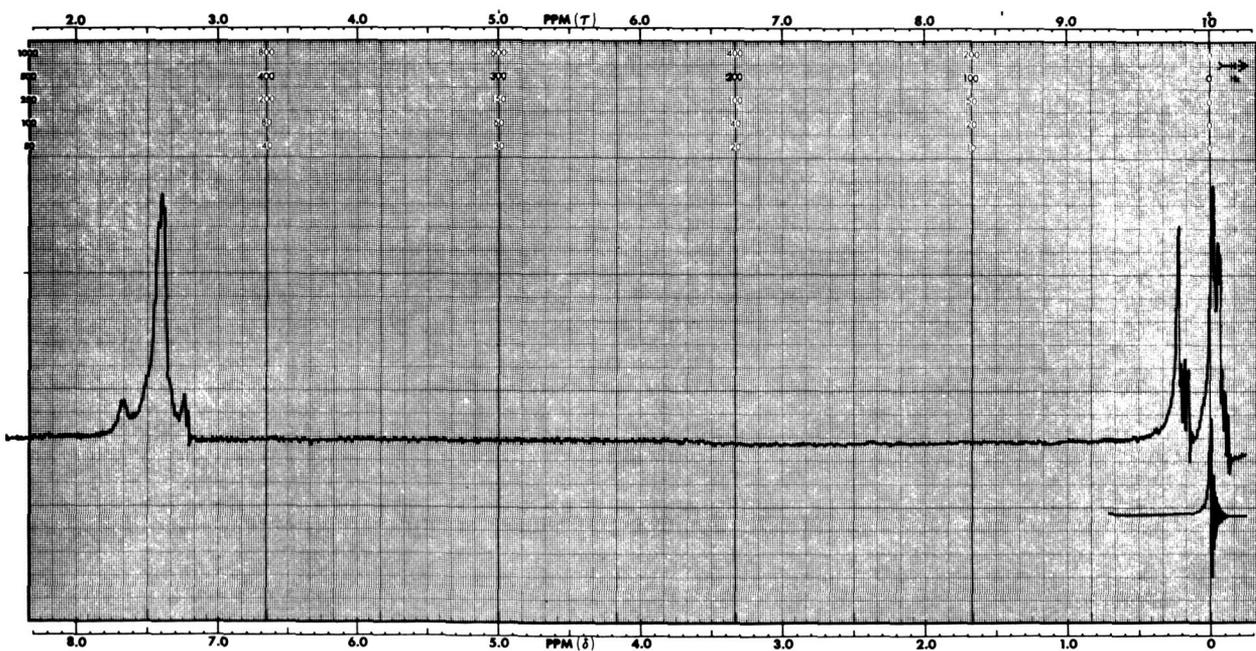


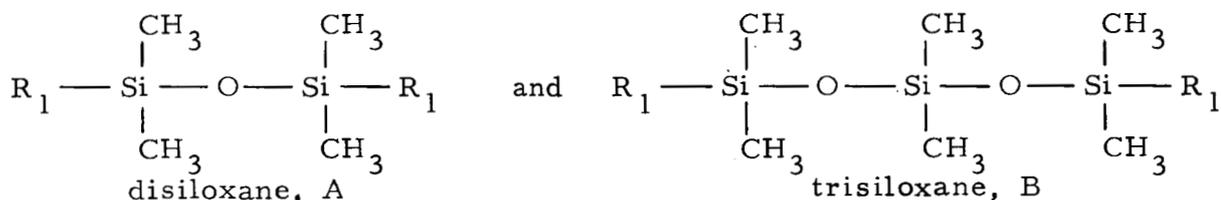
Figure I-17. IR and NMR Spectra of HCP-2800 Final Blend, Irradiated in Vacuum. IR Between Salt Crystals. NMR Parameters: R. F. Field = 0.10 mG; Sweep Time = 500 Sec.; Sweep Width = 500 Hz; Spectrum Amplitude = 16

APPENDIX II

HUGHES SYNTHESIZED LUBRICANTS

Table II-1. Tetramethyldisiloxanes and hexamethyltrisiloxane, disubstituted

General Structures:



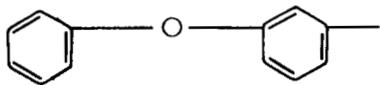
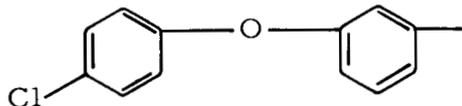
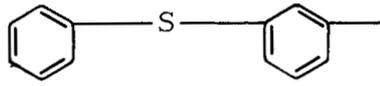
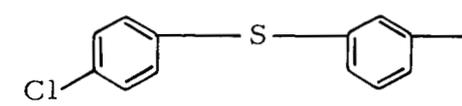
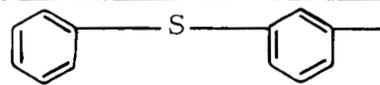
HCP Number	General Structure	R <sub>1</sub>
1500	A	 3-phenoxyphenyl
1600	A	 3-(4-chlorophenoxy)phenyl
C1500/1600	A	(1)
1800	A	 3-(phenylthio)phenyl
1900	A	 3-(4-chlorophenylthio)phenyl
2800	B	 3-(phenylthio)phenyl
(1) Mixed. Some molecules are HCP-1500, some HCP-1600, others are a combination; proportions depend on mole ratios of starting materials.		

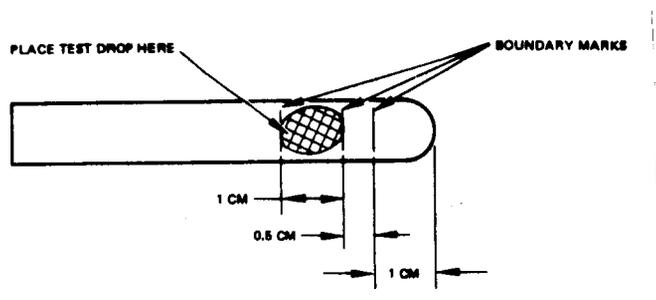
Table II-2. Disiloxanylphenyl ether and the homolog polymer

HCP Number	Chemical Name	General Structure	R <sub>1</sub>	R <sub>2</sub>
4270	Bis[4-(3-phenyl - 1, 1, 3, 3-tetra-methyl-disiloxanyl) phenyl] ether	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{R}_1 - \text{Si} \\   \\ \text{CH}_3 \end{array} - \text{O} - \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} \\   \\ \text{CH}_3 \end{array} - \text{R}_2 \right]_2 \text{O}$	 phenyl	 1, 4-phenylene
4270P	Poly[oxy(dimethyl-silylene)-1, 4-phenyleneoxy-1, 4-phenylene (dimethylsilylene)]	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{O} - \text{Si} \\   \\ \text{CH}_3 \end{array} - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} \\   \\ \text{CH}_3 \end{array} \right]$	--	--

### APPENDIX III

#### NEW MICRO-SAMPLE POUR POINT TESTING PROCEDURE

1. Prepare two 12 x 75-mm test tubes by detergent and chromic acid cleaning, followed by drying in an oven. Scratch boundary marks on the outside of the tubes with a diamond marker as shown in the following sketch:



Rub scratch marks with a pencil tip to increase their visibility.

2. Place ~0.15 g of test fluid (~3 to 5 drops from a 22-gauge hypodermic needle) in the middle of the space bounded by the marks 1 cm apart (see above sketch), while the tube is in the horizontal position. Do not permit spreading of the total amount beyond the boundary lines.

NOTE: Spreading may be effectively controlled by cooling the side of the tube on a slab of dry ice. The phenomenon of increased fluid surface tension with decreasing temperature is utilized to achieve this control. Lifting the tube off and placing it back on the dry ice permits the operator to spread the total test drop to the exact boundaries. Deposition of equivalent amounts of fluids of different densities and surface tension may require the pre-determination of the pendent drop weight obtained from a 22-gauge hypodermic needle.

3. Freeze the bounded test drop to the side of the tightly stoppered tube with dry ice or liquid nitrogen.
4. Rapidly fasten two such charged, stoppered tubes to a low-temperature thermometer, using a rubber band in such a manner that the thermometer bulb is in the immediate vicinity of the two frozen test drops.

5. Immediately immerse the thermometer - tube assembly in a vertical position into a dry-ice/acetone bath cooled 10 - 30°F below the expected melting point. Do not immerse rubber stoppers below the bath fluid surface. During steps 4 and 5 the test drop must remain frozen to the side of the tube. If any visible drop movement does occur during the transfer, discard the sample and prepare a fresh one.
6. Allow bath to warm up by thermal conductance from the surroundings. To achieve a uniform warming rate, utilize a 600-ml charge in an 800-ml capacity transparent Dewar flask.
7. Record the temperature when the average distance traveled by the drop fronts equals 0.5 cm (e. g. , one front just beyond the 0.5 cm mark, the other drop front just approaching its own 0.5 cm boundary mark). This temperature is reported as the pour point of the fluid.

APPENDIX IV  
VAPOR PRESSURE

SPECIMEN PREPARATION AND ASSEMBLY

1. The sample cup, the baffle plate and the spring-damper foil-extender rod assembly are thoroughly rinsed with appropriate solvents, then dried with a gentle stream of dry, filtered air. The cup and the extender rod are coated with the fluid barrier compound. Approximately 0.5 g of the test substance is then transferred to the cup.
2. The cup is placed in a flat-bottomed glass vacuum chamber equipped with a two-way valve. If the compound is a solid at room temperature and expected to be a liquid during the evaporation rate measurements, the product is melted by careful heating of the chamber walls.
3. The pressure is then slowly reduced to  $1 \times 10^{-2}$  torr to remove any air and moisture contained in the liquid. The pressure is restored to atmospheric by admitting pure, dry helium into the chamber. Repeated pump-down and helium saturation cycles prevent any further bubbling of the oil on evacuation. Helium apparently does not bubble out of fluids under reduced pressure.
4. If the cup containing the degassed and helium-saturated test substance is immediately assembled into the balance and rough-pumping is started within a reasonably short period of time (1/2 hour), no frothing or bubbling occurs during the balance evacuation sequence.
5. The permanently sealed spring-foil-extender rod assembly is suspended on a specially prepared stand. The perforated watch-glass baffle plate is sleeved onto the extender rod, the cup suspended from the rod hook, and the baffle plate is lowered onto the cup, just like a movable cap. The operator lifts, then lowers the entire assembly into the balance body. As the assembly is lowered, the baffle plate is caught on the three indentations of the inside balance wall ( $120^\circ$  apart), while the cup, suspended on the extender rod, continues its downward travel to the middle of the furnace zone.
6. After the spring hook is properly positioned on the top vacuum flange rim, the viewing port is attached and sealed, the cooling water tubes are connected, the water flow is started and the evacuation sequence is initiated.

## APPENDIX V

### LOW-VOLUME WEAR TEST PROCEDURE

#### TYPE I - O.K. LOAD

1. Clean ring and high pressure block by rubbing with a clean, acetone-saturated tissue, followed by thorough rinsing with acetone and laboratory-grade trichlorotrifluoroethane in that order. Apply fluorochemical oil-barrier coating to the face and the back of the test ring and to the ring retainer/washer surfaces. \*

CAUTION: Do not apply barrier coating to any portion of the ring wear path.

2. Install specimens in the friction assembly. Prelubricate the ring before installation by applying a thin film of the test lubricant with a degreased Q-tip.
3. Insert a clean\*\*, dry felt lubricant transfer tip (0.25 inch dia., 0.5 inch long) into the mini-reservoir with about two-thirds of its length protruding from the reservoir tube. Tighten reservoir on its support stand, making sure that the felt does not touch the test ring. Transfer 0.3 ml of the test lubricant into the reservoir cavity with a syringe. Allow the lubricant to permeate the felt tip completely, then replenish the lubricant by transferring an additional 0.2 ml of the lubricant into the cavity. Install the loading spring, and close the reservoir by tightening the screw cap over.
4. Loosen, then retighten the reservoir on its stand in such a manner that the felt tip is pressed against the ring by a light, constant load. The constant magnitude of the load is determined by (a) a standard felt tip length, (b) the standard loading spring size and (c) positioning of the reservoir by means of a reference mark.
5. Rotate test ring slowly (3-5 rpm) for ten cycles without load to further redistribute the lubricant. Apply one pound on the bale rod, and start test by rotating the ring at 40 rpm. Monitor the friction throughout the test.

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\* This application enhances retention of the wicked-out lubricant on the wear track.

\*\*Ultrasonically clean the felt using first acetone, then trichlorotrifluoroethane.

6. Apply an additional pound on the bale rod after 40 cycles (1 minute). Continue application of additional one-pound weights at 40 cycle (1 minute) intervals, until at a given load, a continuous, high-pitched scream indicates breakdown in lubrication. At this load terminate the test.

NOTE: A light-to-moderate rhythmic high-pitched noise is acceptable, as long as the noise diminishes to a light scraping sound before the application of the next additional one-pound bale rod load.

7. Note and record the failure load. The O.K. Load is defined as one pound less than the failure load. The maximum O.K. Load is 21 pounds, as this is the limit of the test machine.

#### TYPE II--5000-CYCLE WEAR TEST

1. If the lubricant supported 8 pounds or more in the Type I (O.K. Load) Test, the 5000-cycle Wear Test is done at 8 pounds and 40 rpm, with the entire load applied at once (gently) on the bale rod. If the lubricant had an O.K. Load of 7 pounds or less, the load is applied step-wise, as in the O.K. Load Test.
  - a. If the wear test at 8 pounds full load fails before 5000 cycles are completed, the next trial should be step-wise loading to a maximum of 8 pounds, continuing to a total of 5000 cycles after reaching a load of 8 pounds.
2. Perform steps 1 through 4 as in the Type I Procedure.
3. Rotate ring slowly for ten cycles without load to further redistribute the lubricant. Start test by rotating the ring at 40 rpm.
4. At the end of the loading sequence, continue the test at 40 rpm to 5000 cycles, or to failure. The selection of the failure friction force of each test will have to be made by the operator who must keep the automatic cut-off capability of the LFW-1 machine in mind. Automatic cut-off of the test machine will occur at full scale pen deflection of the recorder under any given attenuation.
5. The operator must, therefore, observe the steady-state friction of each test and select a convenient pen deflection at an optimum attenuation, where (a) the friction readout is accomplished with maximum sensitivity, and (b) the friction force increase on incipient failure will allow some pen travel to a full-scale deflection at that attenuation. Such full-scale deflection will, of course, activate the cut-off mechanism and will automatically

terminate the test. Automatic termination before completion of 5000 cycles, or the development of a high-pitched, continuous scream after the steady-state will constitute failure.

6. After 5000 cycles, disassemble the test specimens and photomicrographically examine the wear scar on the clock, and the appearance of the felt tip.
7. If failure occurs in less than 5000 cycles, there are two options: either (a) there is enough experimental fluid available for further testing, in which case the full-scale run must be repeated at a lighter load (1 lb reduction); if that is successful, repeat that again to provide two, valid, full-scale rating runs, or (b) perform only one additional full-scale run at a load reduced by 1 lb, and rate the lubricant based solely on this single successful test.

## APPENDIX VI

### PREPARATION OF FLUIDS FOR IRRADIATION

1. The sample is introduced into the bulb of the vacuum container through the constriction, without wetting the walls, by using a syringe with a long hypodermic needle.
2. The filled vacuum vial, connected to a chamber for vacuum degassing and helium gas saturation (kept vertical at all times), is placed into a 200°F water bath in a 15 kc ultrasonic cleaner and a vacuum of  $\sim 10^2$  torr is pulled on the vial. De-gassing and helium gas saturation are continued until no further bubbling is observed. Excessive wetting of the bulb wall above the liquid is prevented by occasional venting with the He gas.
3. The vial containing the de-gassed and helium-saturated product is placed on a vacuum train, then pumped down to  $10^{-6}$  torr, using a mechanical pre-pump and a mercury diffusion pump. At the required pressure the constriction is sealed off with a hydrogen-oxygen torch. Helium saturation prevents foaming of the sample during the repeated evacuation process.
4. The pre-weighed "atmospheric" container (weighing bottle) is filled with the test fluid, then the vial is re-weighed.
5. Before being positioned in the irradiation chamber, all primary fluid containers are placed into secondary safety containers which are simply lipless 50-ml glass beakers. This is permitted because the shielding effect of glass is negligible. The "atmospheric" and the safety containers are reusable despite their turning dark brown during irradiation.
6. The containers are placed in the irradiation chamber and the test begun.
  - a. The  $\gamma$ -energy is constantly calibrated by the use of the decay curve of the isotope, and the exposure time is automatically controlled to an accuracy of  $\pm 6$  seconds;
  - b. the temperature of the irradiation chamber is controlled to less than 100°F by blowing dry, filtered air through the chamber during irradiation. The temperature is monitored by a copper-constantan thermocouple.
7. The irradiated samples are removed from the chamber. The "vacuum" vial is opened by filing a mark close to the tip and touching the mark with the white-glowing, melted end of a glass rod.

The contents of both discolored irradiation containers are transferred into clean, pre-weighed glass weighing bottles and the weights of the irradiated samples are determined.