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THE M. W. KELLOGG COMPANY
Petroleum & Chemical
Research Dept.
Jersey City, N. J.

Report No. RL-51-146

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Petroleum And Chemical Research Department

⑨ PROGRESS REPORT. 1 Oct 50-1 Jan 51

⑥ Aratic Rubber.

U. S. Army Contract DA-44-109-qm-222
For the Period October - December, 1950

⑪ 1 Feb ~~1951~~ 51

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Report RL-51-146

⑩ F. J. Horn
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PROGRESS REPORT

Subject: Arctic Rubber, U. S. Army Contract DA 44-109-qm-222

Staff: J. W. Copenhaver, F. J. Honn, W. M. Sims, R. M. Mantell,
F. Schreiner

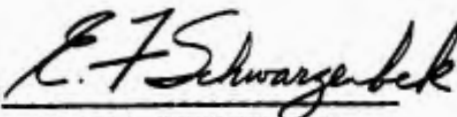
Author: F. J. Honn

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I. Introduction

A. Purpose of the Project

The primary purpose of this project is the preparation of an oil and fuel-resistant elastomer which will retain its rubber-like characteristics between -70°F. and $+160^{\circ}\text{F.}$ To achieve this goal, the M. W. Kellogg Company has been authorized by the Quartermaster Corps to carry out a broad investigation of fluorocarbon polymers, involving (1) monomer synthesis; (2) polymer preparation; and (3) polymer evaluation.

B. Research Program

In the first quarterly report, issued on October 1, 1950, a research program was proposed whereby polymers and copolymers of fluoro-olefins, fluoro-chloro-olefins, hydrocarbons, esters and other monomers are to be prepared and screened in a preliminary fashion. It was recognized then that the ideal "Arctic Rubber" must be composed of polymer chains with a high degree of inherent flexibility and little or no tendency to crystallize on prolonged exposure to low temperatures. These requirements may well be met by preparing a disordered chain, partially or wholly fluorinated, with side groups large enough to prevent packing yet not too bulky to impede rotation about single bonds, with relatively few polar groups to give rise to interchain cohesion, and with a certain amount of residual unsaturation or functionality to permit vulcanization to a network structure inherently more resistant to crystallization and solvent penetration. For the immediate future, progress toward this ideal structure involves copolymerization of the following, currently available monomers: $\text{CF}_2=\text{CFCl}$, $\text{CF}_2=\text{CH}_2$, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$, $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$, and $(\text{CH}_3)_2\text{C}=\text{CH}_2$. As other monomers become available through purchase or synthesis, additional copolymer pairs will be evaluated.

C. Past Progress

Progress during the first quarter ending October 1, 1950 was confined largely to the erection and operation of a unit for the thermal dimerization of $\text{CF}_2=\text{CFCl}$. Approximately 25 pounds of liquid product were obtained, from which the following monomers could be derived by distillation, chlorination and dechlorination: $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$, $\text{CF}_3-\text{CF}=\text{CF}_2$, $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$, $\text{CF}_3-\text{CF}_2-\text{CF}=\text{CF}_2$, $\text{CF}_2-\text{CF}=\text{CF}_2\text{Cl}$, and $\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3$. Initial distillations were completed on about 15 pounds of the crude liquid product.

II. Summary of Current Progress

During the present quarter, laboratory work has been initiated on the copolymerization of $\text{CF}_2=\text{CFCl}$ with $\text{CF}_2=\text{CH}_2$ and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. Rubber-like products have been obtained in satisfactory yield by means of aqueous suspension and emulsion recipes. The synthesis of monomers derived from the thermal dimerization of $\text{CF}_2=\text{CFCl}$ has advanced through the chlorination and distillation stages.

III. Experimental Section

A. Monomer Synthesis

The C-4 cut (boiling range 55-66°C.), which composed 41% of the crude thermal dimer derived from $\text{CF}_2=\text{CFCl}$, has been chlorinated batch-wise according to standard procedures in a five-liter flask, irradiated by ultraviolet light. Approximately 25 pounds of the chlorinated product have been fractionally distilled through a 3/4" x 36" column packed with glass helices and operated at atmospheric pressure with a reflux ratio of about 10:1. Two compounds have been obtained: about 9 pounds of $\text{C}_4\text{F}_6\text{Cl}_2$ (b.p. 59°C.) and about 16 pounds of $\text{C}_4\text{F}_6\text{Cl}_4$ (b.p. 130°C.). These compounds will be dechlorinated with zinc dust to yield the monomers $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$ and $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$.

Following is a list of monomers now immediately available for polymerization:

<u>Monomer</u>	<u>Approximate Quantity on Hand</u>	<u>Supplier</u>
$\text{CF}_2=\text{CFCl}$	Unlimited	M. W. Kellogg Co.
$\text{CF}_2=\text{CH}_2$	10 lbs.	General Chemical Div.
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	17 lbs.	Matheson Co.
$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	6 lbs.	Phillips Petroleum Co.
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	17 lbs.	Matheson Co.
$\text{CF}_3-\text{CF}=\text{CF}_2$	1 lb.	Minnesota Mining and Manufacturing Co.
$\text{CH}_2=\text{CHCl}$	25 lbs.	Matheson Co.
$\text{CF}_2=\text{CF}-\text{CN}$	200 gm.	Minnesota Mining and Manufacturing Co.
$\text{CCl}_2=\text{CFCl}$	100 gm.	Halogen Chem., Inc.
$\text{CCl}_2=\text{CCl}-\text{CF}_3$	100 gm.	Halogen Chem., Inc.

B. Polymer Preparation

The primary aim in this work has been the preparation of a wide variety of copolymers from the available monomers, with minor emphasis on the actual techniques of polymerization. The recipes used have been as simple as possible, consistent with the production of enough polymer for preliminary screening tests. Thus, in the two systems studied to



date, a water-persulfate suspension sufficed for the copolymerization of $\text{CF}_2=\text{CFCl}$ and $\text{CF}_2=\text{CH}_2$, whereas an iron-sugar-cumene redox emulsion system was needed to obtain a product from $\text{CF}_2=\text{CFCl}$ and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$.

1. Apparatus

The high pressures exerted by many of the fluorocarbon monomers have necessitated polymerization equipment somewhat more cumbersome than that conventionally employed in laboratory-scale GR-S polymerization. At the present time reactions involving $\text{CF}_2=\text{CH}_2$ (b.p. -81°C .), are being carried out in a silver-lined, 250 ml. bomb manufactured by the American Instrument Co. In recipes where $\text{CF}_2=\text{CFCl}$ (b.p. -27°C .), is the low-boiling component, 300 ml. heavy-wall, sealed glass tubes suffice. Monomers are charged into both the bomb and the glass tubes on a vacuum transfer system under O_2 -free conditions. The bomb is agitated during the polymerization period in an "Aminco" rocking device, while the glass tubes are vigorously shaken in a horizontal platform shaker. All reactions have been conducted at room temperature because of the difficulty of thermostating accurately either of the agitation devices.

Plans are now being drawn for an end-over-end tumbling polymerization bath capable of operating at temperatures above and below room temperature. Stainless steel bottles, of lighter construction than the Aminco bomb, are under consideration for the lower-boiling monomers. These bottles, sealed glass tubes, and crown-cap beverage bottles can all be accommodated in the proposed polymerization bath.

2. Copolymerization of $\text{CF}_2=\text{CFCl}$ and $\text{CF}_2=\text{CH}_2$

Copolymers of $\text{CF}_2=\text{CFCl}$ and $\text{CF}_2=\text{CH}_2$, in which the molar ratios of charged monomers ranged from 75/25 through 50/50 and 25/75 to 0/100, were prepared in the following suspension system:

Water, distilled	100 pts. by wt.
Monomers	100
$\text{K}_2\text{S}_2\text{O}_8$	0.5

Moderate to high yields were obtained for all charges except 100% $\text{CF}_2=\text{CH}_2$, where it was necessary to add 0.4 part NaHSO_3 activator. Conversion data and polymer compositions (deduced from F content) are presented below:

Run No.	Molar Ratio CF ₂ =CFCl/CF ₂ =CH ₂		% Conversion	Reaction Time
	Charged	Found		
4A	75/25	70	29	63
3	50/50	58	12	24
5	25/75	25	70	21
12	0/100	-	1	87
26 /a/	0/100	-	22	43

/a/ Activator added to recipe.

In contrast to the homopolymers of CF₂=CFCl and CF₂=CH₂ which are powdery solids, the copolymers of these two monomers are distinctly rubber-like at room temperature. Two of the copolymers (50 and 25 mole % CF₂=CFCl) are soluble in acetone; the third (75% mole % CF₂=CFCl) is markedly swollen by this solvent. Neither of the homopolymers is soluble in acetone, however. At room temperature the 50/50 copolymer is precipitated from acetone solution by hydrocarbons (e.g., petroleum ether and benzene) and methanol, but at low temperatures (e.g., -80°C.) it becomes soluble in methanol.

3. Copolymerization of CF₂=CFCl and CH₂=CH-CH=CH₂

The water-persulfate-bisulfite suspension system used successfully in copolymerizing CF₂=CFCl with CF₂=CH₂ was not effective in copolymerizing CF₂=CFCl with butadiene. In five runs, for example, where the charged molar ratios of CF₂=CFCl/CH₂=CH-CH=CH₂ ranged from 94/6 to 80/20, conversions were less than 1% in 70 hours. The addition of 20 and 100 ppm Fe (based on the monomers) in the form of FeSO₄ · 7H₂O was to no avail in increasing the yield.

Nonetheless, the products obtained in these preliminary experiments were rubbery enough to encourage further work with emulsion systems. The first emulsion recipe tested was the following:

Water, distilled	200 Pts. by wt.
CF ₂ =CFCl	89.5)80/20 molar
CH ₂ =CH-CH=CH ₂	10.5
KORR Soap /a/	5.0
(NH ₄) ₂ S ₂ O ₈	0.5
NaHSO ₃	0.3
FeSO ₄ · 7H ₂ O	0.05
pH of soap soln.	10.5-11.0
/a/ (Potassium Rubber Reserve soap purchased from Proctor and Gamble).	

The yield after 63 hours at room temperature, was negligible.

The next recipe tested was of the cumene-redox type.



Water, distilled	200 pts. by wt.
Monomers	100
KORR soap	5
Cumene hydroperoxide (100%)	0.15
$\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	1.00
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.10
Dextrose	1.00
pH of soap soln.	10.0

The charged molar ratios of $\text{CF}_2=\text{CFCl}/\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ranged from 100/0 through 75/25 and 25/75 to 0/100. Three of the polymerizations were continued for 48 hours; the fourth (75 mole % $\text{CF}_2=\text{CFCl}$) coagulated after 24 hours because of a marked decrease in pH. The yields in each case are listed below.

Run No.	Mole % $\text{CF}_2=\text{CFCl}$ Charged	% Conversion	Reaction Time
19	0	99	48 hrs.
20	25	78	48
21	75	1	24
22	100	1	48

On the basis of yield, the product of run 20, which is definitely rubber-like, almost certainly contains elements of both $\text{CF}_2=\text{CFCl}$ and butadiene.

Three attempts to copolymerize $\text{CF}_2=\text{CFCl}$ and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ in molar ratios of 70/30, 50/50, and 25/75 in the following acidic emulsion recipe were unsuccessful:

Water, distilled	200 pts. by wt.
Monomers	100
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.5
NaHSO_3	0.4
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.01
Duponol C	2
pH of aqueous phase	3.0

4. Polymerization of $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2$

A solid polymer of perfluorobutadiene, prepared by Prof. Bridgman at $62^\circ\text{C}.$, under 16,000 atm., has been received for evaluation.

IV. Plans for Future Work

During the next quarter, the copolymerization studies of $\text{CF}_2=\text{CFCl}$ (1), $\text{CF}_2=\text{CH}_2$ (2) and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (3) will be extended to include additional monomer ratios of 1-2 and 1-3, terpolymers of 1-2-3, in which butadiene will be a minor component, and copolymers of 2-3.

Copolymerizations will also be attempted between pairs of the following monomers: $\text{CF}_2=\text{CFCl}$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$, $\text{CF}_2=\text{CCl}_2$, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, and $\text{CH}_2=\text{CHCl}$.

The two chlorinated products, $\text{C}_4\text{F}_6\text{Cl}_2$ and $\text{C}_4\text{F}_6\text{Cl}_4$, will be dechlorinated and purified by careful distillation through a low-temperature column to yield $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$ and $\text{CF}_2-\text{CF}=\text{CF}-\text{CF}_2$ for additional copolymerization studies.


F. J. HONN


J. W. COPENHAVER

References to original records:

Notebook # 97 (Honn), pages 1-22 incl.
Notebook # 86 (Mantell), pages 114-147 inc., pages 154, 155
158, 159, 162, 166, 170, 171, 176.

SUPPLEMENTARY

INFORMATION

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