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SUBJECT Fluorination of n-Heptane with Cobalt Trifluoride (Progress Report)

100XR-2609

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E. I. DU PONT DE NEMOURS & COMPANY

JACKSON LABORATORY

JUNE 30, 1943

HOXR-2609

JWD-2

PROGRESS REPORT

CONTRACT W-7412-eng-2

FLUORINATION OF n-HEPTANE WITH COBALT TRIFLUORIDE

Work Done by:	Under Supervision of:
W. J. Clem	F. B. Downing
R. F. Deese, Jr.	A. F. Benning
K. C. Johnson	

Reported by:

K. C. Johnson

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ABSTRACT

An operating process has been developed for the fluorination of n-heptane in the vapor phase with cobalt trifluoride at 250-350°C. in a special agitated reactor. Yields of crude Ø-heptane of 80-85% of theory have been attained consistently by this method in a laboratory scale model reactor. Approximately 5-10% of cyclic fluorocarbons are formed as byproducts in the reaction. The residual hydrogen containing compounds in the crude Ø-heptane can be fluorinated further by repassing over cobalt trifluoride at 350°C.

The total crude Ø-heptane after a second pass over cobalt trifluoride was within specification limits for coolant grade under the C-716 pilot plant contract. Over 50% of the second pass crud after fractionation through an 18-20 plate column was within specification limits for the sealant grade under the C-716 pilot plant contract.

Yield data on material pressing the proposed specifications for sealant grade C_7F_{16}under the C-816 contract will not be available until further distillation studies are completed.

Preliminary work on analytical methods for determining purity [illegible] the C_7F_{16} has been carried out. An analytical distillation in a Podbielniak high temperature still and examination of reflux boiling points of foreshots from the distillation shows promise as a control method for determining C_7F_{14} compounds in C_7F_{16}. Absolute correlation of this method with infra-red analyses is being held up pending installation of a more efficient Podbielniak column.

A method of determining the amount of hydrogen containing Ø-heptane in a close cut of C_7F_{16} by measurement of its dielectric properties appears to be of interest and details are being worked out. The correlation between the hydrogen content of hydro Ø-heptanes as shown by dielectric properties and the stability to process gas is being investigated.

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The method of determining the stability of Ø-heptane samples to process gas treatment has been worked out satisfactorily within the specification limits in the C-716 contract (0.1 to 1.0% residue).

Mechanical problems have made the stability test in the range of 0.01 - 0.02% residue erratic. Further work is being carried out to improve the consistency of this test for the low range proposed for C_7F_{16} in the C-816 contract.

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Fluorination of n-Heptane with Cobalt Trifluoride

Object of the Investigation:

To develop an operating process for the fluorination of n-heptane with cobalt trifluoride and to develop analytical methods for evaluating the purity of the fluorinated product.

Period Covered by the Report:

December 15, 1942 to June 15, 1943.

Historical Background:

Initial development work on the vapor phase fluorination of hydrocarbons such as n-heptane with CoF_3 was started at Johns Hopkins University early in 1942. The early work was carried out first in static reactors and later in reactors which were simply rotating shells without internal agitation. When the feasibility of this fluorination method had been demonstrated, the problem of developing an operating process for large scale production of φ-heptane was turned over to the duPont Company. Agitated reactors and a pilot plant layout (C-716 contract) were designed on the basis of the experimental results from Johns Hopkins University. (Ref: Report of J. B. Roberts on Comparison of Direct Catalytic and Cobalt Fluoride Process for Manufacture of C_7F_{16} dated 9-1-42). The present report covers the experimental work carried out in Jackson Laboratory in developing an operating process for fluorinating n-heptane with CoF_3 in the vapor phase using the agitated reactor as designed for the pilot plant.

Summary and Conclusions:

A satisfactory operating process has been developed for the fluorination of n-heptane in the vapor phase with CoF_3 in a special agitated reactor. This process consists of the following steps: (1) Preparation of CoF_3 in the reactors by treating CoF_2 with gaseous fluorine at 200-250°C. (2) Vaporizing n-heptane and

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passing the vapors over CoF_3 in the agitated reactor at a graded temperature of 225-350°C. (3) Condensing the fluorocarbon product and HF formed and separating the two liquid phases. (4) Repassing the first pass crude over CoF_3 at 300-350°C. (5) Condensing the crude ϕ-heptane from the second pass and washing with caustic to remove dissolved HF. (6) Drying the crude ϕ-heptane and distilling the dried product. (7) Regenerating the CoF_2 formed to CoF_3 with fluorine and repeating the cycle.

Crude ϕ-heptane was obtained in yields of 80-85% of theory based on complete fluorination in the laboratory scale model reactor.

The principle impurity in this crude was similar to the No. 10 cut (probably ϕ-ethyl cyclo pentane) from Dr. Henne's fractionation of crude ϕ-heptane produced at Johns Hopkins. Some ϕ-methyl cyclohexane was also formed. The total cyclics in a typical laboratory crude ϕ-heptane was about 6% of the total crude. Some high boiling hydro compounds were present even in the second pass crude. By repassing over CoF_3 at 350°C. the high boiling hydro compounds can be converted to ϕ-heptane.

The total crude after second pass was satisfactory quality to meet the specifications for coolant grade in the C-716 contract with respect to boiling range and stability to process gas (less than 1% residue).

A single fractionation of the crude ϕ-heptane in 18-20 plate column gave about 50% of a mid-cut which passed specifications for the sealant grade in the C-716 contract. (Process gas residue less than 0.1%).

Analytical methods have been worked out in a preliminary way for determining the quality of close cut ϕ-heptane to meet the proposed specifications for the second order of C_7F_{16}. (0.5% C_7F_{14} and 0.02% residue to process gas).

A distillation analysis of C_7F_{16} close cuts in a Podbielniak high temperature still and determination of the reflux boiling point of a small foreshot cut shows promise of being a satisfactory control analysis to correlate with the infra-red analysis for cyclic C_7F_{14} compounds. Changes of the order of 0.03°C. in refl[illegible]

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boiling point of the first 1% cut in this distillation analysis are effected by the addition of 0.1% of C_7F_{14} to the C_7F_{16} sample.

The presence of high boiling monohydro compounds in C_7F_{16} can be determined by a measurement of the dielectric capacity of the sample. The specific inductive capacity (S.I.C.) as calculated from this measurement shows an increase from 1.773 for Ø-heptane to 2.750 for the monohydro Ø-heptane (b.p. about 87.3°C.). The Podbielniak distillation analysis used for C_7F_{14} content of a sample of C_7F_{16} can be utilized for monohydro compounds by examining the S.I.C. of the still holdback in which are concentrated the high boilers.

Work is still in progress to standardize the process gas stability test to give consistent blanks and to detect residues of the order of 0.02%. The stability test is satisfactory for testing samples having residues of 0.1 to 1.0% as required for the C-716 contract.

<u>Plans for Future Work:</u>

A more efficient Podbielniak column is being installed. When this is ready, more precise correlation will be made of the C_7F_{14} content of samples of C_7F_{16} as shown by infra-red and distillation methods of analysis.

The use of the S.I.C. value as a measure of the monohydro content of C_7F_{16} will be evaluated further. A correlation between process gas residue tests and monohydro Ø-heptane content of C_7F_{16} will be made.

As soon as production of C_7F_{16} in the pilot plant becomes standardized, an evaluation will be made in a 100 plate column of the plant yield of C_7F_{16} of satisfactory quality to pass specifications for the second order of C_7F_{16}.

The process gas residue test is being studied further to eliminate mechanical troubles and improve the technique of operation to give consistently low residue values (0.01 - 0.02%).

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Experimental

The work done on perfluoro n-heptane (ø-heptane) will be reported under the following headings:

(A) Fluorination of n-heptane

(B) Purification of crude ø-heptane

(C) Analytical Methods

(D) Miscellaneous experimental work.

(A) Fluorination of n-Heptane:

1. Equipment.

The following study of the fluorination of n-heptane with cobalt trifluoride has been carried out in an experimental agitated reactor which is an approximate scale model of the reactor designed for the production of ø-heptane on a pilot plant basis (C-716 contract). A schematic drawing of the laboratory reactor is attached to this report. The reactor itself was made from 4 in. standard steel pipe (36 in. long) with one end flanged and the other end welded. The agitator was made from 1-1/4 in. extra heavy steel pipe to which were welded 12 plow shaped blades cut from 1-1/4 in. angle iron. These blades were arranged in groups of four with the order of breaking the surface 1, 3, 2 and 4 in each group.

The manifold feeder distributed the gas over about 50% of the reactor length. The exit gases were taken off through a dust collector which consisted of a cylinder of nickel wire cloth inside a 2 in. pipe. The dust was collected on the inside of the nickel screen and the gases were conducted out to the condenser.

The stuffing boxes on the ends of the reactor were each packed with 2 1/8 in. carbon rings and several thicknesses of 1/4 in. copper braid. A brass lantern ring was provided in each stuffing box to give a positive pressure of nitrogen into the reactor in the event of leakage.

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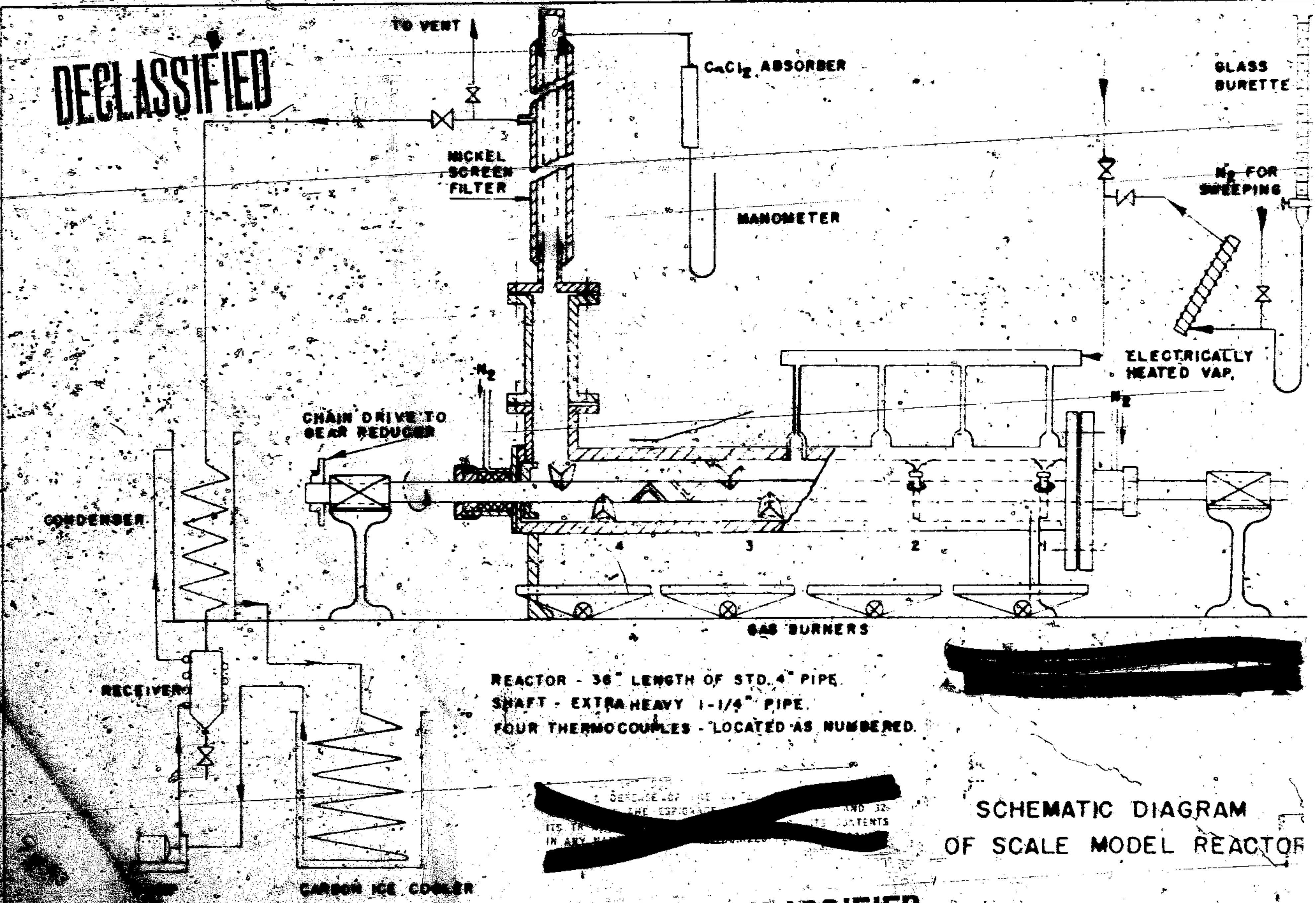

REACTOR - 36" LENGTH OF STD. 4" PIPE.
SHAFT - EXTRA HEAVY 1-1/4" PIPE.
FOUR THERMOCOUPLES - LOCATED AS NUMBERED.

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SCHEMATIC DIAGRAM OF SCALE MODEL REACTOR

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The auxiliary equipment consisted of the following items:

(a) 100 cc. glass burette feeder with an expansion bulb for observing dropwise feed.

(b) Electrically heated copper tube for vaporizing the liquid feed.

(c) Copper coil condenser with circulating trichlorethylene for cooling.

(d) Four gas burners for heating.

(e) Four thermocouples for measuring temperatures in the reactor charge.

(f) Manometer to measure pressure inside dust collector.

2. Preparation of Cobalt Trifluoride.

$$(CoCl_2 + 2HF \Longrightarrow CoF_2 + 2HCl)$$

Anhydrous cobalt chloride (7.8 lbs.) was charged into the reactor and converted to the difluoride by treatment with anhydrous HF at 200-250°C. A total of 13-3/4 lbs. of HF was fed over a period of 44 hours. A considerable excess over theory was used to insure completion of reaction. The difluoride was converted to the trifluoride by reaction with fluorine gas at 200-300°C. This reaction appeared to go to completion with only a small excess of fluorine being used ($2CoF_2 + F_2 \longrightarrow 2CoF_3$). The exit gases gave a flame test with a piece of charred wood when the conversion was complete and the fluorine was no longer being absorbed. After the excess fluorine was swept from the reactor with nitrogen, the reactor was ready for a fluorination cycle. The following typical run will serve to illustrate the process used for fluorinating n-heptane.

3. Fluorination of n-Heptane.

$$(C_7H_{16} + 32CoF_3 \longrightarrow C_7F_{16} + 32CoF_2 + 16\ HF).$$

The temperatures in the reactor were adjusted to 225 ±25°C. at the feed end and graded up to 350°C. at the exit end. The vaporizer was heated to 150°C. and the condenser was cooled to -30 to -40°C. The liquid n-heptane was fed dropwise (0.4 - 0.6 cc. per minute) into the vaporizer.

From the vaporizer the gaseous n-heptane was passed through lagged lines to the manifold feed of the reactor. As soon as the organic feed came in contact with the cobalt trifluoride, the fluorination started as evidenced by a temperature rise in the reactor. The gas burners were adjusted to maintain a temperature of 200 ±25°C. at the feed end with the feed rates given above. The exit gases, HF and crude Ø-heptane, were passed through the nickel screen to remove cobalt fluoride dust and into the condenser. It was found necessary to heat the dust collector in order to avoid condensation in the lines. This was done by leading the hot burner gases up around the dust collector by means of a stack.

During the run the pressure inside the nickel screen was observed by means of a manometer to check for any plugging of the screen or lines. The product was collected in a cold receiver with a conical bottom and bottom drain valve. After the heptane feed was finished, the reactor was swept with nitrogen to displace the fluorocarbon into the condenser. The fluorocarbon layer (Sp. G. - 1.7) was separated from the HF layer (sp. gr. - 1.0) by drawing off the lower layer into dilute KOH.

The HF was drowned into ice and water and a small amount of fluorocarbon was recovered by separation from the aqueous layer. The total crude fluorocarbon was washed with dilute KOH to remove HF, separated from the aqueous layer and dried with anhydrous sodium sulfate.

A normal run of 100 cc of n-heptane (68 grams) gave 212 grams of crude Ø-heptane or 80.3% of theory based on complete reaction. The HF recovery was 190 grams or 87% of theory for complete reaction.

The amount of n-heptane that could be run without exhausting the reactor more than 70% was about 68 grams. With this size run, the handling losses were an appreciable percentage of the total yield. The yields given in this report are based on weight of Ø-heptane recovered after separating the HF, washing and separating the aqueous layer, and do not include any of the above handling losses. It is estimated that approximately 5% of the yield was lost in working up the samples in the average runs.

The following table shows the effect of running the fluorination at various temperatures with the temperature held uniform throughout the length of the reactor. In each run, n-heptane from Westvaco Chlorine Products Co. was used and the feed rates were between 17 and 21 grams per hour. The runs were kept small enough to insure the CoF_3 being less than 50% exhausted. The estimated time of contact in the reactor for these runs was of the order of magnitude of 2-3 minutes. The HF evolved was determined by the difference between the total weight of product and HF and the weight of product after washing with caustic.

TABLE I

Effect of Temperature on Yield and Completion of Fluorination

Run No.	n-Heptane fed (gms.)	Temp. °C.	Yield Crude ø-Heptane (gms.)	Yield Crude ø-Heptane (% Theory)	Yield HF gms.	Yield HF % Theory
16	54.6	150	95.1	44.8	77.3	44.3
24	47.6	200	142.1	76.9	118	77.5
25	40.8	250	126.1	79.8	119.2	90.6
26	40.8	300	134.7	87.9	121.7	93.5
28	40.8	350	126.1	79.6	114.0	87.3
30	50.7	400	167.7	85.0	168.3	104

Considering the amount of HF evolved as a criterion of completion of fluorination, the above results indicate that elevated temperatures, 300°C. or higher, are necessary to force the reaction to approximate completion at the contact times used. The lower [illegible] of both HF and fluorocarbon in run 28 at 350°C. indicated some [illegible] loss. Due to pressure of other work, this run was not [illegible].

In an attempt to high-spot the quality of the crude ø-heptane obtained in these runs, a distillation was made of each crude through

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a small heated jacket column containing a Nichrome spiral. Only a little fractionation was effected, but a distillation range was obtained which gave a rapid method of comparing various crude φ-heptanes.

Fig. 1 shows the comparative distillation ranges for the crudes described above. The temperatures given are head temperatures taken at the stage of the distillation indicated. In each case the holdback of the column was about 7-8%.

These results indicate that the degree of fluorination increases with increased temperature of fluorination as evidenced by disappearance of higher boiling materials. The formation of lower boiling products which resulted from cracking or byproduct ring closure reactions increases with increased temperature of fluorination. However, use of the manifold distributing feed and close control of temperatures and feed rates to avoid hot spots in the reactor, has reduced the amounts of lower boiling products to 5-10% which is considerably below the 20-30% reported earlier by other investigators using static reactors or single feed rotating reactors.

In order to reduce the local overheating to a minimum, most of the fluorinations using n-heptane as feed material have been made with the temperature at the feed end 225 ±25°C. and at the exit end about 300-350°C. The crude φ-heptane obtained under these conditions still contained considerable amounts of incompletely fluorinated compounds and required a second pass over CoF_3 after removal of the diluting HF in order to complete the reaction.

The following table shows the results of a series of fluorinations made with a temperature graded from 225°C. to 350°C. at feed rates of 0.4 to 0.6 cc heptane per min. In each case Westvaco grade n-heptane was used. Since these runs were made by various inexperienced operators, the variations may be considered to be due to differences in controlling feed rates and temperatures.

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FIGURE I

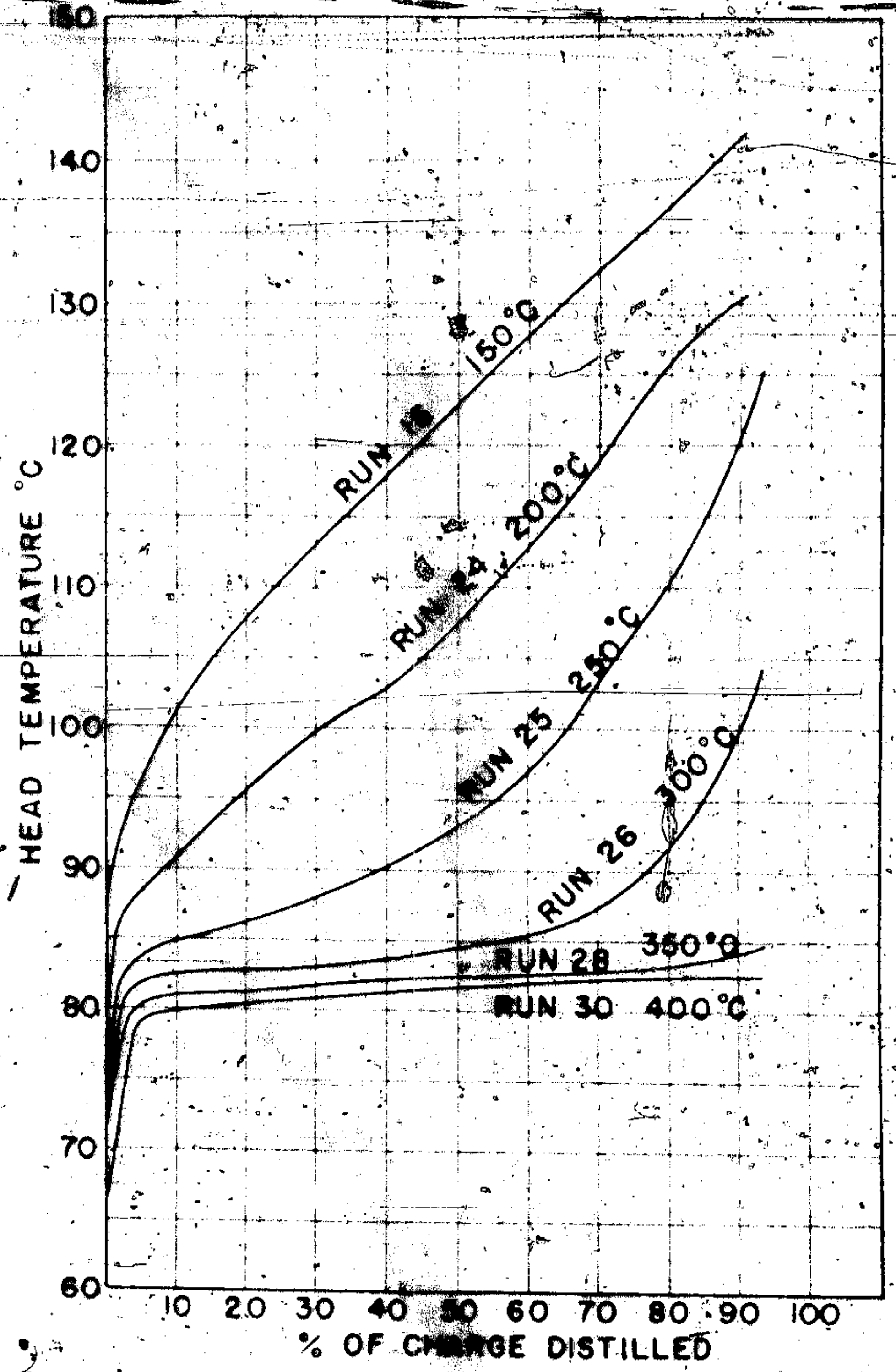

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TABLE II

Fluorination of n-Heptane - Consistency Series

Run No.	n-Heptane fed (gms.)	Yield Crude Ø-heptane gms.	Yield Crude Ø-heptane % Theory	Yield HF gms.	Yield HF % Theory
10	54.6	160	75.5	148	84.8
17	54.2	160	76.1	150	86.5
19	54.0	183.5	88.0	167	97.0
22A	68.0	216.5	81.7	208	95.0
23A	68.0	217.9	82.6	209.4	96.3
27	54.4	176.6	83.8	166.9	93.5
37	68.0	204.6	80.1	207.4	95.0

The higher HF recovery in the latter runs is a reflection of an improved operating technique rather than a real increase in completion of fluorination, since these crudes all showed about the same distillation range.

A typical distillation range (spiral column) for a first pass crude run under the above conditions (Run 23A) is given below.

% Distillation	Head Temp. °C.
Start	72.0
5	81.5
10	82.5
20	83.5
40	84.5
60	85.5
80	90.5
92 (max. temp.)	104.0

The effect of percentage exhaustion of the CoF_3 was checked by making a normal sized run (60-70% exhaustion), collecting the sample and then running an additional 30% of n-heptane through the reactor at the same feed rate to give 75-85% exhaustion. In general, the amount of low boiling material in the second portion was not materially increased over that in the first portion as evidenced by the distillation range, but due to the lower actual contact time the fluorination was not as complete. This less complete reaction was shown by an increase in the amount of high boiling products and may have amounted to about 10% less reaction.

A series of five runs (Runs 38-40, 42-43) were made to give a composite of crude ø-heptane for distillation studies. In these runs a graded temperature was used in the reactor (225-350°C.). The amount of fluorocarbon dissolved in the HF was discarded. The yields of washed crude varied from 73 to 83%, with an average yield of 79.5% of theory based on complete reaction. A composite of the washed and dried crude ø-heptane from these five runs was repassed through the reactor at 300-350°C. at a feed rate of 2-3 cc per minute (run 44). The second pass runs were made in the same manner as first pass except that higher temperatures were used and more rapid feed rates (2-3 cc. per minute). Since there was no appreciable amount of HF formed to act as a diluent, the contact time was about 5 minutes at these feed rates.

The second pass crude was separated from the small amount of HF formed, washed with dilute KOH and dried with anhydrous sodium sulfate as described above for first pass crudes. The yields on second pass for normal first pass crudes were 99-100% of material fed or about 95% of theory based on expected weight gain corresponding to the HF evolution.

These results indicate an overall yield of second pass crude ø-heptane of about 79-80% of theory based on n-heptane used.

Figure 2 shows the distillation range of a typical first pass crude and the corresponding second pass crude. The reduction in amounts of high boiling materials is evidence of more complete fluorination.

A series of 12 additional runs (Runs 45-56) were made to supply additional crude for distillation. No effort was made to recover product dissolved in the HF. The yields in this series varied from 71 to 81% with an average of about 78% of theory.

FIGURE 2

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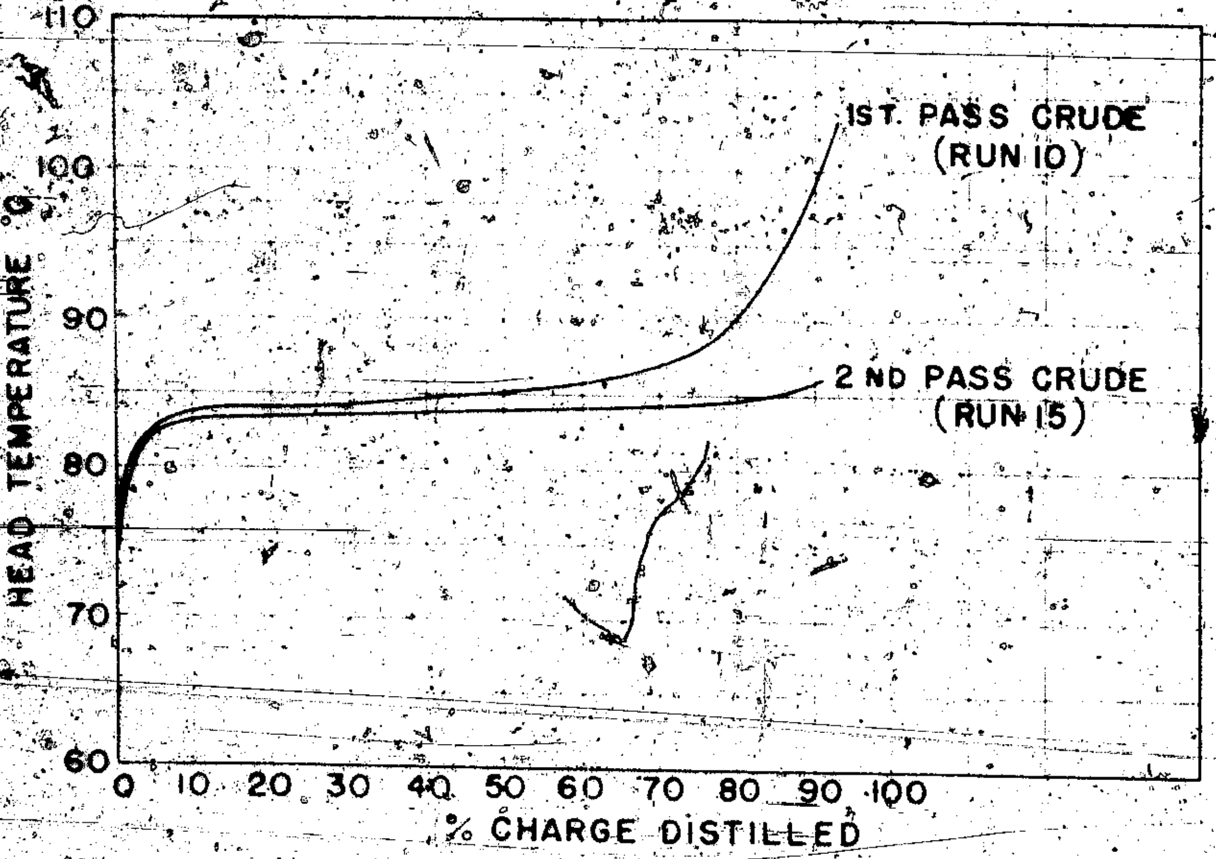

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This composite was given a second pass as run 57 with a return of 100% of material fed. There was some evidence that the second pass of this composite did not give as complete a reaction as usual probably due either to temperatures being slightly below 300°C. or too rapid a feed rate.

(B) Purification of Crude φ-Heptane:

The impurities present in crude φ-heptane as produced by the fluorination of n-heptane with CoF_3 consist of the following general types:

(1) Low boiling cracked products - completely fluorinated.
(2) Cyclic byproducts - completely fluorinated (C_7F_{14}).
    (a) φ-methyl cyclohexane - b.p. 76.33°C.
    (b) Cut No. 10 - probably φ-dimethyl cyclopentane or φ-ethyl cyclopentane - b.p. 74.5°C.
(3) Hydrogen-containing, incompletely fluorinated compounds - boiling above φ-heptane.

The low boiling cracked products are relatively easily removed by distillation.

The cyclic 714's with boiling points closer to φ-heptane are more difficult to separate. Similarly the mono and possibly dihydro φ-heptanes appear to have boiling points only slightly above φ-heptane, and are difficult to remove completely by distillation. Infra-red analyses of crude φ-heptanes prepared at Johns Hopkins University by Dr. R. D. Fowler, indicated an appreciable amount of φ-methyl cyclohexane present and somewhat lesser amounts of the No. 10 cut impurity.

To determine the amounts of C_7F_{14} compounds formed during the fluorination made in agitated scale model reactor described earlier, the composite second pass crude (run 44) described in section (A) was fractionated in a vacuum jacketed column, 48 in. x 0.5 in. packed with 1/8 in. glass helices (estimated 15-20 theoretical plates).

The following table shows the distillation ranges of the various cuts taken and their composition as determined by infra-red analyses by Dr. V. Z. Williams at American Cyanamid Company.

TABLE III

Distillation of Second Pass Crude ∅-Heptane (Run 44)

Cut No.	Reflux ratio	% of Total	Distillation range °C.	% ∅-methyl cyclohexane & Cut 10	High boilers	S.I.C.
I	50:1	6.0	71.00 - 79.13	50		1.80
II	"	8.2	79.13 - 81.58	23		1.795
III	"	10.0	81.58 - 82.38	6		1.795
IV	10:1	23.2	82.38 - 82.55	0.4		1.79
V	"	13.0	82.55 - 82.59	<0.1		1.80
VI	50:1	10.4	82.59 - 82.62	<0.1		1.81
VII	"	6.2	82.62 - 82.72		?	1.828
VIII	"	4.4	82.72 - 83.32		Some	1.876
Holdback		10.8	Above 83.32		Much	2.52

There was a 7.8% handling loss during this distillation which was carried out over a period of several days. Although there was some ∅-methyl cyclohexane detected, the major impurity reported was the No. 10 cut. The ratio of No. 10 cut to ∅-methylcyclohexane was of the order of 20 or 30 to 1.

These values indicate about 5.6% of cyclic bodies formed during the fluorination.

The S.I.C. (specific inductive capacity) which appears to be a measure of the amount of hydrogen containing bodies present will be discussed more fully in section (C) under analytical methods.

The hydrogen containing bodies which have boiling points above ∅-heptane react with process gas to a greater or lesser degree. The repassing of hydro ∅-heptanes over CoF_3 at 300-350°C., seems to be an effective way of reducing the amount of hydro bodies to a minimum. In general, all first pass crude ∅-heptanes show a drop in boiling point on repass over CoF_3.

Further evidence that repassing of high boiling fractions from crude Ø-heptane over CoF_3 at 300-350°C. gives more complete reaction is given by the following table. In each case the overall distillation range of the crude Ø-heptane fraction before and after repass is given. Since the amount of HF evolved was small in most cases, it was not possible to use this value as determined by weight as an indication of completion of reaction during the second pass.

TABLE IV

Effect of Repass over CoF_3 on Crude Ø-Heptane

Sample	Distillation range °C. Original	 After Repass	HF evolved (% by weight)	Process Gas Residue Before repass	 After repass
Johns Hopkins 83-84° cut	82.4-85.6°	78.2-83.6°	Trace	0.8%	0.14%
Johns Hopkins above 83° cut	82 -89.5°	79.5-83.1°	Trace	0.4%	0.10%
Johns Hopkins still residue (above 88°C.)	86 -131°	78.2-83.1	7%	0.54	0.05
Run 10	74 -103°	76 -86°	4%	0.13	0.08

These results indicate that some hydrogen containing bodies which have boiling points above Ø-heptane do not react as readily with process gas at 100°C. as with CoF_3 at 350°C. At present the best method of replacing the residual hydrogen atoms on hydro Ø-heptanes ~~seems~~ to be repeated treatment with CoF_3 at elevated temperatures (300-350°C.).

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First pass crudes showed a process gas residue varying from 0.04 - 0.13%, while second pass crudes showed values of 0.08 - 0.20. These results indicate that the process gas test does not detect quantitatively hydro ø-heptanes.

(C) Analytical Methods:

The two principle types of impurities which it is necessary to determine to a fairly close tolerance in order to meet the specifications for C_7F_{16} in the C-816 contract are as follows:

(1) C_7F_{14} compounds including both ø-methyl cyclohexane and No. 10 cut.

(2) Hydrogen containing bodies which react with process gas or have a molecular weight below 352.

The infra-red method of analysis is the only direct method to date of determining the amount of cyclic C_7F_{14} bodies in ø-heptane.

In the absence of high boiling hydrogen containing compounds, Dr. Williams' accuracy of determining C_7F_{14} cyclic compounds by this method in amounts up to the specification limit of 0.5% is ±0.1%. Attempts have been made to correlate the infra-red analyses with a more simple testing method, such as lowering of the reflux boiling point of ø-heptane, due to the presence of the lower boiling C_7F_{14} compounds.

In order to concentrate the lower boiling impurities in a small portion of the ø-heptane sample, the following distillation scheme was adopted. A 50 cc sample of the ø-heptane to be tested was distilled in a high temperature Podbielniak still with a spiral packed column with the following temperatures and cuts being taken.

(a) Equilibrium temperature at total reflux prior to any take off (E.P.T.).

(b) First 0.5 cc cut.

(c) Equilibrium temperature at total reflux at midpoint of distillation.

(d) Middle 2.5 cc cut.

(e) Holdback of column (approximately 2.5 cc.).

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The reflux boiling point (R.B.P.) was taken of the first 0.5 cc cut, middle 2.5 cc cut and 2.5 cc holdback. The apparatus for determining reflux boiling point was a small tube with sidearm condenser, and thermometer (drawing attached). A microburner was used to heat the constricted tip which had a volume of about 0.4 cc. The reflux boiling point was recorded after equilibrium as the temperature when the refluxing liquid level just covered the immersion mark of the thermometer.

A series of samples of C_7F_{16} were subjected to this Podbielniak distillation method of analysis both alone and with known amounts of ø-methyl cyclohexane (714) and Cut #10 added. The results are given in the following table.

TABLE V

Sample C_7F_{16}	J.L. 122-89 cut 3	J.L. 122-89 + cut 3 0.88% 714	Dr. Henne cut H	Dr. Henne cut H + 0.5% 714	J.L. 167-73	J.L. 167-73 + 0.5% 714	J.L. 167-73 + 0.2% Cut 10	J.L. 167-73 + 0.5% Cut 10
E.P.T.	82.27	82.00	82.37	82.21	82.35	82.17	82.18	82.00
R.B.P.								
Orig'l	82.44	-	82.55	-	82.43			
1st 0.5cc	82.34	82.04	82.41	82.26	82.33	82.22	82.23	82.02
Midpoint	82.43	82.34	82.48	82.41	82.38	82.42	82.40	82.39
Heels	82.71	82.64	83.45	83.49	82.99	82.97	82.96	82.98
ΔE.P.T. 82.44-E.P.T.	0.17	0.44	0.07	0.23	0.09	0.27	0.26	0.44
ΔR.B.P. 82.44-R.B.P. of 1st 0.5 cc	0.10	0.40	0.03	0.18	0.11	0.22	0.21	0.42

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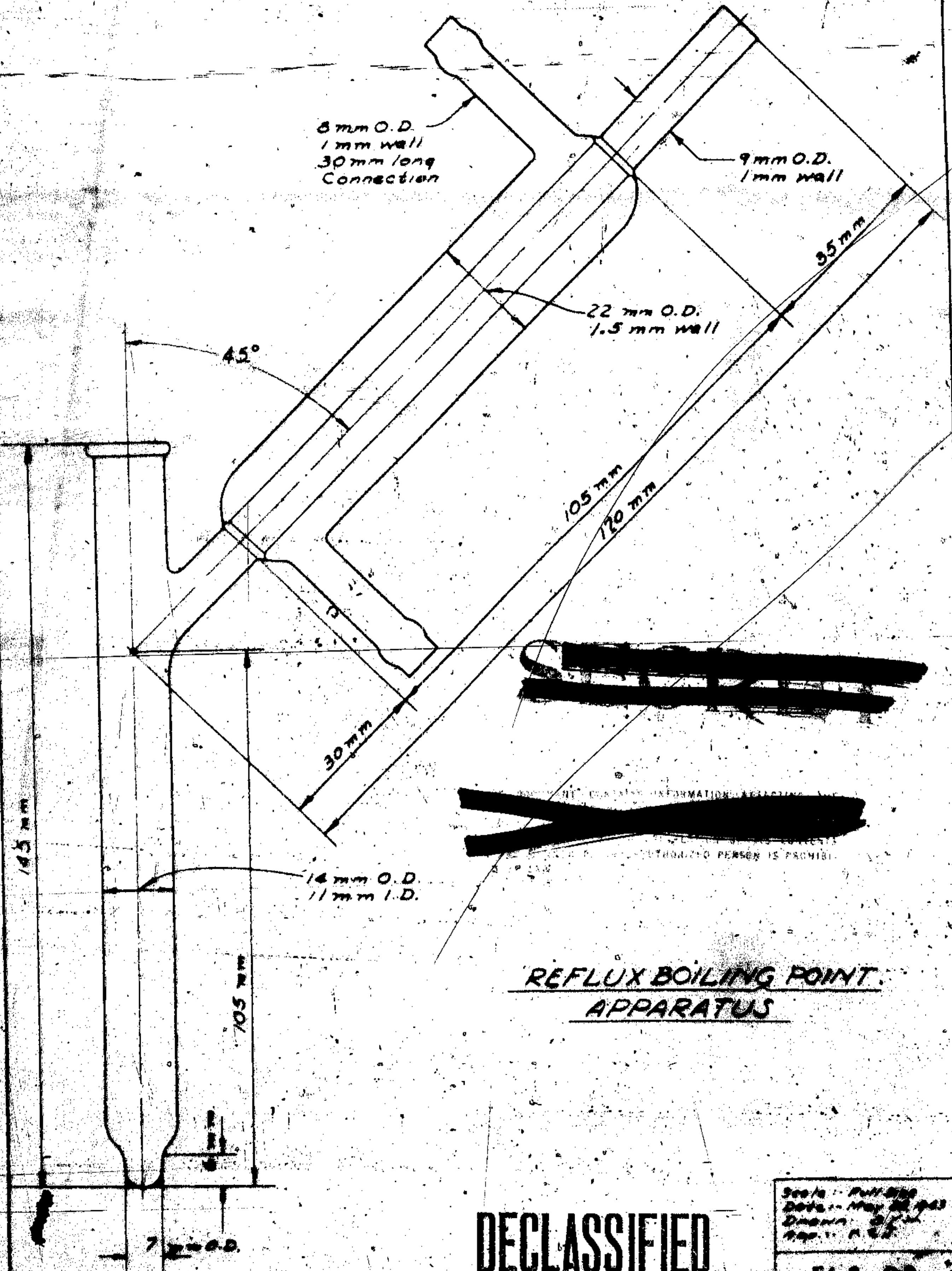

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REFLUX BOILING POINT APPARATUS

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Scale :- Full Size
Date :- May [illegible] 1943
Drawn :- [illegible]
App. :- [illegible]

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The following conclusions can be drawn from the above results:

(1) The presence of appreciable amounts of low or high boiling materials will lower or raise the reflux boiling point of a sample in proportion to the amounts present.

(2) The Podbielniak column used did not have a sufficient number of theoretical plates to remove low boilers early in the distillation as shown by the low R.B.P. of the mid-cut from samples containing added low boilers.

(3) The decrease in E.P.T. and in R.B.P. of 1st 0.5 cc with added C_7F_{14} corresponds to a change of approximately 0.03°C. per 0.1% of C_7F_{14} added to original sample.

(4) Cut No. 10 effects approximately double the change in R.B.P. of 1st 0.5 cc. caused by an equal amount of ∅-methyl cyclohexane or 0.06°C. per 0.1% Cut 10 added to original sample.

(5) The high boiling material is concentrated mainly in the holdback of the column when the original amount present is low.

Infra-red analyses of cuts from a Pod. distillation of a narrow fraction of ∅-heptane indicated an enrichment factor for ∅-methyl cyclohexane in the first 0.5 cc of only 2 to 3 times that of the total sample. The following table shows the change in composition of distillation with amount taken off. In each case a 50 cc sample was distilled. The 5% holdback contained too much high boiling material to be analyzed by infra-red methods for C_7F_{14} content.

24.X 53

TABLE VI

Sample	% of Distillate	% of Ø-methyl cyclohexane in sample	% of original Ø-methyl cyclohexane in sample
219-9			
Original	-	0.07	-
First 0.5 cc	1	0.17	3.0
4.5 cc	9	0.13	20.8
5.0 cc	10	0.06	10.6
37.5 cc	75	0.05	65.6
219-2			
Original	-	0.61	-
First 0.5 cc	1	2.0	3.6
4.5 cc	9	1.55	25.2
5.0 cc	10	1.17	21.1
37.5 cc	75	0.37	50.0

The effect of adding the lower boiling Cut No. 10 was to give a higher concentration of the impurity in the first part of the distillation than in the case of Ø-methyl cyclohexane. Since the main impurity in a narrow cut of Ø-heptane appears to be the Ø-methyl-cyclohexane rather than the No. 10 cut, no further work is contemplated on the effect of Cut No. 10 on boiling point.

Attempts to correlate the Ø-methyl cyclohexane content of a given sample of Ø-heptane with its reflux boiling point have not been entirely satisfactory in view of some uncertainties as to the absolute values of the amounts present. Infra-red analyses express the amount of impurity as an increase over a reference sample. Further work on obtaining a pure sample of Ø-heptane is in progress in other laboratories and the sample obtained will be used for future work in correlating reflux boiling points and composition as shown by infra-red analyses.

Since information available with regard to possible analyses of the hydrogen content of Ø-heptane by infra-red method was definitely unfavorable, an [illegible]pt was made to utilize boiling points or other physical properties for this purpose. All evidence to date has indicated that high boiling fractions from crude Ø-heptane contain hydrogen since they evolve HF on further treatment with CoF_3 at elevated temperatures. The boiling points of retreated crudes approached the boiling point of Ø-heptane itself.

In view of the possible dipole that might be set up in Ø-heptane containing one hydrogen atom, the dielectric properties of various fractions of Ø-heptane were measured.

A small cell was devised to measure the capacity of the organic liquid. This cell consists of an outer brass shell, 0.513" I.D. x 3.5" long with an insulating plug at the bottom. The plug contains a centering pin through it which acts as the electrical connection for an inner brass cylinder (0.5" x 3.0") which is inserted into the shell. The upper end of the insert cylinder centered by an insulating ring machined to fit the outer shell. The second electrical lead was taken off the outer metal shell. The annular space between the shell and insert cylinder is 0.0065" and the cell has a total volume of about 1 cc of liquid.

The dielectrical capacity of the cell containing air was measured as approximately 146 $\mu\mu$farads. The dielectrical capacity of the cell containing the sample to be tested was measured. The specific inductive capacity (S.I.C.) was calculated as the ratio between the dielectric capacity of the cell with the sample and with air. In general it was found that samples of completely fluorinated heptane from different sources had consistently a value for the S.I.C. of 1.77 - 1.78. Samples which contained hydrogen, as shown by evolution of HF on further treatment with CoF_3, showed higher S.I.C. values.

In order to correlate roughly the amount of hydrogen (expressed as percent mono hydro Ø-heptane) with the S.I.C. value, several samples of crude Ø-heptane were treated exhaustively with CoF_3 to evolve HF. This was done by passing the sample (vapor phase) through CoF_3 (350°C.) in a small static laboratory reactor (1" x 9") and absorbing the HF evolved in standard caustic.

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From the amount of sample fed and the moles of HF evolved, the hydrogen content of the sample can be expressed as % monohydro-ø-heptane.

The following table shows the approximate correlation betwee S.I.C. and hydrogen content of some crude ø-heptanes.

TABLE VII

Sample	% Monohydro ø-heptane by HF evolution	S.I.C.
Run 28 (1st pass crude) 350°C.	23	1.93
Run 44 (2nd pass crude)	13	1.88
Run 30 (1st pass crude) 400°C.	3	1.83
ø-Heptane	0	1.78

Assuming a straight line relationship between % monohydro ø-heptane and S.I.C., these results indicate a change of S.I.C. of 0.006 - 0.009 per % of monohydro body present.

The presence of polyhydro compounds which do not show a proportional increase in S.I.C. per hydrogen atom and cyclic bodies such as ø-methyl cyclohexane (S.I.C. 1.85) could account for the discrepancies noted in the results obtained with these crude ø-heptanes.

Samples from a fractionation made by Dr. Henne at Ohio State University of high boiling cuts of ø-heptane were evaluated for S.I.C. and reflux boiling point (R.B.P.). The bulk of these sample was assumed to be substantially free of low boiling cyclic compound and high boiling polyhydro bodies.

The following table shows the relation between S.I.C. and R.B.P. for these samples. The lowest S.I.C. value obtained to date for a ø-heptane fraction essentially free of hydro bodies and ø-

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methyl cyclohexane is 1.772. The cut temperatures for boiling range were read from the distillation curve and are approximate.

TABLE VIII

Cut No.	Boiling range °C. (745 mm.)	S.I.C.	R.B.P. (760 mm.)
1	81.9 - 82.1	1.919	83.00
2	82.1 - 82.3	1.940	83.10
3	82.3 - 82.4	1.968	83.23
4	82.4 - 82.7	2.010	83.38
5	82.7 - 83.4	2.105	83.88
6	83.4 - 85.2	2.362	85.18
7	85.2 - 86.1	2.632	86.63
8	86.1 - 86.4	2.718	87.16
9	86.4 - 86.45	2.738	87.27
10	86.45- 86.55	2.746	87.37
11	86.55- 86.60	2.750	87.39
12	86.60- 86.60	2.756	87.48
13	86.60- 86.75	2.766	87.58
14	86.75- 86.90	2.780	87.68
15	86.90- 87.20	2.808	87.88
16	87.20- 88.90	2.864	88.58
17	88.90- 91.10	2.954	90.98

Assuming Cut 11, which is from the middle of the flat, to be 100% monohydro ø-heptane, the ΔS.I.C. is equal to 0.00977 per % monohydro ø-heptane on a linear basis.

Examination of the midcuts of ø-heptane for high boilers by the Podbielniak distillation method of analysis described above, appears promising. S.I.C. values for cuts from a typical Pod. distillation of a midcut ø-heptane (82.39-82.49°C.) are given below. The % of monohydro ø-heptane present is calculated from the linear ΔS.I.C. value of 0.0098 given above. A 50 cc sample was distilled and the cuts were taken as indicated.

TABLE IX

Sample, cc	S.I.C.	% Monohydro Ø-heptane in sample	Total % of monohydro Ø-heptane in orig. sample
Ø-heptane 219-35 (cut 4) 50 cc	1.775	0.3	100
Cut 1 (0 -0.5)	-	-	-
2 (0.5-5.0)	1.772	0	0
3 (5.0-10.0)	1.772	0	0
4 (10.0-25.0)	1.772	0	0
5 (25.0-27.5)	1.772	0	0
6 (27.5-32.5)	1.772	0	0
7 (32.5-37.5)	1.774	0.2	6.5
8 (37.5-42.5)	1.774	0.2	6.5
9 (42.5-49.5)	1.781	0.92	28.8
10 (Holdback) (2.0cc)	1.815	4.39	57.4

Since the high boiling monohydro Ø-heptane appears to be concentrated in the last 10-20% of the distillation, this Pod. distillation method appears promising as a control method of evaluating narrow cuts of Ø-heptane for the presence of high boiling compounds.

When 2% of monohydro Ø-heptane was added to a cut of Ø-heptan and the mixture subjected to the Pod. distillation analysis, the results indicated that some high boilers were appearing in the earlier cuts. This is additional evidence that the spiral packed Podbielniak column being used is not sufficiently efficient to give good separation.

Calculating the % of monohydro Ø-heptane by the S.I.C. method in the various cuts as compared to the original sample gives a close agreement on the total.

Additional work is required on the measurement of S.I.C. to determine the effect of temperature and to ascertain whether a linear or a logarithmic law of mixture applies. The latter method of calculation (Ref: Physik. Zeit. 27, 115-158, (1926)) is given by the following expression:

$$\varepsilon_m = \varepsilon_1^{\theta_1} \cdot \varepsilon_2^{\theta_2}$$

where ε_m = dielectric constant of a mixture
θ_1 = mole fraction of compound 1 with a dielectric constant of ε_1
θ_2 = mole fraction of compound 2 with a dielectric constant of ε_2

In the lower concentration of monohydro ø-heptane both methods of calculation give good agreement.

Additional investigation of the Podbielniak column as an analytical method for determining both low and high boilers will await the installation of a new Podbielniak column of high efficienc

Stability Tests:

The stability of various samples of ø-heptanes to process gas has been tested by the method proposed in the specifications for the C-716 contract. This test consists in heating a dry sample of the ø-heptane (100 grams) with about 10% of its weight of process gas for 3 hours at 100°C. and weighing the residue remaining in the reactors after pumping out the excess process gas and ø-heptane.

The principle difficulties encountered to date in these tests are as follows:

(1) Difficulty in getting consistent blanks of less than 10 mg. with process gas alone.
(2) Mechanical troubles involving leaking valves on the reactors and in the loading system.
(3) Difficulty in differentiating between residue forming materials inherent in the ø-heptane cut and extraneous material such as moisture, oxygen or grease introduced with the sample.

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It has not been difficult to prepare samples of Ø-heptane which pass the specification limit of 0.1% residue given in the C-716 contract. Additional work will be required to determine the consistency with which a residue test of 0.02% can be met.

(D) Miscellaneous Experimental Work:

Solubility data

The solubility of water in Ø-heptane and of Ø-heptane in wate were estimated roughly by adding a small amount of the material to be tested to a large volume of the solvent, shaking vigorously for a period of time and observing the disappearance of the second phas

At 28°C. water will dissolve less than .003% of Ø-heptane an at the same temperature Ø-heptane will dissolve less than .003% of water.

While no quantitative results are available, evidence obtained to date indicates that the solubility of Ø-heptane in anhydrous hydrogen fluoride decreases appreciably as the degree of fluorination is increased.

Samples of liquid HF separated from crude Ø-heptanes after the fluorination step have contained from 1.2% to 7.0% of dissolved fluorocarbons depending on the quality of crude Ø-heptane. The more nearly complete the fluorination as shown by the distillation range of the fluorocarbon, the lower the solubility of the product in HF.

Purity of Intermediates

The bulk of the work in this report is based on the use of synthetic grade n-heptane as produced by Westvaco Chlorine Product Co. By infra-red analysis, this material is equivalent in quality to the Rossini standard n-heptane with respect to methyl cyclohexane content (less than 0.5%).

Samples of n-heptane have been received from Phillips Petroleum Co. which are poorer in this respect than the Westvaco material. One sample of n-heptane was obtained from Phillips whic represented material isolated from a petroleum fraction by repeate azeotropic distillations and fractionations. This material was judged by Dr. Williams at American Cyanamid Co. to have about 1% more methyl cyclohexane than the Westvaco material.

Three runs were made fluorinating this sample of n-heptane in the manner described in Section (A). After repassing, the composite crude Ø-heptane was distilled and found to have appreciably more low boiling material than Ø-heptane from the Westvaco grade n-heptane.

In view of the fact that any methyl cyclohexane would consume fluorine and give no usable product, it was agreed that n-heptane supplied for production of C_7F_{16} in the C-816 contract would be similar in quality to Westvaco grade synthetic n-heptane.

Final page of Progress Report
Fluorination of n-Heptane with CoF_3

Jackson Laboratory
June 30, 1943
ahs

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