July 26, 1949. D. E. BADERTSCHER ET AL 2,477,538

PRODUCTION OF POLYMERIC OIL

Filed Nov. 9, 1945 4 Sheets-Sheet 1

Fig. 1a,

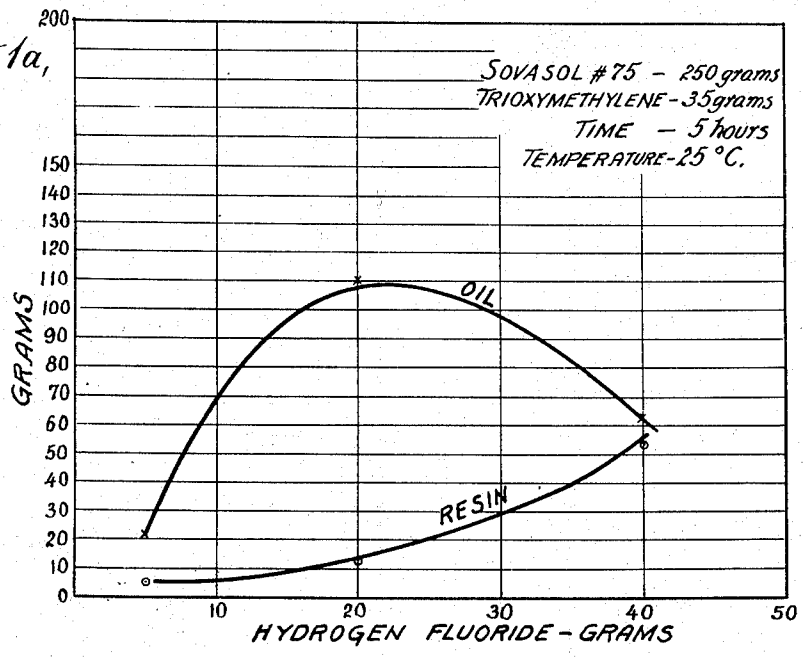
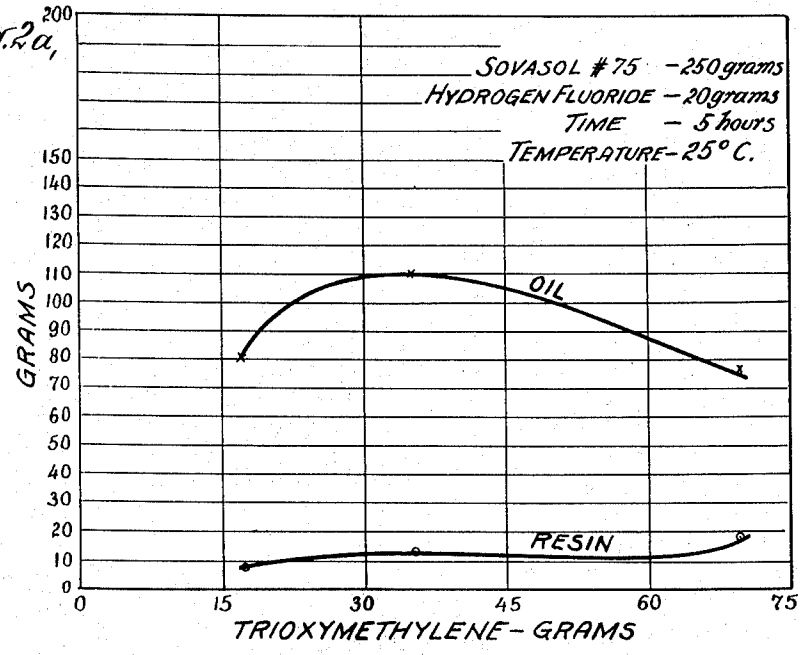


Fig. 2a,



INVENTORS
DARWIN E. BADERTSCHER and
RICHARD B. BISHOP
BY Francis J. Johnston
AGENT OR ATTORNEY

July 26, 1949. D. E. BADERTSCHER ET AL 2,477,538

PRODUCTION OF POLYMERIC OIL

Filed Nov. 9, 1945 4 Sheets-Sheet 2

Fig. 1b,

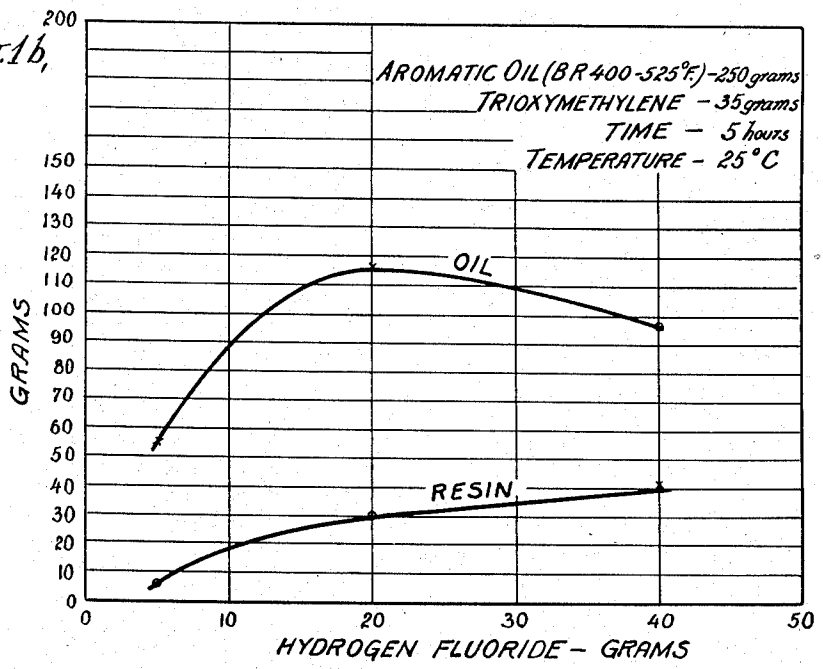
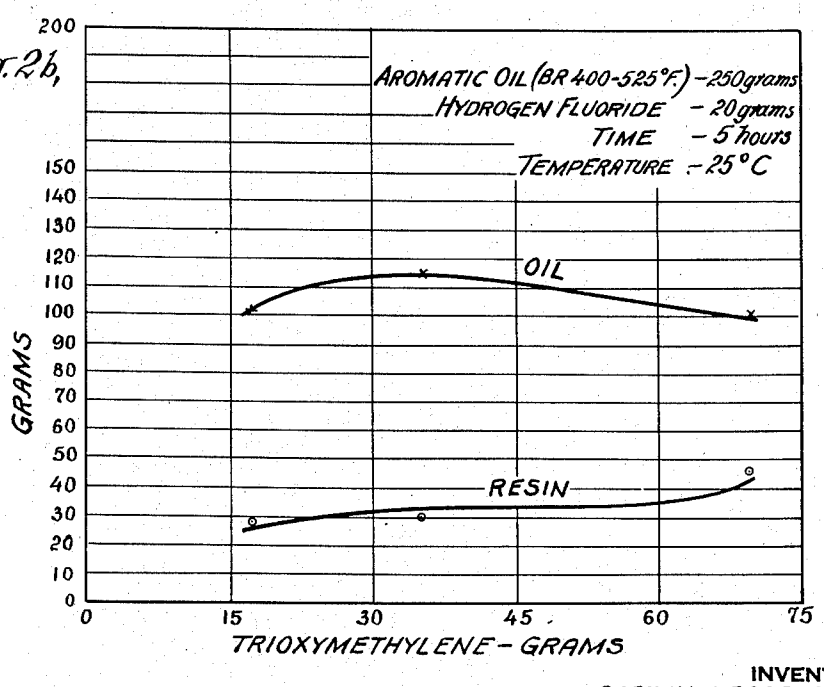


Fig. 2b,



INVENTORS
DARWIN E. BADERTSCHER and
RICHARD B. BISHOP
BY Francis L. Johnston
AGENT OR ATTORNEY

July 26, 1949. D. E. BADERTSCHER ET AL 2,477,538

PRODUCTION OF POLYMERIC OIL

Filed Nov. 9, 1945 4 Sheets-Sheet 3

Fig. 3a,

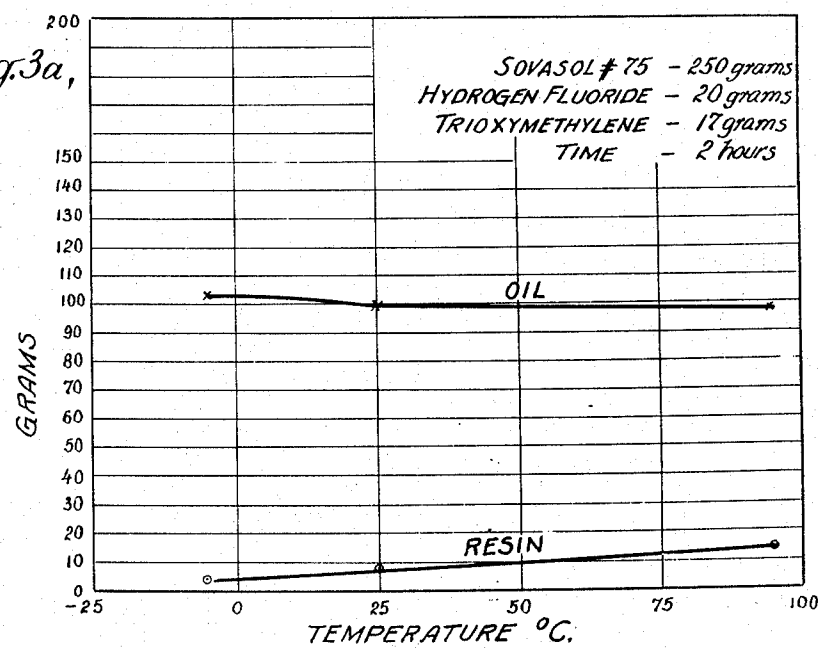
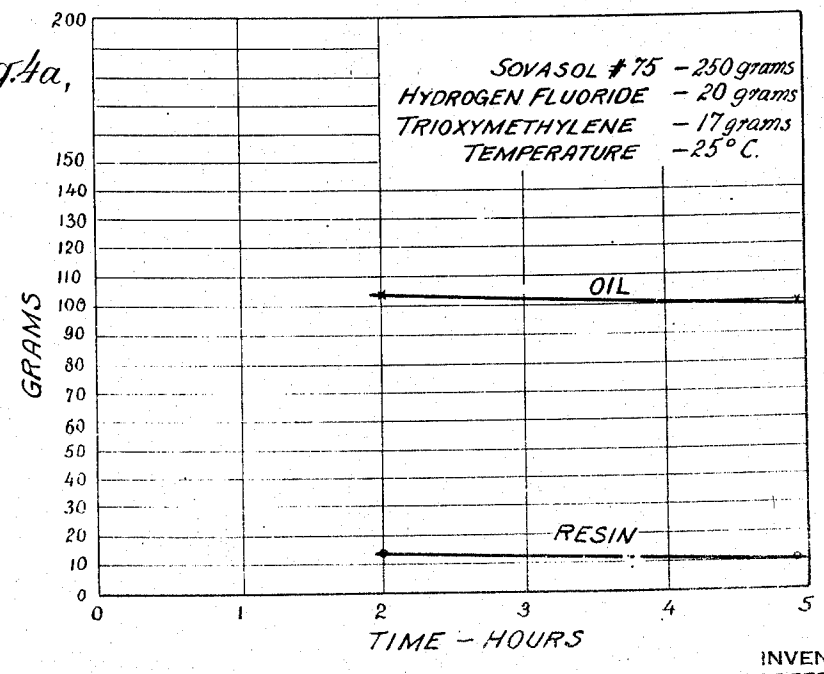


Fig. 4a,



INVENTORS
DARWIN E. BADERTSCHER and
RICHARD B. BISHOP
BY Francis J. Johnston
AGENT OR ATTORNEY

July 26, 1949. D. E. BADERTSCHER ET AL 2,477,538

PRODUCTION OF POLYMERIC OIL

Filed Nov. 9, 1945 4 Sheets-Sheet 4

Fig. 3b,

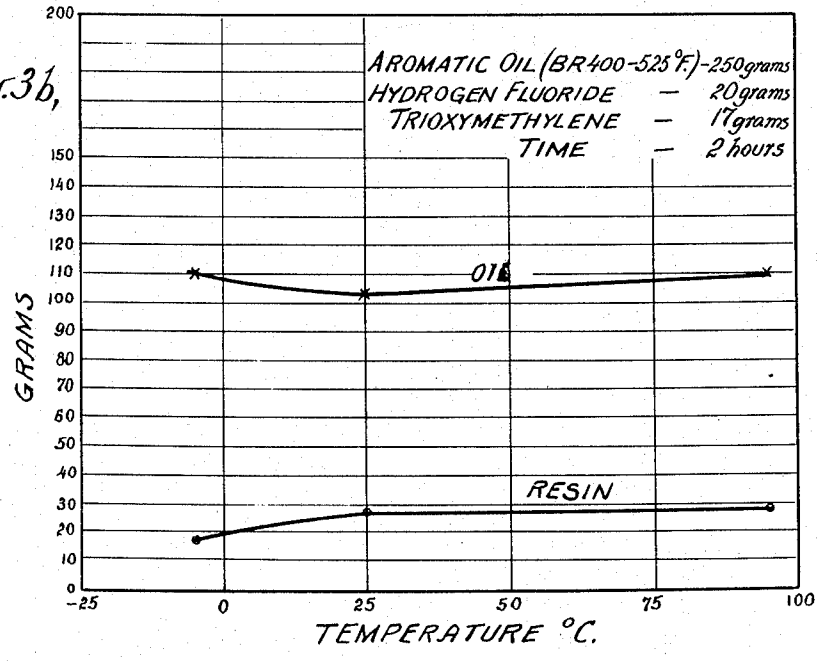
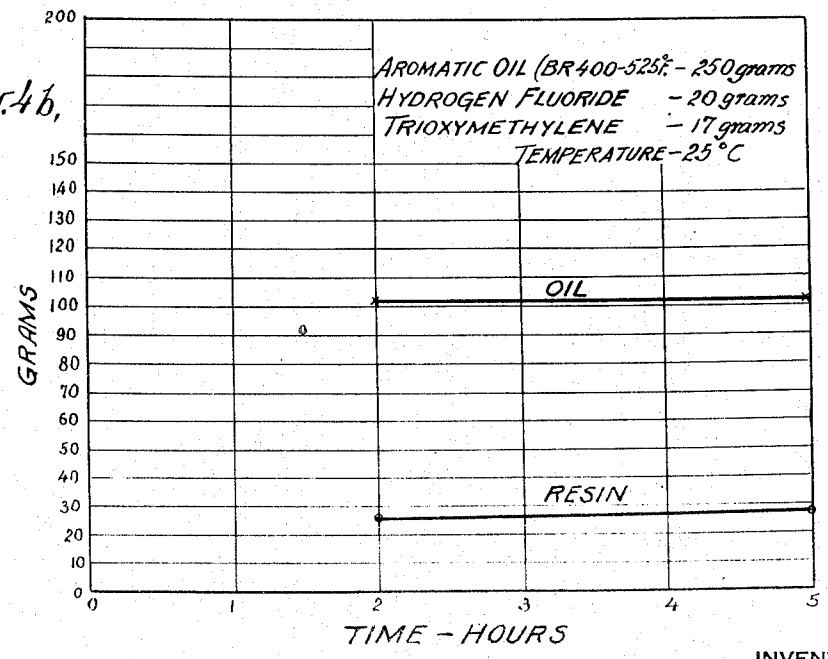


Fig. 4b,



INVENTORS
DARWIN F. BADERTSCHER and
RICHARD B. BISHOP
BY Frances F. Johnston
AGENT OR ATTORNEY

Patented July 26, 1949 2,477,538

UNITED STATES PATENT OFFICE

2,477,538

PRODUCTION OF POLYMERIC OIL

Darwin E. Badertscher, Woodbury, and Richard B. Bishop, Haddonfield, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

Application November 9, 1945, Serial No. 627,758

5 Claims. (Cl. 196—78)

1

This invention relates to the production of viscous oils suitable for use as plasticizers for various resins such as the vinyl resins, softeners for synthetic rubbers, fluids for hydraulic systems, liquids for quartz testing and the like.

The present application is a continuation-in-part of our application Serial No. 463,938, filed October 30, 1942, now Patent No. 2,397,398, wherein there is disclosed a process for producing resinous materials, particularly light-colored resinous materials having relatively high melting points from aromatic hydrocarbon materials such as benzene, toluene, xylenes, mesitylenes, naphthalene, alpha- and beta-methyl naphthalenes, polymethyl naphthalenes, anthracene, etc. Preferred as inexpensive aromatic hydrocarbon materials are petroleum fractions rich in aromatic hydrocarbons. Typical, and particularly preferred, of such aromatic petroleum fractions are those obtained by catalytic cracking or cyclization, or catalytic cracking and cyclization, of petroleum stocks and having boiling ranges from about 300° F. to about 400° F., and from about 500° F. to about 750° F.; and those obtained by thermal cracking of petroleum stocks and having boiling ranges from about 400° F. to about 600° F.

In general, all aldehydes are contemplated herein for condensation with the foregoing aromatic hydrocarbons in the presence of hydrogen fluoride. Representative aldehydes are formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, toluic aldehydes, etc. The aliphatic aldehydes are preferred and particular preference is given herein to formaldehyde which may be used either in the gaseous phase, the aqueous phase as 37 per cent Formalin, or in the solid phase such as trioxymethylene or paraformaldehyde.

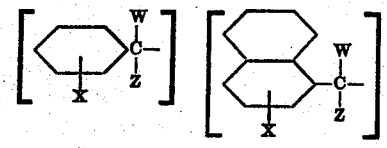
The hydrogen fluoride used as the catalyst or condensing agent herein may be the anhydrous product or it may be employed in aqueous solutions of a wide range of concentrations. Anhydrous hydrogen fluoride, however, is preferred. The amount of hydrogen fluoride used may be varied from about 1.5 per cent to about 25 per cent by weight of the reaction mixture but, in general, most satisfactory results are obtained with concentrations of about 5 per cent to about 15 per cent by weight of the reaction mixture. The aldehyde may be varied within a wide range and the temperature for batch operation may be between −5° centigrade and 95° centigrade. However, in continuous operation employing a heating zone and a zone in which the reaction products are rapidly cooled, temperatures above 100° centigrade and of the order of 400° C. to 1000° C. with residence times of the order of two minutes or less may be employed.

2

The relation of the variables time, temperature and hydrocarbon : aldehyde : hydrogen fluoride is established for batch operation in Table I and the drawings Fig. 1 and Fig. 2. These data were obtained in the following manner. The hydrocarbon, trioxymethylene and hydrogen fluoride were placed in a small, cold (0° C.) 500 cubic centimeters bomb (copper lined) which was then immediately capped and placed in a violent reciprocating shaker, where it was maintained at the desired temperature for the desired reaction time. After shaking for the desired period, the bomb was opened and the HF neutralized with 20 per cent potassium hydroxide. The emulsion which usually formed was broken with petrohol and benzene. The layers were then separated and the hydrocarbon layer was passed through a filter bed of Super Filtrol. The filtrate, a clear yellow-red colored liquid was then distilled using a side arm flask equipped with a total take-off condenser. That material which boiled above the boiling range of the charge material and below 300° C. at 10 millimeters was defined as oil. The portion remaining in the flask after such a distillation was recorded as resin.

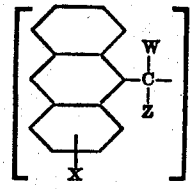
Using this procedure a series of runs were made on each variable. Studies were made on the effect of (*a*) concentration of hydrogen fluoride, (*b*) concentration of trioxymethylene, (*c*) effect of temperature, and (*d*) effect of time. Two stocks ("Sovasol" #75 and aromatic petroleum stock boiling range 400–525° F.) were treated in this manner. The results of this work are itemized in Table I. Figures 1*a*, 2*a*, 3*a* and 4*a* illustrate graphically the results itemized in Table I employing an aromatic petroleum stock in which the aromatic compounds comprise essentially alkylated benzenes. Figures 1*b*, 2*b*, 3*b*, and 4*b* illustrate in a graphical manner the results itemized in Table I for an aromatic petroleum stock in which the aromatic compounds comprise essentially polynuclear aromatic hydrocarbons, such as naphthalene and alkylated naphthalenes.

The resinous materials boiling above the boiling range of the charge material and below 300° C. at 10 millimeters of mercury have as an essential constituent at least one polymer of an aromatic hydrocarbon, which polymer has a unit which may be represented by one or more of the following formulae depending upon the character of the charge stock:



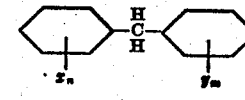
I II

and



III

which may be represented by Formula II. Similarly, when the charge stock is either a hydrocarbon of the anthracene series, a mixture of hydrocarbons of the anthracene series or a material of which the predominant constituents are hydrocarbons of the anthracene series, the resinous oil as defined hereinbefore has as an essential constituent a polymer which has a basic unit which can be represented by the Formula III. When an aromatic hydrocarbon of the benzene series or a charge stock containing hydrocarbons of the benzene series and formaldehyde or its polymers are employed, the resinous oil boiling above the boiling point of the charge stock and below 300° C. at 10 millimeters of mercury has as an essential constituent a polymer, predominantly the dimer represented by the formula:



in which x and y are alkyl groups having 1 to 4 carbon atoms and n and m are small integers not greater than 5.

TABLE I

Oil intermediates and resin from "Sovasol" #75 and aromatic petroleum stock, boiling range 400–525° F.

Run No.	Reactants						Time	Temp.	Stripping Temp.	Stripping Press	Resin		Oil	
	"Sovasol" #75		Trioxymethylene		Hydrogen Fluoride									
	Gms.	*Mols.*	*Gms.*	*Mols.*	*Gms.*	*Mols.*	*Hrs.*	*°C.*	*°C.*	*mm.*	*Gms.*	*Percent*	*Gms.*	*Percent*
1	250	2.08	35	1.1	20	1	5	25	300	10	13	5.2	110	44.0
2	250	2.08	35	1.1	40	2	5	25	300	10	53.5	21.4	63	25.2
3	250	2.08	35	1.1	5	.25	5	25	300	10	5	2.0	21	8.4
4	250	2.08	17	0.6	20	1	5	25	300	10	7–8	3.0	98	32.0
5	250	2.08	70	2.2	20	1	5	25	300	10	17	6.8	76	30.4
6	250	2.08	17	.6	20	1	2	25	300	10	12	4.8	103	41.2
7	250	2.08	17	.6	20	1	20	run not necessary, compare 4 and 6; fig. 2, *d*						
8	250	2.08	17	.6	20	1	2	−3	300	10	4	1.6	103	41.2
9	250	2.08	17	.6	20	1	2	+95	300	10	14	5.6	98	39.2
Aromatic Petroleum Stock Boiling Range 400–525 F.														
10	250	1.5	35	1.1	20	1	5	25	300	10	30	12.0	115	46.0
11	250	1.5	35	1.1	40	2	5	25	300	10	95	37.9	40	16.0
12	250	1.5	35	1.1	5	.25	5	25	300	10	6	2.4	56	22.4
13	250	1.5	17	.6	20	1	5	25	300	10	28	11.2	103	41.2
14	250	1.5	70	2.2	20	1	5	25	300	10	46	18.4	100	40.0
15	250	1.5	17	.6	20	1	2	25	300	10	26	10.4	103	41.2
16	250	1.5	17	.6	20	1	20	25	300	10	run not necessary, compare 13 and 15; fig. 2, *d*			
17	250	1.5	17	.6	20	1	2	−5	300	10	18	7.2	110	44.0
18	250	1.5	17	.6	20	1	2	+95	300	10	28	11.2	112	44.8

Remarks

"Sovasol" #75 resin—after stripping run at 10 millimeters and 300° C. the remaining material is defined as resin.
Oil—that product which comes over at 10 millimeters between 80–300° C.
Molecular weight of "Sovasol" #75, 121.
Aromatic petroleum stock boiling range 400–525° F.—after stripping run at 10 millimeters and 300° C. the remaining material is defined as resin.
Oil—that product which comes over at 10 millimeters between 130–300° C.
Molecular weight of aromatic petroleum stock boiling range 400–525° F., 163.

where x represents 1 to 5 alkyl groups having 1 to 2 carbon atoms attached to the nucleus in any position, W and Z are selected from alkyl, aryl, alkaryl groups and hydrogen. For example, when a mononuclear hydrocarbon or a mixture of mononuclear hydrocarbons are the predominant constituents of the charge stock, the resinous oil obtained as described hereinbefore has as an essential constituent at least one polymer the structure of the basic unit of which may be represented by Formula I. When the charge stock is either a hydrocarbon of the naphthalene series or a mixture of hydrocarbons of which the predominant constituents are hydrocarbons of the naphthalene series, the resinous oil obtained as described hereinbefore has as an essential constituent at least one polymer the basic unit of

In general, these data show that for the highest yield of oil from these stocks a molar ratio of hydrocarbon to trioxymethylene to hydrogen fluoride of 2–1–1 should be used. Figure 1*a* (the effect of increasing concentration of hydrogen fluoride) shows that the oil production increases up to a maximum at 1 mol of hydrogen fluoride for 2 moles of hydrocarbon, after which it begins to fall off with an increase in resin formation. Figure 2*a* shows the same general type of curve for increasing trioxymethylene concentrations with the maximum at a concentration of 1 mol of trioxymethylene to 2 moles of hydrocarbon. The change obtained by varying the concentration of trioxymethylene is not as marked as that obtained by varying the concentration of hydrogen fluoride. Thus a molar ratio of 4–1–2 shows al-

most as much effectiveness as a molar ratio of 2–1–1. The temperature of the reaction has no appreciable effect between —5° C. and 95° C. However, at higher temperatures short reaction times well below the two hours minimum used in these operations can be used.

The properties of the resinous materials obtained as contemplated by this invention may be modified by varying one or more of a number of influencing factors. The materials may be of various degrees of hardness or softness, of brittleness or toughness, and may be light or dark in color, etc., depending upon the reaction conditions. Temperature, time, concentration of hydrogen fluoride, ratio of reactants, treatment following resinification (such as distillation) etc., all may be regulated to obtain resinous materials of different properties. The products obtained may be used in paints, varnishes and lacquers, in molding compositions, as shellac replacements, as electrical insulating materials, and waxes or extenders for more expensive resins such as the polystyrene resins and carnauba wax, etc.

As aforesaid, hydrogen fluoride is effective for the condensation of aromatic hydrocarbons and aldehydes over a wide range of temperatures including both low temperatures and relatively high temperatures. In this respect, hydrogen fluoride differs substantially from the related halogen acids, hydrochloric and hydrobromic acids which are effective as catalysts for their reactions at relatively high temperatures only. To demonstrate this difference in activity, comparative results of the preparation of resinous materials of the type contemplated herein are set forth in Table II below. The preparations were carried out in sealed stainless-steel reaction vessels and, in all cases, 250 grams of an aromatic-rich hydrocarbon stock obtained from a catalytic cracking operation of a petroleum stock and identified by the characteristics: boiling range 310–395° F., Kauri-Butanol No. 80, flash point (Tag closed cup) 100° F. were used with 35 grams of trioxymethylene and about 40 grams of anhydrous hydrogen halide. Each reaction was carried out for about 6 hours at either about 25° C. or about 180° C. as indicated in Table II. With each reaction, the reaction vessel was opened at the end of about 6 hours and the contents taken up in benzol. The benzol solution was filtered, the filtrate neutralized with dilute (10 per cent) sodium hydroxide solution and then washed with water, separated and filtered. The washed benzol filtrate was then distilled to a pot temperature of about 250° C. under about 10 millimeters pressure, leaving the resin as the residue. The yield obtained in each case is given below in Table II:

TABLE II

Catalyst Used (Anhydrous)	Temperature, ° C.	Yield, grams
HF	25	83.5
HF	180	105
HCl	25	2.4
HCl	188	65
HBr	25	2
HBr	180	59

The results tabulated in Table II clearly indicate that hydrogen fluoride is effective at both low temperatures (25° C.) and at relatively high temperatures (180° C.). The results also demonstrate that hydrogen fluoride is a much more effective condensing agent than either hydrochloric or hydrobromic acids at such temperatures.

To further demonstrate the superiority of hydrogen fluoride over the related halogen acids, hydrochloric and hydrobromic acids, resinous materials were prepared in the presence of the aqueous halogen acids. The preparations were carried out in sealed metal flasks maintained at 100° C. In each case, 250 grams of the hydrocarbon used above (Table II) and 35 grams of trioxymethylene were used. The products were treated as described above in discussion of the products shown in Table II. These results are given in Table III which follows and are self-explanatory:

TABLE III

Catalyst Used (Aqueous)	Conc.	Flask	Wt., Grams	Time, Hrs.	Yield, Grams
	Per cent				
HF	48	Copper	100	3	85
HCl	38	Steel	100	3	2.2
HBr	48	Copper	100	6	24

The effects of various factors, such as concentration of reactants, temperature, etc., on the yield of resin obtained from an aromatic hydrocarbon (that used in connection with Tables II and III) and trioxymethylene are illustrated by the results tabulated in Table IV below. All products were worked up as described above in connection with Table II.

TABLE IV

Variable Changed	Reaction No.	Wt. of Hydrocarbons, grams	Wt. of $(HCHO)_3$, grams	Wt. of Anhydrous HF, grams	Temp., ° C.	Time, hrs.	Yield, grams
Wt. of HF	24	250	35	5	100	6	68
	29	250	35	15	100	6	84
	26	250	35	25	100	6	74
	33	250	50	15	100	6	94
	31	250	50	25	100	6	124
	32	250	50	35	100	6	140
Wt. of $(HCHO)_3$	35	250	25	5	100	6	49
	24	250	35	5	100	6	68
	34	250	25	15	100	6	56
	29	250	35	15	100	6	84
	33	250	50	15	100	6	94
Temperature	22	250	30	25	100	3	81
	27	250	35	25	100	3	80.5
	20	250	35	25	0	6	42
	26	250	35	25	100	6	74
Time	27	250	35	25	100	3	80.5
	26	250	35	25	100	6	74
	28	250	35	25	100	16	85

Inspection of the results in Table IV show the following features in connection with the factors susceptible of variation. In general, an increase

in the concentration of hydrogen fluoride, other factors remaining constant, appears to increase the yield of resin and an increase in concentration of aldehyde (trioxy-methylene), with other factors the same, also increases the yield of resin; the yield is also affected by temperature as shown by reactions 20 and 26 above, and by the data in Table II. As aforesaid, however, and as is shown by Table II, yields in commercial quantities of superior resins can be obtained with hydrogen fluoride at low temperatures, for example, 0° C. (reaction 20 above) which is not the case with the other hydrogen halides. The period of reaction, at least within the range of time intervals represented by reactions 26, 27 and 28, does not appear to have any material effect on the yield.

Reaction 20, of Table IV, demonstrates that hydrogen fluoride is effective at temperatures in the neighborhood of 0° C. Although the highest reaction temperatures illustrated are at about 180° C., it would appear from the results shown in Tables II and IV that hydrogen fluoride would be effective for the purposes contemplated herein at still higher temperatures, such as, for example, about 200° C.

It will be apparent to those familiar with the art that glass equipment cannot be used effectively for the condensation contemplated herein in view of the well-known chemical action of hydrogen fluoride on glass. Equipment made of various metals and alloys of such metals may be used in the preparation of the resinous materials described above. In general, copper, stainless steel and iron reaction vessels are considered most desirable for our purposes.

As aforesaid, the resinous materials contemplated herein may have different physical properties depending upon the various factors referred to above. The following examples of typical preparations clearly indicate several of these typical resinous materials.

Example I

A mixture of 250 grams of an aromatic rich hydrocarbon fraction, described above in connection with Table II, 50 grams of trioxymethylene and 35 grams of anhydrous hydrogen fluoride was shaken in a tightly-capped copper flask, in a 100° C. steam bath for 18 hours. The mixture was then cooled, neutralized with 20–25 per cent sodium hydroxide, taken up in benzene, water washed, filtered and the filtrate distilled to a pot temperature of 250° C. under 10 millimeters pressure. The residue, 140 grams, is a light-colored resin with a ball-and-ring melting point of about 89° C.

Example II

A mixture of 200 cubic centimeters of an aromatic rich hydrocarbon fraction obtained from a thermally-treated recycle stock from a thermal cracking operation and having a boiling range of about 400–600° F., 40 grams of trioxymethylene and 25 grams of anhydrous hydrogen fluoride was stirred in a tightly-capped copper flask for 6 hours in an ice bath, and then stirred for 16 hours at room temperature. The reaction mixture was then worked up as in Example I. A light-colored resin, 148 grams, with a ball-and-ring melting point of about 77° C. was thus obtained.

Example III

A heavy fuel distillate from a catalytic cracking operation having the following properties:

Boiling range:		
Initial boiling point	°F.	504
10%	°F.	520
50%	°F.	540
90%	°F.	660
End point	°F.	735
ASTM pour point	°F.	0
S. U. V. @ 100° F	seconds	50

was used in this preparation.

A mixture of 1000 grams of this aromatic rich hydrocarbon fraction, 200 grams of trioxymethylene and 105 grams of hydrogen fluoride was shaken in a tightly-capped iron bomb for 16 hours at about 25° C. The reaction mixture was worked up as in the preceding Examples I and II. A light-colored resin, 290 grams, with a ball-and-ring melting point of about 143° C. was thus obtained.

This application is a continuation-in-part of our copending application Serial No. 463,938, filed October 30, 1942 now Patent No. 2,397,398.

The examples and procedures given hereinabove are intended to be illustrative only, and the invention is not to be construed as limited thereto. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples and procedures may be included within the scope of the appended claims.

We claim:

1. A process for producing polymeric oil from petroleum products which comprises reacting an aromatic-rich hydrocarbon fraction having a boiling range of about 310° F. to about 395° F. at atmospheric pressure and obtained by catalytic cracking of a petroleum stock with about 6 to about 27 weight per cent of trioxymethylene based on the weight of the hydrocarbon fraction in the presence of about 3 to about 15 weight per cent of hydrogen fluoride based upon the weight of said aromatic-rich fraction at temperatures up to about 1000° C. for a reaction time not greater than about 2 hours for temperatures of minus about 5° C. to plus about 100° C. and for a reaction time not greater than about 2 minutes for temperatures of about 400 C. to about 1000° C., cooling the reaction mixture, neutralizing the cooled reaction mixture with aqueous alkali metal hydroxide solution, separating the hydrocarbons from the aqueous solutions, separating insoluble material from said hydrocarbons and recovering polymeric oil from said separated hydrocarbons as a fraction boiling above about 395° F. at atmospheric pressure and below about 572° F. at a pressure of 10 millimeters of mercury.

2. A process for producing polymeric oil from petroleum products which comprises reacting an aromatic-rich hydrocarbon fraction having a boiling range of about 400° F. to about 600° F. at atmospheric pressure and obtained by thermal cracking of petroleum stocks with about 6 to about 27 weight per cent of trioxymethylene based upon the weight of the aromatic-rich fraction in the presence of about 3 to about 15 weight per cent of hydrogen fluoride based upon the weight of the aromatic-rich fraction at temperatures up to about 1000° C. for a reaction time not greater than about 2 hours for temperatures of minus about 5° C. to plus about 100° C. and for a reaction time not greater than about 2 minutes for temperatures of about 400° C. to about 1000° C., cooling the reaction mixture, neutralizing the reaction mixture with aqueous alkali metal hydroxide, separating hydrocarbons from aqueous solution, separating liquid hydrocarbons from insoluble material and recovering polymeric oil as

a fraction of said liquid hydrocarbons boiling above about 600° F. at atmospheric pressure and below about 572° F. at a pressure of 10 millimeters of mercury.

3. A process for producing polymeric oil from petroleum products which comprises reacting an aromatic-rich hydrocarbon fraction having a boiling range of about 400° F. to about 525° F. at atmospheric pressure and a Saybolt Universal Viscosity at 100° F. of about 50 seconds and obtained from a catalytic cracking operation with about 6 to about 27 weight per cent of trioxymethylene based upon the weight of said aromatic-rich fraction in the presence of about 3 to about 15 weight per cent of hydrogen fluoride based upon the weight of said aromatic-rich fraction at temperatures up to 1000° C. for a reaction time not greater than about 2 hours for temperatures of about minus 5° C. to about 100° C. and for a reaction time not greater than about 2 minutes for temperatures of about 400° C. to about 1000° C., cooling the reaction mixture, neutralizing the reaction mixture with aqueous alkali metal hydroxide, separating hydrocarbons from aqueous solution, separating liquid hydrocarbons from insoluble material and recovering polymeric oil as a fraction of said liquid hydrocarbons boiling above about 735° F. at atmospheric pressure and below about 572° F. at a pressure of 10 millimeters of mercury.

4. A process for producing polymeric oil from petroleum products which comprises reacting an aromatic-rich hydrocarbon fraction having a boiling range within the limits about 300° F. to about 750° F. at atmospheric pressure and obtained by cracking petroleum stock with about 6 to about 27 weight per cent of formaldehyde based upon the weight of said aromatic-rich fraction in the presence of about 3 to about 15 weight per cent of hydrogen fluoride based upon the weight of said aromatic-rich fraction at temperatures up to 1000° C. for a reaction time not greater than about 2 hours for temperatures of about minus 5° C. to about 100° C. and for a reaction time not greater than 2 minutes for temperatures of about 400 C. to about 1000° C., cooling the reaction mixture, neutralizing the reaction mixture, separating hydrocarbons from the reaction mixture, separating liquid hydrocarbons from insoluble material, and recovering polymeric oil as a fraction of said liquid hydrocarbons said fraction of liquid hydrocarbons having an initial boiling point higher than the final boiling point of the aforesaid aromatic-rich fraction and a final boiling point below about 572° F. at a pressure of 10 millimeters of mercury.

5. A process for producing polymeric oil from petroleum products which comprises reacting an aromatic-rich hydrocarbon fraction having a boiling range within the limits about 300° F. to about 750° F. at atmospheric pressure and obtained by cracking petroleum stock with about 6 to about 27 weight per cent of formaldehyde based upon the weight of said aromatic-rich fraction in the presence of about 3 to about 15 weight per cent of hydrogen fluoride based upon the weight of said aromatic-rich fraction, the reaction time being not greater than 2 hours for temperatures of about minus 5° C. to about 100° C., and not greater than 2 minutes for temperatures of about 400° C. to about 1000° C., cooling the reaction mixture, neutralizing the reaction mixture, separating hydrocarbons from the reaction mixture, separating liquid hydrocarbons from insoluble material, and recovering polymeric oil as a fraction of said liquid hydrocarbons, said fraction of liquid hydrocarbons having an initial boiling point higher than the final boiling point of the aforesaid aromatic-rich fraction and a final boiling point below about 572° F. at a pressure of 10 millimeters of mercury.

DARWIN E. BADERTSCHER.
RICHARD B. BISHOP.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,237,634	Rosen	Apr. 8, 1941
2,275,312	Tinker et al.	Mar. 3, 1942
2,397,398	Badertscher et al.	Mar. 26, 1946

FOREIGN PATENTS

Number	Country	Date
403,264	Germany	Aug. 9, 1919

OTHER REFERENCES

Calcott et al.: Journal American Chem. Soc., April 1939, volume 61, pages 949–51.

Fulton et al.: Industrial and Engineering Chemistry, vol. 32, No. 3, March 1940, pages 304–309.

Simons: Industrial and Engineering Chemistry, vol. 32, 1940, pages 178–180.