first production of a high temperature type, demanding that the reactors be in the neighborhood of 300° C. at the inlet end. These higher temperatures resulted in a proportionately decreased crude yield, and the average fell to about 70%, based on the conversion of $—CH_2—$ to $—CF_2—$; the average composition of this crude is shown by means of typical distillation data:

Boiling Range	% of Still Charge
<180° C. (atm. pressure)	15
180° (atm.) to 147° C. (10 mm.)	45
147° to 208° C. (10 mm.)	36
>208° C. (10 mm.)	4

Only 45% of the material corresponded to specification grade solvent. Although it was possible to increase this figure significantly by changes in feed stock, this was not done, as the fraction boiling in the range 147–208° C. at 10 mm. was equally desirable as the lubricant described in the following section.

PERFLUORO LUBRICANT. The highest boiling fluorocarbon produced in quantity by this unit was fluorinated lubricating oil having an average molecular weight in the neighborhood of 1000 which corresponded to a chain length of about 20 carbon atoms. This material boiled from 147° to 208° C. at 10 mm. although it was frequently possible to blend in higher boiling and lower boiling materials and still meet the viscosity specification. The increase in molecular weight was again reflected in the higher boiling point of the starting material (325–410° C.) and the necessity for operating the reactor entirely above 350° C. The most common starting material was an SAE 10 lubricating oil known as Diol 45 (made by the Standard Oil Company of New Jersey). The crude yield with this material fell to about 50%, based on the conversion of $—CH_2—$ to $—CF_2—$. A typical distillation analysis follows:

Boiling Range	% of Still Charge
<160° C. (atm. pressure)	23
160° (atm.) to 147° C. (10 mm.)	24
147° to 208° C. (10 mm.)	46
>208° C. (10 mm.)	7

A typical specification cut of this material had a viscosity of 980 Saybolt seconds at 37.8° C. and 57.2 seconds at 98.9°.

Variations in feed stock did not benefit the total production per run, despite the rather high percentage of the crude which lay outside the desired distillation range, nor was it possible to increase the crude yield significantly by variations in the operating technique. Nevertheless, approximately 2800 pounds were produced within the stipulated specifications, and the lighter by-product cuts found application as solvents.

ACKNOWLEDGMENT

This paper represents work done for the U. S. Army Corps of Engineers, Manhattan District. R. Rosen and E. V. Murphree of the Standard Oil Company of New Jersey were instrumental in getting the pilot plant work started. Much profitable knowledge was derived from contact with men of the Du Pont Company, particularly H. W. Elley, A. F. Benning, F. B. Downing, J. D. Compton, W. O. Jewett Jr., and J. B. Roberts. The interest of D. H. Andrews in the early work of R. D. Fowler on the preparation of fluorine and UF_6 led directly to the work described in this paper; the interest and generous financial support of H. A. B. Dunning made that early work possible.

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PRESENTED before the Symposium on Fluorine Chemistry as paper 65, Division of Industrial and Engineering Chemistry, 110th Meeting of the 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.

Fluorocarbons by fluorination of hydrocarbons with COBALT TRIFLUORIDE

THE effects of variables in the fluorination of *n*-heptane and diperfluoromethylbenzene with cobalt trifluoride were determined. The most suitable method for purification of the resulting perfluoroheptane and perfluorodimethylcyclohexane was fractional distillation. Measurement of the dielectric constant of the crude and distilled products proved useful as a means of controlling quality, whereas infrared methods were relied on for final analysis of the purified product.

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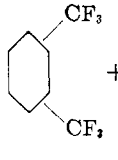
LIQUID fluorocarbons were first prepared by Simons and Block (*4*) by the action of fluorine on carbon black. Cady and co-workers (*1*) made fluorocarbons by fluorination of hydrocarbons with elemental fluorine over various catalysts. Fowler and associates (*2*) fluorinated hydrocarbons indirectly with cobalt trifluoride; the cobalt trifluoride was converted to the difluoride, which was then reconverted to the trifluoride with fluorine gas.

The purpose of this work was to develop processes for the large scale manufacture of perfluoroheptane and perfluorodimethylcyclohexane. The method developed and demonstrated on a semiworks scale by Fowler *et at.* appeared the most suitable for large scale manufacture. Accordingly, this method was studied further with the object of determining the effect of operating variables as well as developing methods of control and analysis.

The high heats of reaction in both the fluorination of hydrocarbons with cobalt trifluoride (Equations 1 and 2) and the conversion of the resulting cobalt difluoride with elemental fluorine (Equation 3) complicated the production of the fluorocarbons on a large scale.

$$C_7H_{16} + 32CoF_3 \longrightarrow C_7F_{16} + 32CoF_2 + 16HF + 1000 \text{ kg.-cal.} \qquad (1)$$



$$+ 14CoF_3 \longrightarrow C_8F_{16} + 14CoF_2 + 4HF + 460 \text{ kg. cal.} \qquad (2)$$

$$2CoF_2 + F_2 \longrightarrow 2CoF_3 + 58 \text{ kg.-cal.} \qquad (3)$$

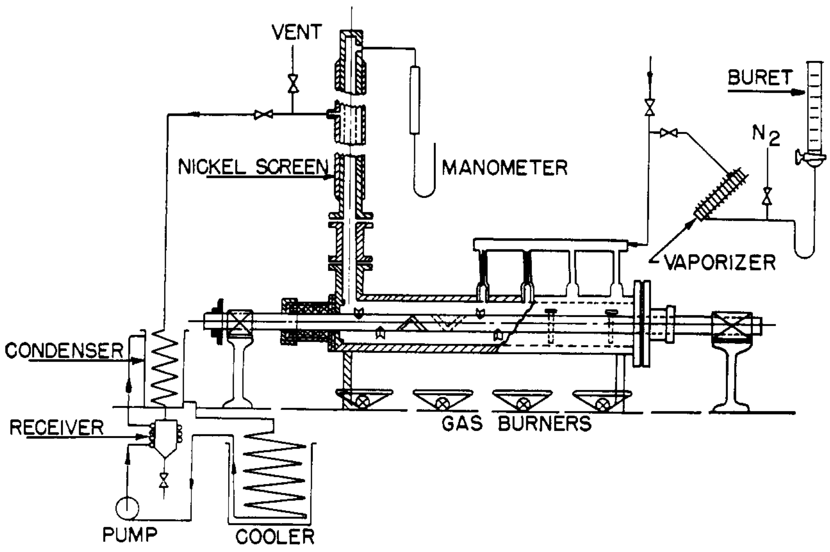


Figure 1. Equipment for Fluorination of Heptane

The heat of reaction for reactivation of the cobalt difluoride was measured at the National Bureau of Standards, whereas that for the fluorination of heptane and diperfluoromethylbenzene was estimated by comparison of observed heat transfer rates for both reactions. The value for the regeneration reaction is much lower than the calculated value given by Ruff and Ascher (*3*).

FLUORINATION WITH CoF_3

FLUORINATION OF HEPTANE. The reactor (Figure 1) was 36 inches long and 4 inches in diameter. It contained 3200 grams of cobalt trifluoride, which was sufficient for a total feed of about 70 grams of heptane. In operation, the temperatures of the reactor were adjusted to 225° C. at the inlet end and 350° C. at the outlet by regulation of gas burners.

Liquid *n*-heptane was fed dropwise into the vaporizer from the buret at a rate of about 20 grams per hour. The heptane vapor entered the reactor through the manifold feed system. For a feed rate of 20 grams per hour the estimated time of contact was 2 to 3 minutes. As soon as the organic feed came in contact with the cobalt trifluoride, fluorination started, as evidenced by a temperature rise in the reactor, and it was necessary to decrease the flame on the gas burners to maintain the temperature at 225° to 350° C. The exit gases, hydrogen fluoride and crude perfluoroheptane, passed through the nickel screen to allow removal of cobalt fluoride dust and then into the condenser. The product collected in the cold receiver. At the end of the run the reactor was swept with nitrogen to displace fluorocarbon from the reactor into the condenser.

The lower layer of crude fluorocarbon (specific gravity, about 1.7) was separated from the upper layer of hydrogen fluoride (specific gravity, about 1.0). The latter was drowned in water and a small amount of fluorocarbon recovered by separation from the aqueous layer. The crude fluorocarbon was washed with dilute caustic soda, separated from the aqueous layer, and dried. A run of 68 grams of *n*-heptane gave 212 grams of crude perfluoroheptane and 190 grams of hydrogen fluoride, which is equivalent to an 80% yield of fluorocarbon and 87% recovery of hydrogen fluoride based on heptane (Equation 1).

FLUORINATION OF DIPERFLUOROMETHYLBENZENE. For small scale experimental work, equipment similar in design to that used for perfluoroheptane was employed. The chief differences were in the size of the reactor and the method of heating and cooling. The reactor was 12 inches in diameter by 4.5 feet long and was heated and cooled by circulating air. It contained 85 pounds of cobalt difluoride which was converted to the trifluoride at 250–275° C. by addition of fluorine from the generators at 0.5 to 1.5 pounds per hour. The heat of reaction raised the temperature to about 350° C. When fluorine was detected in the exit gas, the generators were shut off and the reactor was swept with nitrogen. While being swept with nitrogen, the reactor was allowed to cool to 290–300° C. Diperfluoromethylbenzene was then fed at 15 cc. per minute. During the reaction the temperature in the reactor rose to 300–345° C.; a temperature peak of 340–350° C. moved slowly from forepart of the reactor to the exit end. At the end of the feed the reactor was swept with nitrogen to displace the fluorocarbon vapors from the reactor into the condenser. The liquid products were collected in the receiver and then worked up in a manner similar to that used for the crude perfluoroheptane.

A normal charge of 8.9 pounds of diperfluoromethylbenzene gave 15.1 pounds of perfluorodimethylcyclohexane, or 91% of theory based on diperfluoromethylbenzene. The recovery of hydrogen fluoride was 80% of theory, and the cobalt trifluoride was 70% exhausted.

EFFECT OF TEMPERATURE

The effect of various operating temperatures was determined by a series of runs in which the temperature of the reactor was varied from 150° to 400° C. in the fluorination of heptane and from 210° to 390° C. in the fluorination of diperfluoromethylbenzene. The quality of the crude fluorocarbons was determined by distillation through a four-plate column. The distillation curves are shown in Figures 2 and 3. Column head temperatures are plotted against the amount distilled. Pure perfluoroheptane has a boiling point of 82.5° C. The pure perfluorodimethylcyclohexane has a boiling point of 101.0° C. (ortho) to 102.6° C. (para). The boiling points of the incompletely fluorinated products are higher, a rise in distillation range indicating incompleteness of reaction. The curves show that the degree of fluorination increases with the temperature of fluorination and that a reactor temperature of 300–350° C. gives the largest amount of material distilling within the range for the pure fluorocarbons.

Products of decomposition generally boil lower. The region covering the first part of the distillation shows the effect of temperature on these products. In the fluorination of heptane (Figure 2), low boilers to the extent of 5 to 10% of the crude fluorocarbons were obtained at 350–400° C., whereas with diperfluoromethylbenzene 10 to 20% of low boilers were obtained at the higher temperature (Figure 3).

EFFECT OF CONTACT TIME

The products obtained by a single pass of heptane and diperfluoromethylbenzene through the reactor were far from being completely reacted, and it was advantageous to repass the crude fluorocarbon rather than use a longer time of contact in a single pass. Feed rates giving a contact time of 3 to 6 minutes were satisfactory. Slower feed rates were of no great advantage, although the amount of cracking was not greatly increased. The effect of repassing crude perfluoroheptane made at 300° C. is illustrated in Figure 4, which shows distillation curves of products obtained by one and two passes through the reactor. The decrease in high boiling compounds or incompletely reacted products can readily be seen.

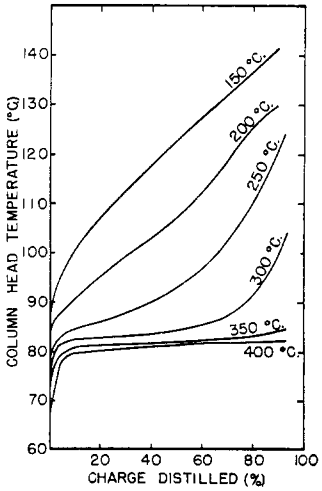


Figure 2. Comparative Distillation Ranges of Crude Perfluoroheptane Prepared at Various Reaction Temperatures

Crude perfluoroheptane was repassed through the reactor at rates ten to fifteen times greater than the rate used for heptane in the first pass, and crude perfluorodimethylcyclohexane at rates four to five times greater than that for diperfluoromethylbenzene. Although the feed rates were considerably greater, the time of contact was longer in the second pass because comparatively little hydrogen fluoride was evolved to dilute the reaction mixture. Yields by weight on repassing the first-pass fluorocarbons were 98 to 100%, making the over-all yield of perfluoroheptane based on heptane 75 to 80% and that of perfluorodimethylcyclohexane based on diperfluoromethylbenzene 90%.

COMPOSITION OF CRUDE PERFLUOROHEPTANE

Table I shows the principal compounds found in material made by two passes through the reactor. The compounds are listed in the order of their boiling points. The desired product, perfluoroheptane, and its isomers boil at 82.49° C. Decomposition products and the cyclic fluorocarbons, perfluoroethylcyclopentane and perfluoromethylcyclohexane, have lower boiling points. Generally, the incompletely reacted or hydrogen-containing compounds boil higher. It is evident that fractional distillation should provide a means of separation of most of these impurities. However, the isomers and the unknown hydrofluorocarbon ($C_xF_yH_z$) boil too close for separation. These compounds were detected by infrared examination. Isomers were not objectionable, but the unknown hydrofluorocarbon was. The unknown is probably monohydroperfluoroethylcyclopentane, since it forms perfluoroethylcyclopentane on exhaustive treatment with cobalt trifluoride.

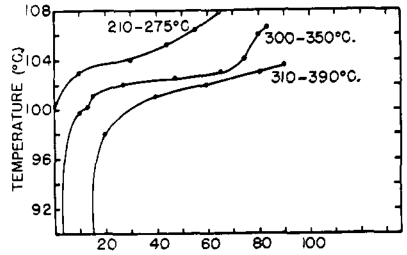
Table I. Fluorocarbons Obtained by Fluorination of Heptane with Cobalt Trifluoride

Compound	B.P., ° C.	S.I.C.
Decompn. products	<75	
$C_5F_9(C_2F_5)$	75.1	1.80
$C_6H_{11}(CF_3)$	76.4	1.85
$C_xF_yH_z$ (unknown)	82(?)	2.00+
C_7F_{16}	82.49	1.765
C_7F_{16} (isomers)	82.49 ± 0.2	1.765 ± 0.005
$C_7F_{15}H$	87.39	2.47
$C_7F_{15}H$	91.92	2.93
$C_7F_{14}H_2$	95.71	3.18
C_7H_{16}	98.42	1.90
$C_7F_{13}H_3$	122–130	..

CONTROL AND ANALYSIS OF PERFLUOROHEPTANE

Inasmuch as fluorocarbons are extremely stable chemically, physical methods had to be found for analysis. Infrared methods were invaluable, but sufficient equipment was not available for routine analyses.

The low boiling impurities were determined by precision boiling point determination after an empirical curve had been established for boiling point *vs.* quantity of cyclic impurities present. However, this method of analysis was not satisfactory for the high boiling impurities, and other physical measurements were considered. It was found that the dielectric constant or specific indu



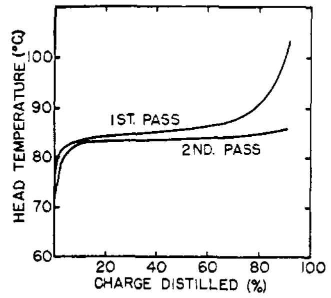


Figure 4. Distillation Curves of Crude Perfluoroheptane Obtained by One and Two Passes over Cobalt Trifluoride

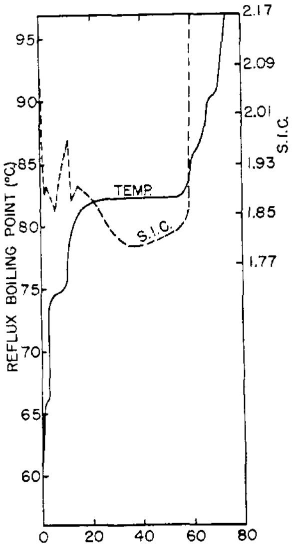
compounds and that measurement of this physical constant was a rapid method for detection. It was readily determined using a Schering bridge and a small capacitance cell (*5*). Perfluoroheptane has an S.I.C. of 1.765; the two monohydrofluorocarbons, 2.47 and 2.93; and the dihydro, 3.18. The dielectric constants of fluorocarbons with more than two hydrogen atoms were not measured. However, at an unknown point as fluorine is replaced with hydrogen the S.I.C. value decreases again, since that of heptane is only 1.9.

PURIFICATION OF PERFLUOROHEPTANE

Specific inductive capacity was used for determination of the quality of the crude as well as the distilled products. If the S.I.C. of a sample of crude was above 1.90, the reaction was not sufficiently complete to purify the product by distillation, and a third pass through the reactor was necessary.

Crude perfluoroheptane with an S.I.C. below 1.9 contained no unreacted heptane and only negligible amounts of the unknown material and di- and trihydro compounds. All other objectionable materials can be separated by fractionation.

A distillation curve of poor quality material distilled in a 100-plate Podbielniak column is shown by the solid line in Figure 5, derived by plotting the boiling points of the distillate against per cent of material distilled. The broken line is the S.I.C. curve. A reflux ratio of 100 to 1 was used on the rises and of 10 to 1 on the flats. The curve shows a small inflection at 66–67° C., which represents a binary mixture containing highly unreacted material, possibly some heptane. The flat at 74–75° C. represents the cyclic fluorocarbons, perfluoromethylcyclohexane and perfluoroethylcyclopentane. The main flat corresponds to perfluoroheptane. The inflections at 87° and 91° C. represent monohydroperfluoroheptane. The S.I.C. falls very sharply at the cyclic fluorocarbon cut, then shows a pronounced rise and falls slowly. The peak of the S.I.C. curve is caused by the unidentified hydro compound. Only a small amount of the material distilled from this crude was completely reacted.



A distillation curve (solid line) and S.I.C. curve (broken line) of the same material after it was repassed through the reactor is shown in Figure 6. It has an S.I.C. of 2.44 before repassing and 1.80 after. The S.I.C. curve (dotted line) of the material be-

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

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-

Table II. Physical Constants of Reaction Products

	Diperfluoromethylbenzene	Perfluorodimethylcyclohexane	Perfluoromethylcyclohexane	Perfluorocyclohexane
Formula	$C_8H_4F_6$	C_8F_{16}	C_7F_{14}	C_6F_{12}
Mol. wt.	214	400	350	300
Sp. gr. at 25° C.	1.3799	1.854	1.7860	...
S.I.C.	12.39	1.863	1.85	...
Refractive index at 25° C.	1.3765	1.286	1.2816	...
B.p. at 760 mm., ° C.	115.7	o = 101.0 m = 102.1 p = 102.6	76.33	50.2
Freezing point, ° C.	−47.12	Approx. −55	...	...
Soly. in HF at 15° C., %	5.8	<1	...	...
Soly. of HF in compound at 15° C., %	0.63	0.1	...	...

than the average material produced on a larger scale. It was well reacted and contained little besides cyclic fluorocarbons and high boiling materials. The material obtained on the rises between the cyclic fluorocarbon flat and perfluoroheptane flat could be returned to the still with subsequent charges. The high boilers represented by the rise of both the distillation and the S.I.C. curves could be converted to perfluoroheptane by repassing over cobalt trifluoride.

CRUDE PERFLUORODIMETHYLCYCLOHEXANE

As with perfluoroheptane, the crude perfluorodimethylcyclohexane contained over-reacted and under-reacted products. The former were compounds with boiling points lower than perfluorodimethylcyclohexane and were formed by cracking. The principal cracked product was perfluoromethylcyclohexane. The under-reacted products consisted of unsaturated compounds and compounds containing hydrogen. These boil in the range of, or higher than, perfluorodimethylcyclohexane. Table II shows some of the physical constants of the materials involved.

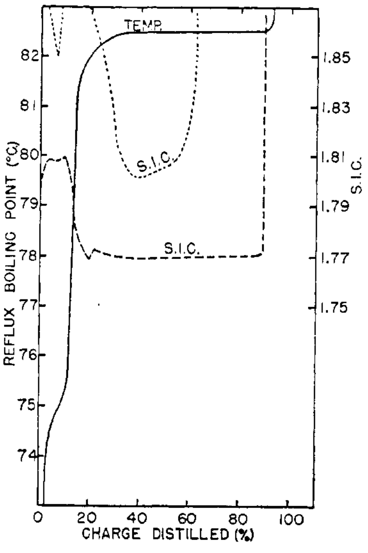


Figure 6. Distillation Curve and S.I.C. Curve of High Grade Crude Perfluoroheptane

Most of the physical properties of the cracked products were similar to those of perfluorodimethylcyclohexane. They differed from it and from one another in boiling point; consequently they could be separated readily by distillation. In general, data are lacking for the incompletely fluorinated compounds. It is known that they had much larger values for refractive index and specific inductive capacity than did the completely fluorinated compounds, and that many of them had specific gravity and boiling point values close to those of the completely fluorinated compounds. The incompletely reacted products were more soluble in hydrogen fluoride than were the perfluoro compounds, and their presence tended to increase the solubility of the perfluoro compounds in that solvent. Accordingly, a considerable separation of impurities was accomplished in the receiver of the apparatus.

CONTROL AND ANALYSIS OF PERFLUORODIMETHYLCYCLOHEXANE

The primary method for determining all of these impurities was by infrared spectrographic analysis. Ordinary distillation range or specific gravity determinations were rapid but gave only approximate indication of the purity of crude perfluorodimethylcyclohexane. The dielectric constant or its practical equivalent, the specific inductive capacity, was a much better criterion for judging the completeness of fluorination. The latter increased almost linearly with hydrogen content.

Neither specific gravity nor S.I.C. was suitable for determining the completely reacted cracked products. Precision fractionation would show and separate them but was time consuming. The principal impurity of this type was perfluoromethylcyclohexane. A rapid method for determining this compound in small amounts was developed. A small sample was topped in a little fractionating still, and the reflux boiling point of the toppings was determined. The still and reflux boiling point apparatus were calibrated with known mixtures of pure material, and the whole determination was carried out under carefully controlled conditions. This method gave results accurate to within ±0.05% on samples containing less than 1% of perfluoromethylcyclohexane, with infrared analysis as a standard.

PURIFICATION OF PERFLUORODIMETHYLCYCLOHEXANE

As with perfluoroheptane, fractional distillation was the best method for purifying perfluorodimethylcyclohexane. In this case it was again necessary to obtain crudes which were well reacted in order to obtain a distilled material of suitable quality. The upper graph of Figure 7 shows the distillation curve of a sample of single-pass crude product distilled in a 100-plate Podbielniak column. The S.I.C. curve is also given; these values are all above 1.93, although much of the temperature curve lies within the range for perfluorodimethylcyclohexane (101° to 103° C.). Less than 25% of the distillate was of suitable quality. The lower graph shows the effect of repassing this crude product over

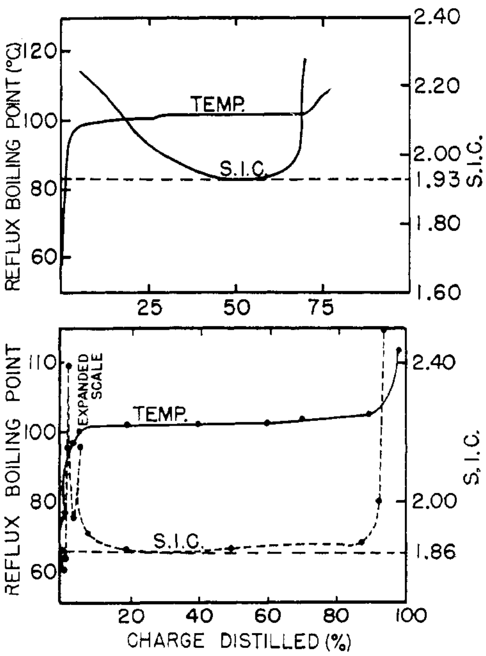


Figure 7. Distillation of First-Pass and of Second-Pass Perfluorodimethylcyclohexane

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 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.

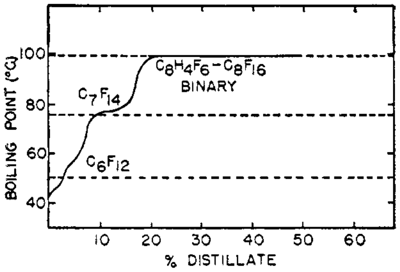


Figure 8. Fractional Redistillation of Perfluorodimethylcyclohexane Foreshots

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.

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 hydrocompounds, were relied on for final analysis of the purified products.

ACKNOWLEDGMENT

The authors wish to acknowledge the work of J. B. Roberts, W. Menges, and W. O. Jewett, who designed the reactor and its auxiliary heating apparatus, that of F. G. Brickwedde of the Bureau of Standards, and that of V. Z. Williams of American Cyanamid Company, who developed and carried out the infrared analyses.

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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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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 (7). 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:

$$CF_2Cl—CFCl_2 \xrightarrow[\text{alcohol}]{\text{Zn}} CF_2{=}CFCl$$

2. Polymerization of chlorotrifluoroethylene:

$$CF_2{=}CFCl \xrightarrow[CHCl_3]{\text{peroxide}} R(CF_2—CFCl)_nR'$$

3. Fluorination of crude polymer:

$$R(CF_2—CFCl)_nR' \xrightarrow{CoF_3} R''(CF_2—CFCl)_nR'''$$

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