

cobalt trifluoride. Repassing caused the S.I.C. curve to flatten out and drop lower; consequently most of it lies in the correct range for perfluorodimethylcyclohexane, except at the beginning where two peaks are shown corresponding to about 0.5% of material

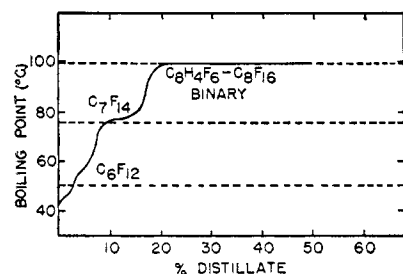


Figure 8. Fractional Redistillation of Perfluorodimethylcyclohexane Foreshots

boiling at 96.5° and about 1% of material boiling at 99.6° and at the end where it rises with the boiling point curve. Material taken between 20 and 80% on this distillation was very pure. The high boiling material could be repassed through the reactor to form perfluorodimethylcyclohexane. On redistillation of the foreshots, the distillation curve of Figure 8 was obtained. The small inflection at about 55° C. is due to perfluorocyclohexane. The flat at 75° to 80° C. is perfluoromethylcyclohexane. Both of these products were discarded. The main flat is an azeotropic mixture of diperfluoromethylbenzene and perfluorodimethylcyclohexane boiling between 99.4° and 99.6° and containing 12-13% of the former. The azeotropic mixture could be repassed through the reactor in order to obtain more material of suitable quality.

#### FLUORINATION OF MONOCHLORODIPERFLUOROMETHYLBENZENE

Monochlorodiperfluoromethylbenzene was fluorinated in the same manner as was diperfluoromethylbenzene and gave similar results, with about three fourths of the chlorine being replaced with fluorine. The corresponding dichloro compound gave a mixture containing excessive amounts of incompletely reacted material.

Material taken between 20 and 80% on this distillation was very pure.

The high boiling material could be repassed through the reactor to

#### LARGE SCALE PRODUCTION

The laboratory reactors were scaled up to a large size. Laboratory yields were not obtained on the larger scale because of greater mechanical losses, more decomposition, and greater by-product formation. The chief problem was dissipation of the heat of reaction for both the organic and the reactivation cycles. Purification of the fluorocarbons by fractional distillation using the S.I.C. method previously described for control was found satisfactory on a large scale. Much has been said about S.I.C. analysis because it was the most suitable control method readily available. However, infrared methods, which were much more accurate for the determination of small quantities of the cyclic fluorocarbons and hydrocarbons, were relied on for final analysis of the purified products.

#### ACKNOWLEDGMENT

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PRESENTED before the Symposium on Fluorine Chemistry as paper 66 and 69, Division of Industrial and Engineering Chemistry, 110th Meeting of AMERICAN CHEMICAL SOCIETY, Chicago, Ill. The work described in this paper is covered also in a comprehensive report of work with fluorine and fluorinated compounds undertaken in connection with the Manhattan Project. This report is soon to be published as Volume I of Division VII of the Manhattan Project Technical Series.

## LOW POLYMERS OF CHLOROTRIFLUOROETHYLENE

### Preparation and utilization in chlorofluorocarbon lubricants

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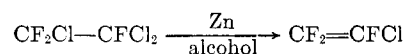
CORNELL UNIVERSITY AND THE S.A.M. LABORATORIES OF THE  
MANHATTAN PROJECT, ITHACA, N. Y., AND NEW YORK, N. Y.

THE purpose of this work was to develop a practical synthetic method for the production of fluorocarbon-type oils and greases, materials which were required because of their unusual properties of chemical stability (?). The processes developed were based on the preparation of low-molecular-weight polymers of chlorotrifluoroethylene and furnished a general method for the production of fluorocarbon-type materials to replace the procedures based on the direct substitution of hydrogen in hydrocarbons by fluorine (6). The polymerization type of process had some inherent advantages as compared with the substitution method. The basic starting material, 1,1,2-trichlorotrifluoroethane had already been developed as a commercial product (Freon 113), and its production involved the cheapest available method for the production of C—F bonds—that is, by

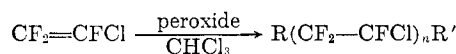
the replacement of chlorine by fluorine using hydrogen fluoride. Relatively little elementary fluorine or highly specialized equipment was required, and a range of products could be produced from the same starting material.

The polymer oil process consisted of the following basic steps:

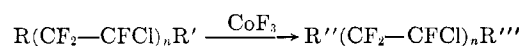
1. Preparation of monomer:



2. Polymerization of chlorotrifluoroethylene:



3. Fluorination of crude polymer:



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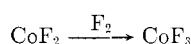
Table I. PREPARATION OF LOW POLYMER CHLOROTRIFLUOROETHYLENE AND FLUORINATION BY COBALT TRIFLUORIDE TREATMENT

Run No.	Polymerization Conditions (Deviation from Standard)	Polymer Yield, % of CF <sub>2</sub> =CFCI Charged	Polymer of B.P. 120-220° C. <sup>a</sup> at 0.3 mm., Wt. % <sup>b</sup>	Polymer of B.P. >220° C. at 0.3 mm., Wt. % <sup>b</sup>	CoF <sub>3</sub> Required, G. CoF <sub>3</sub> /100 G. Oil	Polymer Oil of B.P. 100- 200° C. at 0.3 mm., Wt. % <sup>a,b</sup>
1	Standard conditions	86	26	51	97	27
2	CCl <sub>2</sub> =CCl <sub>2</sub> as solvent	66	16	74	..	..
3	CCl <sub>4</sub> as solvent	71	<10	>80	..	..
4	CHCl=CCl <sub>2</sub> added equimolar to CF <sub>2</sub> =CFCI	60	24	7	..	..
5	CF <sub>2</sub> =CFCI/CHCl <sub>3</sub> ratio, 1/18	76	33	39	99	26
6	(C <sub>2</sub> H <sub>5</sub> COO) <sub>2</sub> /CF <sub>2</sub> =CFCI ratio, 1/10	94	37	49	98	27
7	C <sub>2</sub> H <sub>5</sub> OH added, 1 g./100 g. CHCl <sub>3</sub>	27	..	..	..	..
8	CHCl <sub>3</sub> used was U.S.P. grade	52	..	..	..	..
9	Extra care to remove oxygen	86	28	61	95	16 <sup>c</sup>
10	Oxygen added, 50 lb./sq. in. gage	26	..	..	..	..
11	(CH <sub>3</sub> COO) <sub>2</sub> promoter; (CH <sub>3</sub> COO) <sub>2</sub> /CF <sub>2</sub> =CFCI ratio, 1/20	82	29	52	63	25
12	(CH <sub>3</sub> COO) <sub>2</sub> /CF <sub>2</sub> =CFCI ratio, 1/10	85	41	40	76	29
13	(CH <sub>3</sub> ClCOO) <sub>2</sub> promoter; (CH <sub>3</sub> ClCOO) <sub>2</sub> /CF <sub>2</sub> =CFCI ratio, 1/20	48	20	54	63	18 <sup>c</sup>
14	(CH <sub>3</sub> ClCOO) <sub>2</sub> /CF <sub>2</sub> =CFCI ratio, 1/10	49	39	48	52	33

<sup>a</sup> Comparable data were available for 120-220° C. b.p. fractions in all cases. The stabilized yields were obtained from a crude oil fraction of b.p. 110-240° C. at 0.3 mm.

<sup>b</sup> Yields calculated on the basis of reacted CF<sub>2</sub>=CClF. <sup>c</sup> Large manipulative loss.

#### 4. Preparation of cobalt trifluoride:



Additional oil fraction was obtained by thermally cracking polymers of higher molecular weight.

#### PREPARATION OF MONOMER

Chlorotrifluoroethylene was prepared by dechlorinating 1,1,2-trichlorotrifluoroethane (Freon 113) with zinc dust in alcohol (3, 10). At the temperature of boiling alcohol this reaction proceeded more readily than was indicated in the literature to give essentially quantitative yields. The olefin product was separated continuously from the reaction mixture by distillation at atmospheric pressure with a short, low temperature column mounted above a reflux condenser, the latter operated so as largely to retain the alcohol vapor. The olefin was handled in glass or metal systems with refrigeration or at room temperature under pressure. Inhibitors such as tributylamine were added during storage.

#### POLYMERIZATION OF CHLOROTRIFLUOROETHYLENE

The preparation of solid polymers of chlorotrifluoroethylene was reported in the patent literature (9), and in the present work friable solid polymers, apparently of the type previously claimed, were found comparatively easy to make. However, considerable difficulty was experienced in developing a satisfactory method for the production of material of the lower molecular weight desired. The type of process finally found most effective depended on the use of solvents which could function as chain transfer agents to control molecular weight while maintaining high monomer conversions. The recommended production procedure consisted of rapid polymerization in chloroform solution using a relatively high promoter concentration. The general solvent chain transfer mechanism was first presented by Flory (4) and has been investigated experimentally with styrene (8).

The following general experimental procedure was adopted for the preparation of polymers of low molecular weight:

Small steel high-pressure gas storage cylinders were used for the experimental polymerizations. In changing they were evacuated, and the liquid reaction mixture was drawn in at temperatures near that of dry ice. Normally four duplicate bombs were filled for each run. Each bomb contained 2700 grams of chloroform, 300 grams of chlorotrifluoroethylene, and 15 grams of benzoyl peroxide. The chloroform was alcohol-free, prepared by distillation from phosphorus pentoxide, and the monomer was carefully purified by distillation. Benzoyl peroxide was added in freshly prepared and assayed chloroform solution. Polymerization was carried out by heating in a liquid bath at 100° C. for 1.75 hours. The temperature inside the bomb did not rise appreciably over 100° C. during the reaction period, and polymerization results were readily duplicated. It was found that the time of reaction could be appreciably shortened. After reaction excess olefin was bled off into a cold trap, and the residual chloroform solution transferred to a distillation assembly. The chloroform was removed and the polymer residue distilled at 0.3 mm. pressure, using a short-necked simple distillation flask and oil-bath heating. In the oil process the fraction boiling at 110-240° C. at 0.3 mm. pressure was collected for treatment with cobalt trifluoride. The fluorination treatment with cobalt trifluoride reduced the boiling point of the oil fraction, and after treatment the final polymer oil product was collected (b.p. 100-200° C. at 0.3 mm.).

Table I summarizes the results of a number of polymerization experiments with different reaction mixtures. Example 1 lists the results of a typical run made under the conditions described; these conditions were considered as standard for comparison with

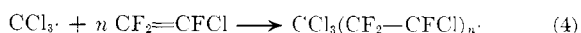
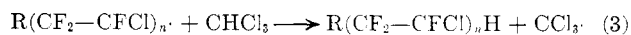
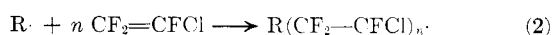
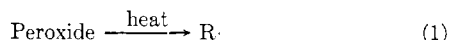
other experiments for which data are given in the table. All reactions were run for 1.75 hours at 100° C.

**EFFECT OF SOLVENT**  
Preliminary polymerization experiments were carried out with the following halogenated solvents of commercially available purity: chloroform, carbon tetrachloride, 1,1,2-trichlorotrifluoroethane, 1,2-dichloroperfluorocyclobutane, and *n*-perfluorohexane. The results indicated that chloroform was the best solvent, both as regards conversion of olefin to polymer and yield of crude oil. Carbon tetrachloride produced a comparatively high conversion, but the yield of low polymer was

**HIGHLY stable chloroperfluorocarbon polymer oils, greases, and waxes were prepared from chlorotrifluoroethylene. This work was part of a program on the development of polymerization procedures for the preparation of fluorocarbon materials. Low polymers of chlorotrifluoroethylene in the desired range of molecular weight were prepared by solution polymerization with peroxide promotion. The solvent functioned as a chain transfer agent to control molecular weight while maintaining high monomer conversions. Final products were produced by treating appropriate fractions with cobalt trifluoride to fluorinate reactive end groupings introduced during the polymerization process. Thermal cracking of chlorotrifluoroethylene polymers was developed to increase the over-all yield of oil and to recover monomer. The polymer oils were shown to be satisfactory lubricants. They exhibited greater change in viscosity with temperature than did petroleum oils but less than the perfluorocarbon oils available for comparison; solubility behavior was normal.**

poor. Low conversions were observed with the remaining chlorinated solvents, and, significantly, little reaction took place in perfluoroheptane. This was interpreted to mean that the perfluoroheptane was stable to the radicals formed in the system and failed entirely as a chain transfer agent. Investigations on a larger scale were carried out with purified carbon tetrachloride (run 3) and tetrachloroethylene (run 2). However, with both solvents lower monomer conversions and lower crude oil yields were obtained than with chloroform.

Analysis of the crude oil for chlorine indicated clearly that the chloroform entered into the polymerization. The chlorine content of the crude oil was 39% as compared with a chlorine content for the monomer of 30.4%. The increased chlorine content may be explained by the chain transfer mechanism, in which a growing polymer chain interacts with a solvent molecule; the result is termination of the polymer chain and production of a new radical from the solvent. This process may be represented as follows:



In Equation 3  $\text{CHCl}_2\cdot$  and  $\text{R}(\text{CF}_2-\text{CFCl})_n\text{Cl}$  were presumably also formed.

Chain termination by radical combination furnished another obvious process for the formation of products with increased chlorine content. It is also probable that polymer chains were initiated by free radicals resulting from the reaction of peroxide and chloroform. Boeseken and Gelissen (2) found that benzoyl peroxide and chloroform reacted to form benzene and  $\text{CCl}_3(\text{C}_6\text{H}_4)\text{COOH}$  as main products.

With tetrachloroethylene as the solvent the chlorine content of the crude oil was 38.4%, an indication that this solvent also entered into the polymer molecule. An interesting result was obtained when equal molar quantities of trichloroethylene and chlorotrifluoroethylene were used (run 4). Sixty per cent of the  $\text{CF}_2=\text{CClF}$  and 20% of the  $\text{CHCl}=\text{CCl}_2$  reacted, and, in addition to the dimer of trichloroethylene,  $\text{C}_4\text{H}_2\text{Cl}_6$  (12), a considerable fraction of low-boiling fluorine- and chlorine-containing compounds was formed. The yield of crude oil was 24%, but the yield of polymer boiling above 220° C. at 0.3 mm. was only 7%; this indicated a large reduction in the average molecular weight. The oil fraction contained 47.5% chlorine as compared with 39% for the standard product; this pointed to the incorporation of  $(\text{CHCl}-\text{CCl}_2)$  units into the polymer chains.

**EFFECT OF OLEFIN CONCENTRATION.** Preliminary work on the effect of chlorotrifluoroethylene concentration at constant peroxide-olefin ratio demonstrated that increased dilution with chloroform gave increased yields of the crude oil fraction. The optimum concentration was in the neighborhood of a 10% solution, and a ratio of 9 parts of chloroform to 1 part of olefin was adopted as a standard reference point. With this dilution the yield of polymer of b.p. 120–220° C. at 0.3 mm. was 26% and the yield of polymer of boiling above 220° at 0.3 mm. was 51%. When the olefin concentration was reduced to 5%, the yield of crude oil was increased to 33% and the yield of residue was decreased to 39%. Although the conversion to crude oil was higher than in the standard runs, this increase was largely due to an increase in the lower molecular weights. As a result there was a comparatively large forerun after stabilization, and the over-all oil yield was the same as that under standard conditions. The olefin conversion of the 5% run was 76%, not far below the 86% of the standard runs. This relatively small dependence of conversion upon olefin concentration was in accord with a chain transfer mechanism.

**EFFECT OF PEROXIDE CONCENTRATION.** The effect of peroxide concentration was similar to that observed in other peroxide-promoted vinyl polymerizations: Increased peroxide concentration resulted in lower molecular weights. The weight ratio of peroxide to olefin was 5 to 100 for most runs, and, when this ratio was increased to 10 to 100, the yield of crude oil was 37% and that of polymer boiling above 220° C. at 0.3 mm. was 49%. Here again the increased oil yield was primarily due to the fractions of lower molecular weight, and the yield of stabilized oil was no better than that obtained with a 5% peroxide concentration.

**EFFECT OF INHIBITORS.** The role of possible inhibitors was studied with regard to those which might be encountered. Ethyl alcohol was first investigated, since it was present in commercial chloroform. When the solvent contained 1% ethyl alcohol (run 7) the conversion was reduced from 86 to 27%; with U.S.P. chloroform (run 8) containing about 0.5% ethyl alcohol, the conversion was reduced to 52%. These data verified the need for alcohol-free chloroform in the polymerization.

Traces of oxygen were present in most of the polymerizations, and its effect was tested in runs 9 and 10. In the former experiment oxygen was removed from the bomb by distilling out a quantity of olefin with a vapor volume equal to twenty times the free volume of the bomb. There was little effect on the conversion or yield of crude oil, but the yield of polymer boiling above 220° C. at 0.3 mm. was 61%, or somewhat higher than the 51% of the standard run. The introduction of 3 atmospheres of oxygen into the free volume (about 1 liter) of the bomb resulted in a decrease of the conversion to 26%. Under the conditions utilized, small amounts of oxygen appeared to reduce the molecular weight but did not greatly affect the yield of crude oil; large quantities of oxygen inhibited polymerization.

#### FLUORINATION OF CRUDE POLYMER

The general method developed for stabilizing the polymer oils involved heating the crude polymer in a nickel vessel to 200° C. and adding an equal weight of cobalt trifluoride in three portions. The mixture was stirred with a slow paddle scraper-type stirrer, and heating was continued for about 5 hours; after that time the cobalt salts had changed from a light tan to red or purple-red. Hydrogen fluoride was given off at first, whereas chlorine was more slowly liberated during the last stages. The unsaturation present in the crude oil was removed by the treatment, and properly treated polymer did not decolorize potassium permanganate in dilute acetone solution or yield appreciable acidity on heating with aqueous alcohol. Average chloride analyses on crude oil fraction ran about 39%; the stabilized oil averaged 31%. For example, 234 grams of crude oil fraction (boiling range, 110–220° C. at 0.3 mm.) which contained 39.1% of chlorine were treated at 170–200° C. with three portions of cobalt trifluoride totaling 227 grams. The reaction product was dissolved in carbon tetrachloride, the cobalt salts were filtered off, and the carbon tetrachloride was removed by distillation. The colorless residue was then vacuum-distilled at 0.3 mm. and the following fractions obtained: forerun (b.p. 65–100° C.), 14.4 grams; oil cut (b.p. 100–200° C.), 191.3 grams containing 30.9% chlorine; and residue, 6.5 grams. The stabilized oil fraction represented 81.6% of the crude oil weight.

It has been demonstrated that peroxide fragments are incorporated into the polymer molecule in peroxide-promoted polymerizations (11), and in the polymers of chlorotrifluoroethylene the end groupings derived from benzoyl peroxide, as well as those from the solvent, were a source of cobalt trifluoride consumption in the fluorination reaction. In addition, products formed from the thermal decomposition of benzoyl peroxide and incompletely removed from the crude oil accounted for some of the cobalt trifluoride required. These considerations suggested that the cobalt trifluoride consumption could be reduced by employing different peroxides. It was found that with acetyl peroxide (runs

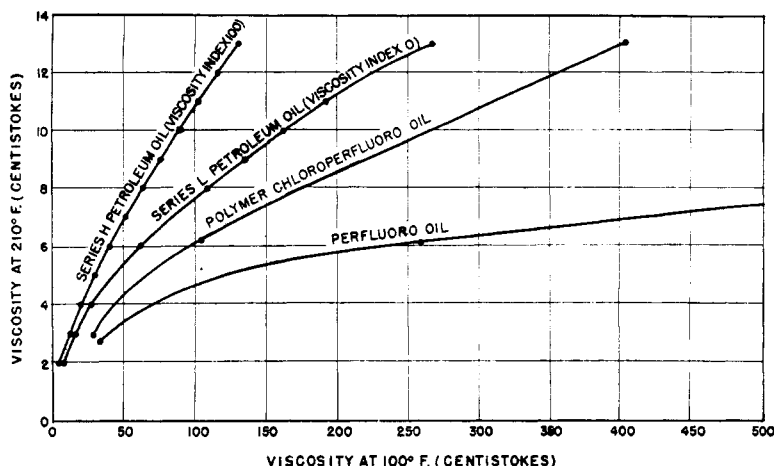


Figure 1. Viscosities of Various Oils at 100° and 210° F.

11 and 12) satisfactory stabilization was achieved with 63 and 76 grams of cobalt trifluoride per 100 grams of crude oil for the 5 and 10% peroxide concentrations, respectively, and with chloroacetyl peroxide (runs 13 and 14) satisfactory stabilization was achieved with 63 and 52 grams of cobalt trifluoride for the 5 and 10% peroxide concentrations, respectively. These polymerizations were carried out with the maximum temperature of reaction 110–120° C.

#### PREPARATION OF COBALT TRIFLUORIDE

The preparation and regeneration of cobalt trifluoride was carried out by the methods developed by Fowler (5) and represented the process requirement for fluorine. (The cobalt trifluoride utilized experimentally in the present work was largely supplied by the Johns Hopkins group and by the Hooker Electrochemical Company.)

**THERMAL CRACKING OF CHLOROTRIFLUOROETHYLENE POLYMER.** Thermal cracking was developed as a synthetic method, complementary to the polymerization procedure, to prepare additional oil from the solid polymer fractions and to recover monomer. Experiments were carried out with three different molecular weight ranges of polymer:

1. Residue which was obtained from the polymer oil process as described (under the conditions of run 1, Table I) of b.p. >240° at 0.3 mm. The residue was a dark-colored solid melting largely between 90° and 120° C., completely soluble in carbon tetrachloride.

2. A polymerization product obtained by heating a solution of 4 parts of chlorotrifluoroethylene, 6 parts of chloroform, and 0.5 part of benzoyl peroxide at 100° C. for 5 hours. As would be expected, this more concentrated olefin solution gave a higher molecular weight product as compared with the standard oil polymerization, which was incompletely soluble in carbon tetrachloride.

3. A material of still higher molecular weight was obtained by the polymerization of 75 parts of chlorotrifluoroethylene, 1 part of chloroform, and 0.24 part of benzoyl peroxide at 60° C. for 3 days. This product melted largely from 195° to 200° C. and was essentially insoluble in carbon tetrachloride.

The polymer was heated in a 1-liter round-bottom flask with a melted lead bath, and the products were distilled off as formed. The more volatile compounds were collected in dry ice and liquid nitrogen traps. In the course of the experiments various devices were incorporated into the design of the flask to reduce the amount of foaming during the reaction. Foaming over was prevented by use of an anchor-type stirrer with a lubricated ground-glass shaft seal and a method of feeding melted polymer into the reaction pot during the run so as to keep down the weight of material in the pot at any one time. The effect of agitation on cracking yields was small, since the bubbling caused by monomer elimination furnished effective agitation. In general, the pyrolysis products could be roughly divided into two parts: low-molecular-weight

oils and waxes, and regenerated monomer and its thermal reaction products. Carbon formation was never a problem; very little was formed under any of the conditions used.

Table II summarizes illustrative data from the cracking of each of the molecular weight ranges.

The high percentage of monomer and low boiling compounds relative to compounds of intermediate weight indicated appreciable true depolymerization of thermally formed polymer-free radicals to yield monomer molecules.

#### PROPERTIES OF LOW POLYMER

All evidence indicated that the crude oil polymer was composed of low polymers of chlorotrifluoroethylene containing end groupings derived from the peroxide promoter and from the solvent. The effect of the solvent on the polymerization suggested that most of the end groupings were derived from this source. Experimentally the low hydrogen content, the high chlorine content relative to monomer, and the loss of chlorine on stabilization, together with the low molar ratio of cobalt trifluoride required for stabilization of the polymer, all supported this view. Analytical results were consistent with a ratio of chloroform to peroxide fragments incorporated into the polymer of the order of 10 to 1. Crude oil fraction obtained by thermal cracking contained fewer reactive end groupings and hence required less cobalt trifluoride for stabilization.

The chlorine content of the low polymer oil (b.p. 100–240° C. at 0.3 mm.) which was obtained directly by polymerization varied from about 39 to 41%. A hydrogen content of 0.25% was found by the Pregl combustion method. The accuracy of the hydrogen determination was not demonstrated, but the fact that the hydrogen must have been present in the chloroform or peroxide fragments made complete oxidation to water probable. The index of refraction of the oil fraction was approximately 1.43, and the density 1.94, at 20° C. Its viscosity was greater than that of the stabilized oil, and for one sample values of 301 centistokes at 100° F. and 11 centistokes at 210° F. were measured.

The melting point of the standard oil polymer (unfractionated; run 1, Table I) was indeterminate. After removal of the chloroform, it was a soft tacky grease at room temperature. However, by varying the polymerization conditions, higher melting materials could be readily prepared. The standard oil polymer was soluble in the common halogenated solvents but incompletely soluble in low boiling petroleum ether. As would be expected, solubility diminished with increasing molecular weight, and fractionation could be carried out by solvent extraction. Alcohol, low boiling petroleum ether, acetone, chloroform, and 1,1,2-trichlorotrifluoroethane may be listed in order of increasing solvent power.

**POLYMER OIL.** The standard oil for which data are given was prepared experimentally. It had a boiling range of 100–200° C. at 0.3 mm., a chlorine content very near that of the monomer (31–32% as compared with 30.4%), and was a water-white free-flowing liquid. The index of refraction at 20° C. varied from 1.39 to 1.40. The density of the oil as normally prepared was within the ranges 1.94 to 1.97 at 20° and 1.83 to 1.86 at 100° C.

TABLE II. THERMAL CRACKING OF (CFC1—CF<sub>2</sub>)<sub>n</sub>

Polymer Type	Pressure, Mm. Hg	Bath Temp., ° C.	Wt. % of Degraded Polymer	
			Cold traps	Oil (b.p. range at 0.3 mm.)
1	25	351	37	55 (100–230° C.)
2	25	401	46	42 (100–210° C.)
3	21	409	20	59 (100–225° C.)

TABLE III. VISCOSITIES OF POLYMER AND PERFLUORO OIL FRACTIONS

Sample	Boiling Range		Viscosity, Centistokes	
	° C.	Mm.	100° F.	210° F.
Polymer oil	100-110	0.3	22.9	2.88
	110-120	0.3	59.4	4.73
	120-130	0.3	104	6.19
	130-140	0.3	185	8.20
	140-160	0.3	403	13.0
Perfluoro oil	127-137	10	33.2	2.73
	137-147	10	75.7	4.1
	147-157	10	249	6.1

In the large scale production of the polymer oil by the Hooker Electrochemical Company, molecular distillation equipment from Distillation Products, Inc., was utilized for separation of volatile fractions; the fractions were blended to give a product closely paralleling the experimental oil in average properties but including a somewhat wider molecular weight range.

The low polymers of chlorotrifluoroethylene within the liquid range of molecular weight exhibited normal solubility. The oil fraction was miscible with ethyl acetate, diethyl ether, carbon tetrachloride, benzene, chloroform, 1,1,1-trichlorotrifluoroethane, acetone, trichloroethylene, and *n*-pentane. It was less soluble in hydroxyl-containing solvents, and the presence of small amounts of water in the solvent led to a marked decrease in the solubility. At room temperature the stabilized polymer oil was soluble to the extent of 50 grams in 100 grams of absolute ethyl alcohol but only 6% soluble in 95% alcohol. In comparison it is interesting to note that fully fluorinated oils were sparingly soluble in common hydrogenated solvents and only miscible with fluorinated solvents. The chlorofluorocarbon oils were good solvents for fluorocarbons and for nonpolar hydrogenated solvents as well.

Based on ebullioscopic measurements in carbon tetrachloride and  $C_6F_{16}$  the number-average molecular weight of the polymer oil fraction was about 770, as determined by F. A. McKenna at S.A.M. laboratories. Since relatively few end groups were derived from the peroxide, both end groups may be considered as  $-CF_2Cl$ . On this basis the number-average chain length was approximately twelve carbon atoms.

The viscosity of the polymer oil was generally between 10 and 20 centistokes at 210° F. The variation of viscosity with the temperature was quite large, as shown by the following table, for a production sample of oil. When these data were plotted as the logarithm of viscosity against the reciprocal of temperature, the graph deviated appreciably from a straight line:

Temperature, ° C.	Viscosity, Centipoises
37.8	143.5
65.6	29.3
98.5	8.86

The viscosity at two temperatures for a series of polymer and perfluoro oil fractions is given in Figure 1 and Table III. (The perfluoro oil fractions were prepared at the Du Pont Company by vapor-phase fluorination of a hydrocarbon oil using the Cady-Grosse procedure.)

These curves were compared with the viscosity data of two petroleum oils. Oil *H* had a viscosity index (*I*) of 100 and represented a relatively small variation of viscosity with temperature. The other, series *L*, had a viscosity index of 0 and represented a comparatively large variation of viscosity with temperature. Data for these oils are employed as standards for evaluating the viscosity-temperature characteristics of lubricating oils, and most petroleum oils fall between these two curves. Both the polymer chloroperfluoro oil and the perfluoro oil fall below the *L* series oil, and the change in viscosity with temperature for the sample of perfluoro oil available was significantly greater than that observed for the polymer oil. H. S. Taylor of Princeton University sug-

gested that the high viscosity temperature coefficients for the perhalogen oils implied hindered rotation about the carbon-carbon bonds. The method of preparation of the perfluoro oil indicated the presence of cyclic and branched chain structures, whereas the polymer oil was presumably composed of straight chains.

**LUBRICATING PROPERTIES OF POLYMER OIL.** A practical test of the lubricating properties of the polymer oil was carried out by operating a Beach-Russ Series 6 vacuum pump continuously for 6888 hours, pumping air, and using the polymer oil as the seal oil. The polymer oil was as satisfactory as the prescribed petroleum seal oil, as indicated by lack of mechanical wear during tests carried out by I. P. Sharpe at The Kellogg Corporation. Another test was carried out by running a 3-horsepower motor continuously for 6 months with polymer oil lubrication of the bronze sleeve bearings. At the end of the test period examination of the bearing surfaces showed no signs of inadequate lubrication. The unsaturation test of the oil had not changed, this indicated freedom from breakdown.

**POLYMER GREASES AND WAXES.** Fractionation of the fluorinated residues from the polymer oil distillation at 0.3 mm. yielded greases which were characterized loosely by their stiffness at room temperature: light grease, b.p. 200-220° C. at 0.3 mm.; medium grease, b.p. 220-240° at 0.3 mm.; and heavy grease, b.p. 240-260° at 0.3 mm.

Stable polymers of higher melting point could be prepared by successive extraction of the crude polymer residue with different solvents, followed by fluorination by reaction with cobalt trifluoride as described for the oil. The stabilized polymer of higher molecular weight was recovered from the fluorination mixture by extraction.

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