

Production of POLYPERFLUOROVINYL CHLORIDE

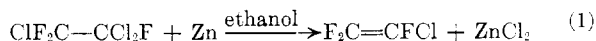
E. A. Belmore, W. M. Ewalt, and B. H. Wojcik

HOOKEE ELECTROCHEMICAL COMPANY, NIAGARA FALLS, N. Y.

THE method developed by Miller and associates at Columbia University for the preparation of the polyperfluorovinyl chloride was successfully applied to pilot plant operation. Perhalovinyl polymers varying in consistency from colorless, stable oils to solid resins were readily obtained. Reaction conditions employed for the polymerization of perfluorovinyl chloride were significant in influencing the degree of polymerization and the type of polymer isolated. A molecular still was utilized for the segregation of the oily constituents from the resinous products. Final treatment of the polyperfluorovinyl chloride oils with cobalt trifluoride increased the thermal and chemical stability of the oils. A procedure was developed for the conversion of solid resinous material to oily products. A flow sheet shows the various steps in the synthesis, and data accumulated during pilot plant operation are included.

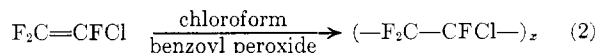
A LABORATORY method for the preparation of a fluorine-containing oil having a high chemical inertness and certain definite physical properties was worked out by W. T. Miller and associates at Columbia University. To make this oil, perfluorovinyl chloride was prepared and then polymerized, and the desired oil was separated from the crude polymer by distillation under vacuum. The Hooker Electrochemical Company was assigned the task of developing the laboratory process into a suitable plant operation. This paper describes briefly the development work carried out in connection with this problem; four steps were involved.

The first is the preparation of perfluorovinyl chloride monomer:



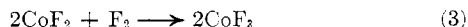
The 1,2,2-trichloro-1,1,2-trifluoroethane is dechlorinated by zinc suspended in ethanol to give perfluorovinyl chloride. This compound boils at about -27°C . and is removed from the reaction mixture through a fractionating column.

The second step is polymerization of perfluorovinyl chloride:



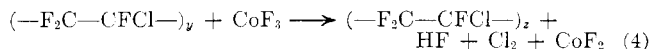
The pure monomer, dissolved in chloroform containing the benzoyl peroxide catalyst, is heated in a pressure vessel where polymerization rapidly occurs. When the reaction is complete, the chloroform and other volatile materials are stripped off to leave behind the polymer concentrate. The desired oil fraction is separated from this concentrate by distilling under high vacuum.

The third step is the preparation of cobalt trifluoride:



Cobalt trifluoride is used in the following step and is prepared by treating anhydrous cobaltous fluoride with elemental fluorine, which readily oxidizes it to the trivalent state.

The fourth step is the treatment of distilled polymer:



The selected fraction, distilled from the crude polymer of step 2, is treated at 200°C . with an equal weight of cobalt trifluoride. This treatment saturates double bonds and replaces hydrogen and loosely attached chlorine atoms with fluorine.

PREPARATION OF PERFLUOROVINYL CHLORIDE

A 5-gallon reactor, patterned after one used by Miller and co-workers, was set up and a number of preliminary runs made to acquire firsthand experience with the reaction. From this study a 110-gallon reactor was built, equipped with a packed column for removing the perfluorovinyl chloride. Figure 1 is a diagram of this unit.

Anhydrous ethanol was mixed with finely divided zinc dust in an agitated iron tank, and the slurry charged into the reactor. The circulating trichloroethylene, used as a cooling medium, was cooled to a temperature between -50° and -60°C . with dry ice. The trichlorotrifluoroethane, obtained from Kinetic Chemicals, Inc., was fed directly into the reactor, which was heated to 70°C . The rate of feed was controlled by means of a rotameter. Vapor temperature, reactor temperature, and the pressure drop through

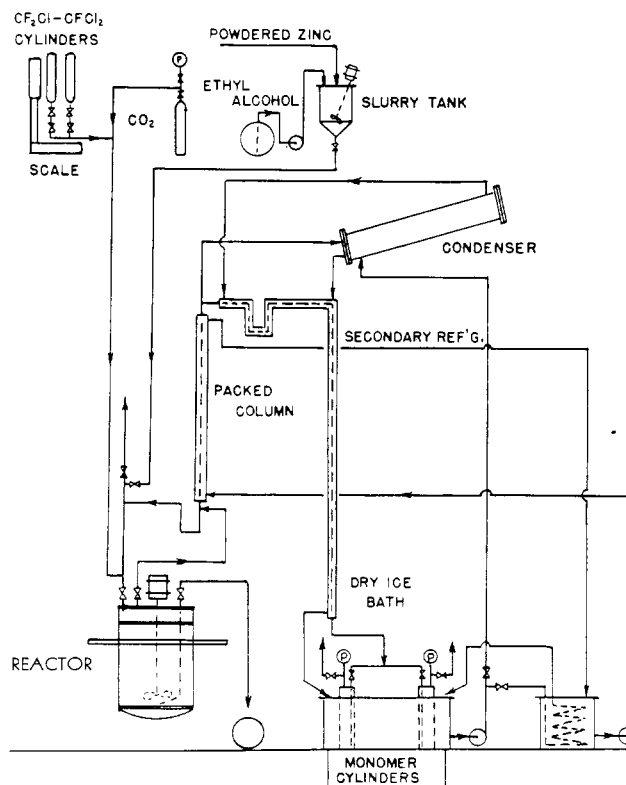


Figure 1. Apparatus for Monomer Preparation

the column were the primary indications of proper operating conditions. The fractionated product was collected in steel cylinders surrounded by a trichloroethylene-dry ice bath. All lines handling the product were either jacketed with the trichloroethylene coolant or thoroughly insulated.

In general the reaction seemed to be rapid and straightforward and presented no unusual problems. Table I shows the data from five runs carried out with this equipment.

The yields of perfluorovinyl chloride varied from 79 to 92% of theory based on the weight of trichlorotrifluoroethane used. This variation was not due to any inherent characteristic of the reaction but to the skill and care of the operator. The use of adequate control instruments would probably have produced consistently high yields. The amount of zinc used was approximately 40% in excess of the theory required, but no attempts were made to recover this excess or the alcohol from the residue in the reactor. After these runs, arrangements were made with the Du Pont Company to supply the monomer necessary for future work, so this phase of the problem was discontinued by the Hooker Company.

POLYMERIZATION OF THE PERFLUOROVINYL CHLORIDE MONOMER

Preliminary polymerization experiments were carried out in a 22-gallon pressure vessel, but for the pilot plant operation a 110-gallon steel autoclave was used. A standard charge for this unit consisted of 900 pounds of alcohol-free chloroform, 100 pounds of

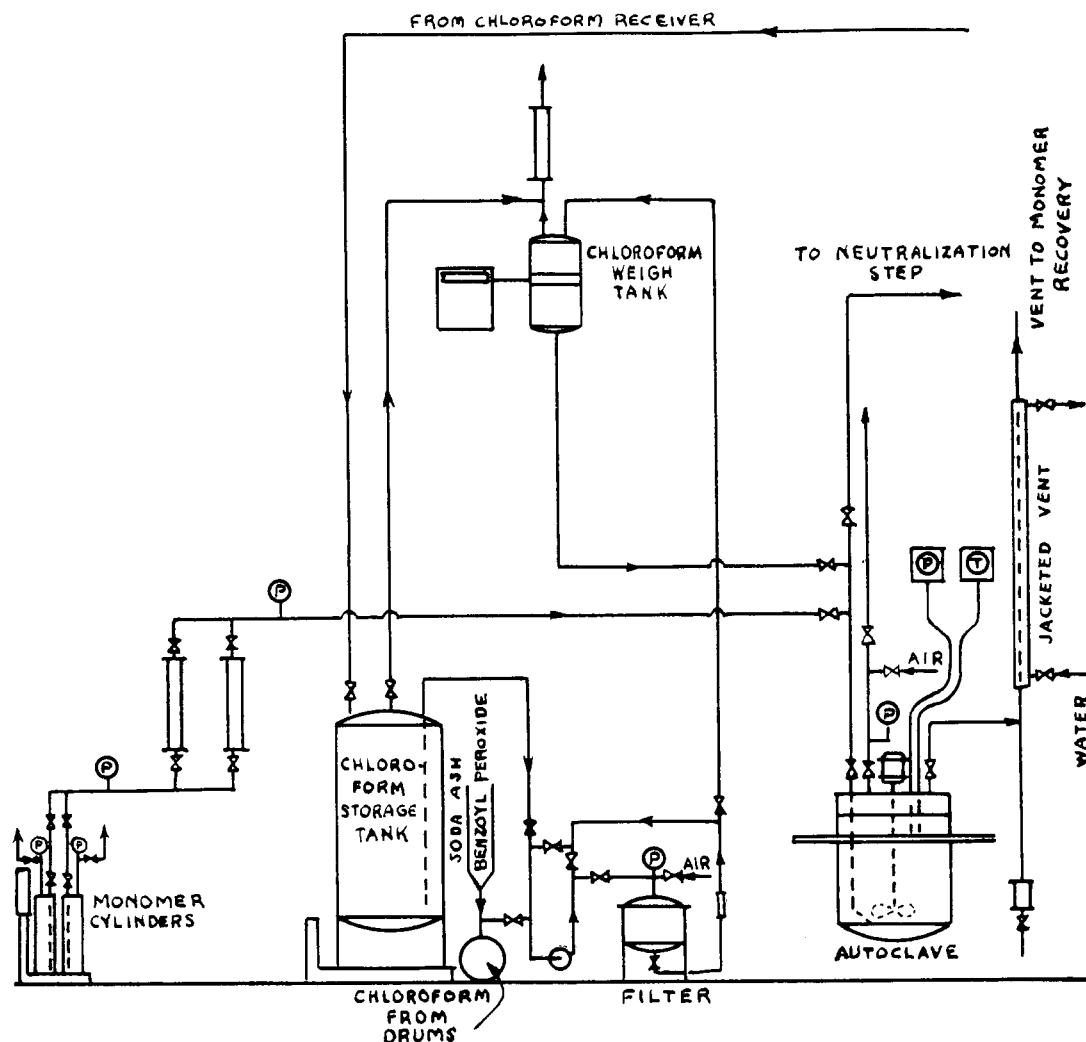


Figure 2. Flow Sheet for Polymer Preparation

perfluorovinyl chloride, and 8 pounds of benzoyl peroxide. Reaction conditions recommended by Miller were 100° C. for 90 minutes. In order to increase the productivity of each autoclave, pilot plant operations were carried out at 150° C. for 15 minutes. This change gave a polymer of a lower average molecular weight but did not markedly decrease the amount of the fraction suitable for the final product. Figure 2 is the flow diagram for the autoclave operation.

The benzoyl peroxide, which contained about 10% water, was dissolved in chloroform, treated with anhydrous sodium carbonate, and charged into the autoclave. Since most of the perfluorovinyl chloride contained a nonvolatile stabilizer, the monomer was removed from the cylinders in the gas phase and passed through phosphorous pentoxide to remove traces of moisture and alcohol before being led into the autoclave.

The reaction was carried out by starting the agitator and heating the autoclave to 150° C. in about 6 or 7 minutes. The pressure quickly rose to a maximum of about 300 pounds per square inch and then rapidly decreased as the monomer was consumed. After 15 minutes at 150° C. the autoclave was cooled to 40–50° C. and slowly vented through a dry ice-cooled condenser to recover the unreacted monomer. This was collected in cylinders and recharged into the autoclave in subsequent runs. The recovery of the monomer was complicated by the gradual accumulation of an appreciable quantity of hydrogen fluoride which had to be disposed of from time to time. The losses from this crude system were probably high, but during 100 autoclave batches an

TABLE I. PREPARATION OF PERFLUOROVINYL CHLORIDE IN 110-GALLON REACTOR

Run No.	Materials Charged, Lb.			Product	
	CF ₂ Cl—CFCl ₂	Abs. ethanol	Zinc ^a	CF ₂ =CFCl, lb.	% of theory
1	273	195	150	151	88.8
2	300	200	150	157	84.0
3	300	200	150	148	79.0
4	300	200	150	172	92.0
5	348	232	174	200	92.0
Total	1521	1027	774	828	87.3

^a A small amount of spent sludge was left in the reactor at the end of each run.

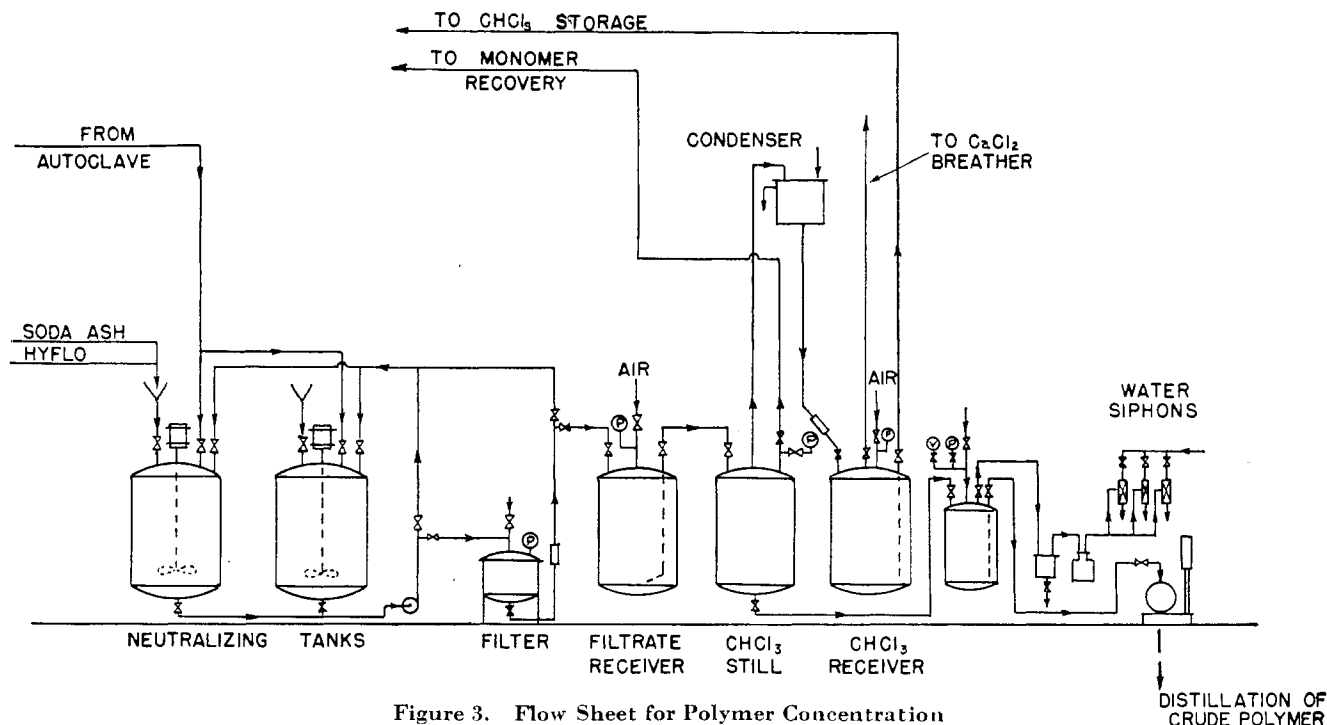


Figure 3. Flow Sheet for Polymer Concentration

average of 17% (17 pounds per batch) of the monomer charged was recovered. After venting, the autoclave was further cooled to about 25° C. and discharged into a 500-gallon holding tank (Figure 3). When five autoclave batches were accumulated, the material was treated with sodium carbonate and filter aid and pumped through a pressure filter. This step was added primarily to remove any iron that might have been picked up in the preceding operations. From preliminary work it had been found that small amounts of iron in the crude concentrated polymer greatly accelerated the rate of cracking and made distillation under high vacuum practically impossible.

The filtered chloroform solution was next transferred to a simple 500-gallon enameled still, equipped with lead accessories, where the chloroform and polymers boiling below 100° C. were removed and returned to the storage tank. The filtered solution still contained some dissolved monomer; this was recovered by returning the uncondensed gases to the monomer recovery system. The residual polymer was transferred to a 100-gallon enameled vessel and further heated to 150° C. while a vacuum was gradually built up to the maximum obtainable with water aspirators. At the same time a slow stream of air was bubbled through the polymer. This treatment served to remove volatile materials and to decompose some of the more unstable components. After this, the remaining polymer was cooled to 100–125° C. and discharged into clean steel cans. At this temperature the polymer was a tan oil which solidified into a sticky grease before room temperature was reached.

In order to isolate a fraction of the oil suitable for further processing, it was necessary to distill the crude polymer under high vacuum. At distillation temperatures the crude polymer was unstable and cracking readily occurred, accompanied by the evolution of much gas. Arrangements were made with Distillation Products, Inc., to carry out this distillation in commercial molecular stills. In their equipment the crude polymer was separated into five fractions of distillate, each containing polymer of successively higher average molecular weight, and a residue which was a brittle resinlike material melting at approximately 90° C. All fractions were returned to the Hooker Company where they were blended in the following manner: Low boiling fractions containing no usable polymer were discarded, fractions containing

less than 80% usable polymer were returned to Distillation Products, Inc., for redistillation, fractions containing more than 80% usable polymer were processed through the next step, and the rest was residue.

Table II consists of data taken from a report by Distillation Products, Inc., on the distillation of the first two samples of crude polymer submitted to them. These results were obtained on a laboratory still and are not strictly comparable to those from production units. The molecular weight determinations, however, give a good indication of the type of polymer that was being processed.

PREPARATION OF COBALT TRIFLUORIDE

Figure 4 shows the flow sheet for this operation. The elemental fluorine, from a single cell of the type described by Murray, Osborne, and Kircher¹, was led into the bottom of an insulated

¹ Murray, R. L., Osborne, S. G., and Kircher, M. S., *IND. ENG. CHEM.*, **39**, 249 (1947).

TABLE II. DATA FROM REPORT OF DISTILLATION PRODUCTS, INC., ON FIRST TWO SAMPLES OF CRUDE CONCENTRATED POLYMER SUBMITTED TO THEM

Run 12, Polymerized at 100° C. for 90 Minutes				Run 15, Polymerized at 160° C. for 10 Minutes			
Fraction No.	% of charge		Mol. wt., approx.	Fraction No.	% of charge		Mol. wt., approx.
Original	Fraction	Total		Original	Fraction	Total	
1	1.63	100.0	1040	1	4.25	...	540
2	3.92	5.55	640	2	2.90	7.15	...
3	5.00	10.55	700	3	7.17	14.32	582
4	4.73	15.28	...	4	5.10	19.42	...
5	4.10	19.38	772	5	5.35	24.77	660
6	4.03	23.41	...	6	8.62	33.39	...
7	4.73	28.14	872	7	2.92	36.31	760
8	2.38	30.52	...	8	3.62	39.93	...
9	4.72	35.24	1050 ^a	9	5.40	45.33	960 ^a
10	8.10	43.34	...	10	4.10	49.43	...
11	3.45	46.79	1260	11	5.40	54.83	1080
12	0.83	47.62	...	12	1.94	56.77	...
13	6.04	53.66	1580	13	3.46	60.23	1260
Cold trap	10.70	64.36	...	14	5.04	65.27	...
Residue	28.80	93.16	2000	Cold trap	6.04	71.31	...
				Residue	21.6	92.9	2040

^a These and subsequent fractions were waxy solids at room temperature.

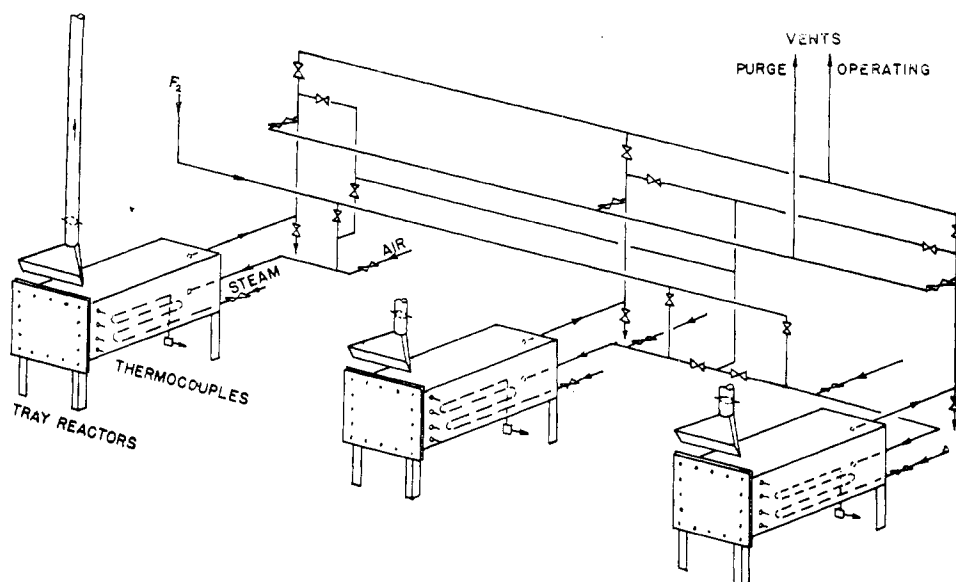


Figure 4. Flow Sheet for Cobalt Trifluoride Preparation

steel reactor which contained six removable steel trays, each charged with a uniform layer of cobalt difluoride. The trays were so arranged in the reactor that the fluorine was forced to pass over the surface of each tray in series. The gas emerging from the first reactor was passed through a second one and finally out the vent. This reaction proceeded rather slowly until a temperature of approximately 75° C. was reached, but after this it was quite vigorous. The temperature increased rapidly to about 200° C. and then decreased slowly as the reaction neared completion. On a few occasions a reaction too rapid and too localized caused a sufficient rise in temperature to burn large holes in the trays.

Material averaging 91% cobalt trifluoride was obtained from new cobalt difluoride. No attempts were made to regenerate any used cobalt salts.

TREATMENT OF DISTILLED POLYMER

In this operation the selected blend of distilled crude polymer was treated with successive portions of cobalt trifluoride at increasingly higher temperatures. A total weight of cobalt trifluoride equal to the weight of the polymer was added, and a maximum temperature of 200° C. was reached.

A 115-gallon steel vessel was constructed for carrying out this reaction. It was equipped with a heavy scraping-type agitator driven by a 25 horsepower motor and an electrically heated oil jacket for maintaining the proper temperatures. A maximum charge consisted of 130 pounds of distilled polymer and an equal amount of cobalt trifluoride. The entire charge of polymer, together with one third the cobalt trifluoride, was added to the reactor and heated to 135–140° C. After cooling to 100° C. the second portion of cobalt trifluoride was added and the temperature raised to 150–160° C. The third portion was added in a like manner, but this time the temperature was raised to 200° C. and held there for 1.5 hours. After each addition the heating had to be carried out slowly and with care. The reaction was quite vigorous, and copious quantities of chlorine and hydrogen fluorine were given off. Care was taken to see that each heating cycle was continued for a sufficient length of time to drive off essentially all the gases.

Upon the addition of each portion of cobalt trifluoride the contents in the reactor became increasingly more viscous and more difficult to agitate. After the last addition the mixture was a semisolid paste resembling wet sand in appearance. A heavy

load was thus thrown on the agitating mechanism and caused much mechanical difficulty. This reactor was later replaced by a powerful kneading machine manufactured by Baker Perkins, Inc. This unit gave little operating difficulty. Figure 5 shows the flow sheet for this operation.

At the end of the heating period the reactor was cooled and a small sample of product tested for unsaturation with aqueous potassium permanganate solution. If the test was positive, another heating with additional cobalt trifluoride had to be carried out; if the test was negative, however, the material was assumed to be suitable for further processing. Enough

carbon tetrachloride was added to the reactor to form a slurry, and the mixture was discharged into an agitated tank where the oil was extracted with carbon tetrachloride several times and then filtered through a pressure filter. The dry salts were later put through another extraction step in order to recover the small amount of polymer that remained.

The filtered extract was transferred to a simple iron still where the carbon tetrachloride was removed at atmospheric pressure and any low boiling polymer stripped off under partial vacuum. The residual polymer was returned to Distillation Products, Inc., for the final distillation. Here again the polymer was put through a molecular still and separated into a number of different fractions of increasingly higher molecular weight. At this point the polymer was quite stable and had little tendency to crack at the temperatures necessary for high vacuum distillation.

Selected fractions of the distilled polymer were blended to make up the finished product and to meet the specifications shown in the following table:

Color	Water white
Acidity	Nil
Max. water, %	0.005
Max. vapor pressure at 140° F., mm.	8.0×10^{-3}
Max. viscosity at 210° F., centipoises	25.0
Stability	Inert to CoF_3 at 200° C.

Table III shows the over-all yield of the desired product, together with the various losses during the polymerization and subsequent processing steps. These values are the actual ones obtained during a pilot plant operation which consumed over 8000 pounds of perfluorovinyl chloride. The over-all efficiency of the entire process was lower than it should have been because of the pressure of time and the necessity of using equipment that was immediately available.

TABLE III. MATERIAL BALANCE FOR PERFLUOROVINYL CHLORIDE DURING POLYMERIZATION AND PROCESSING

Operation	Main Product	Residues	Low Boilers	Unaccounted for
Monomer input	100.0	—	—	—
Polymerization and concn.	66.4	—	8.0	25.6
Distn. of crude concentrate	33.6	24.4	6.0	2.4
Stabilization of distd. crude	28.6	—	5.0	—
Final distn.	18.3	0.6	9.0	0.7
Total as % of monomer	18.3	25.0	28.0	28.7

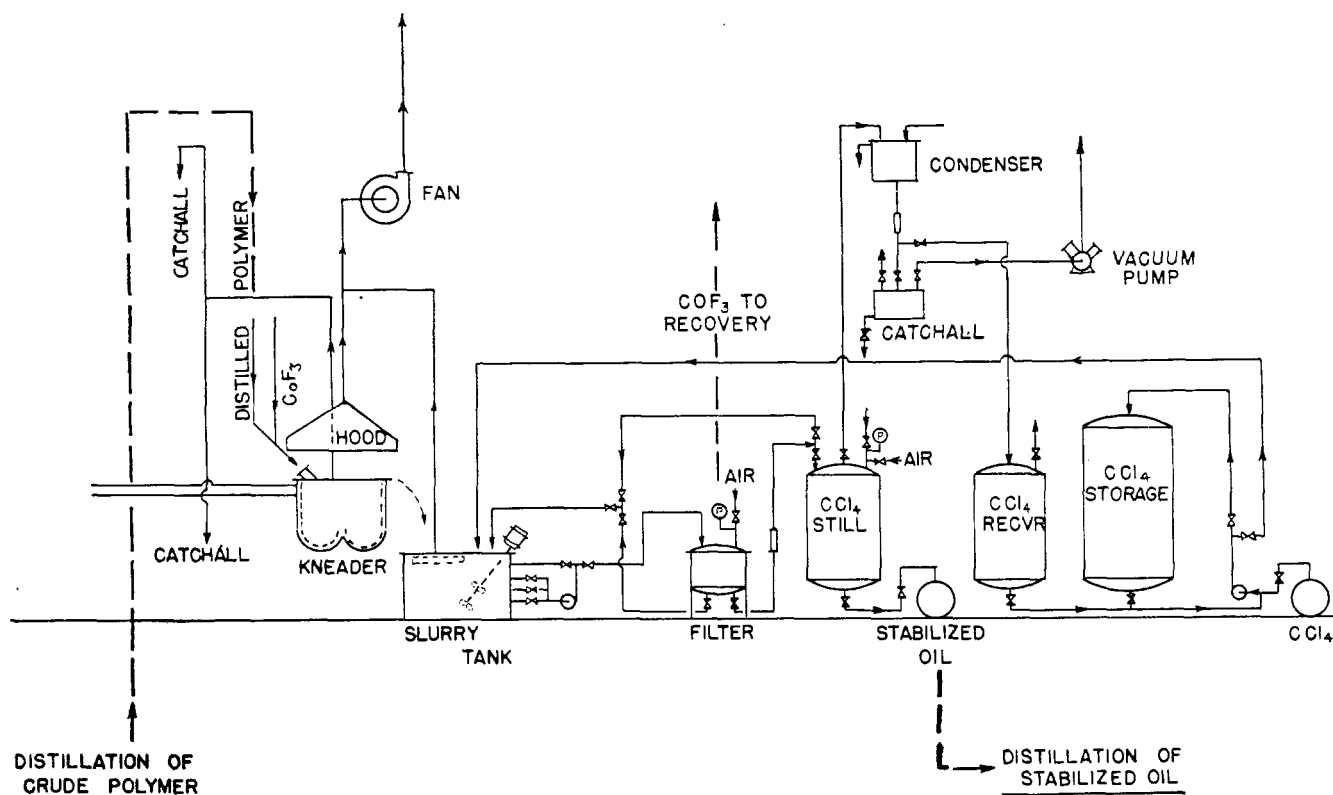


Figure 5. Flow Sheet for Stabilization of Distilled Polymer

The total monomer used is taken as 100 units so that the other values will read directly as percentages of this number. Values in the horizontal line to the right of the indicated operation represent the materials recovered from this operation. The value in the first column represents the number of the original 100 units used in the following operation.

Although the losses during polymerization and concentration were undoubtedly high, this value appears much worse than it actually was. During the recovery of the chloroform the vapor temperature of the still was taken to 100° C. or higher, and this resulted in the inclusion of low boiling polymers in the recirculating chloroform. Since this was not measured, it appears as an unaccounted-for loss.

It was later discovered that the solid residue from the first distillation, representing about 25% of the original monomer, could be cracked to yield about 60% of usable polymer. The cracking of all these residues would have increased the over-all yield of usable oil to about 30% of the original monomer.

Table IV shows a series of laboratory experiments with the cracking of several types of high boiling polymers into usable oil.

The procedure consisted essentially in heating the residue in a single still under pressure of 15–20 mm. At about 275° C. cracking began, and the entire contents of the still distilled over to form a heavy viscous oil. This oil could be processed to yield the finished product in the same manner as the crude material from the original polymerization.

Based on laboratory work, a small nickel still was built which would crack about 200 pounds of residue per batch. A number of runs were made in this unit, and the results obtained were similar to those obtained from the laboratory experiments. It was also learned that the degree of cracking could be controlled to a considerable extent by the pressure maintained on the still during the cracking operation. As the distillation pressure increased, the molecular weight of the product tended to become progressively lower.

ACKNOWLEDGMENT

The authors express their thanks to the Manhattan District, U. S. Army Corps of Engineers, who helped in the guidance of this project and whose financial support made it possible. The authors also wish to thank W. T. Miller and associates at Columbia University for their many helpful suggestions.

TABLE IV. RESIDUE CRACKING EXPERIMENTS

Source of Residue	Apparatus	Fore-shot, %	Good Fraction, %	Residue, %	Loss, %	Final Pressure, Mm.	Final Temp., C.	
							Vapor	Body
Step 2 residue + 50% foreshot and treated with COF_3	Glass	44	38	6	12	30	320	350
Step 2 residue + 50% foreshot and treated with COF_3	Nickel	44	36	8	12	30	200	365
Unstabilized residue (hard, black, resinlike)	Glass	4	67	9	20	40	300	330
Same	Nickel	3	65	12	20	40	280	370
Crude polymer from plant	Glass	16	70	5	10	35	330	360
Same	Nickel	16	74	4	6	20	300	330
Same	Nickel	16.5	67.5	..	16	25	190	360
Same	Nickel	16.5	71.6	..	10	20	185	380
Same	Iron & glass	16.5	67.5	6	10	30	320	350
Same	Iron & nickel	16.5	70	6	7	30	195	385

PRESENTED before the Symposium on Fluorine Chemistry as paper 85, 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.