United States Patent Office

2,817,647

Patented Dec. 24, 1957

2,817,647

THERMAL POLYMERIZATION OF PETROLEUM HYDROCARBON FRACTION

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No Drawing. Application July 6, 1954, Serial No. 441,658

Claims priority, application Great Britain July 3, 1953

14 Claims. (Cl. 260—82)

This invention relates to a process for the production of polymers. More particularly it relates to a process for the production of hydrocarbon polymers including residual polymers, from petroleum.

It is known that cyclopentadiene, by the action of heat, undergoes polymerization with formation of the dimer and higher polymers and that cyclopentadiene is usually a constituent of gasoline obtained by the cracking of naphthas. By the treatment of a C_5 cut from such gasolines, followed by distillation, it is possible to obtain a dicyclopentadiene fraction which has applications in drying oil, paint and varnish manufacture, since, by reaction with vegetable drying oils, products are obtained which are superior to vegetable drying oils alone.

In has hitherto been disclosed that by the heat treatment of a distillation fraction of a steam cracked naphtha, said fraction containing polymers of cyclopentadiene and its homologues, it is possible to depolymerize said polymers to monomers.

We have found that under conditions of long residence time at elevated temperatures and pressure, some of the C_6 and higher constituents of a distillation fraction obtained by cracking a petroleum cut are converted to valuable resinous polymers.

It is an object of the present invention to provide a process for the production of new hydrocarbon polymers, including resinous polymers.

According to the present invention there is provided a process which comprises subjecting a cracked hydrocarbon fraction of petroleum origin having an initial boiling point of at least 15° C. and a final boiling point not higher than 200° C., to a heat treatment in the liquid phase at a temperature in the range 100°–300° C. and at a pressure in the range 50–2000 lbs./sq. in. gauge for a period of at least 30 mins. and thereafter distilling the product to recover a hydrocarbon polymer fraction.

Preferably the cracked hydrocarbon fraction has an initial boiling point in the range 15–120° C. and in particular in the range 15–50° C. and a final boiling point in the range 140 to 200° C.

For ease of separation of distillate polymer as distinguished from resinous polymer, as described hereinafter, and in order to obtain maximum recovery of this product, it is preferred that the feedstock fractions, which boil within the range 15–200° C., have a boiling range extending over not more than 100° C. within this range.

According to a modification of the process of the present invention, said process comprises subjecting a cyclopentadiene-containing cracked hydrocarbon fraction of petroleum origin having an initial boiling point in the range 15 to 30° C. and a final boiling point in the range 50–70° C. to a preliminary heat treatment at a temperature in the range 70°–120° C., whereby cyclopentadiene

contained in the fraction is converted to its dimer, thereafter distilling the product to remove said dimer, subjecting the cyclopentadiene free cracked hydrocarbon fraction obtained overhead to a heat treatment at a temperature above the temperature of said preliminary heat treatment and a superatmospheric pressure and distilling the product to recover a hydrocarbon polymer fraction. Preferably the pressure of the second heat treatment lies in the range 100 to 2000 lbs./sq. in. gauge. Preferably the period of the second heat treatment is at least 60 mins.

In general a suitable cracking stock is a petroleum distillate fraction, for example, naphtha, gas oil or primary flash distillate. The preferred feedstock to the cracking is a petroleum naphtha. More particularly it is preferred that a naphtha cut boiling within the range 90° to 250° C. is subjected to steam cracking. Suitably the naphtha is cracked at a cracking coil exit temperature in the range 600° to 750° C. and at a pressure in the range from atmospheric to about 200 lbs./sq. in.

A particularly preferred feedstock is a cracked naphtha fraction having an initial boiling point in the range 35 to 50° C., and a final boiling point in the range 140° to 170° C. obtained by steam cracking a 90 to 210° C. naphtha cut at a cracking coil exit temperature of 670 to 730° C.

The main heat treatment may be carried out at a temperature in the range 100–250° C. or higher for a period of time dependent upon the temperature of the treatment but usually within the range 1–12 hours. Preferably the treatment is carried out at a temperature in the range 150–275° C. and for 3–6 hours. The pressure should be sufficient to maintain the feedstock in the liquid phase at the temperature employed for the heat treatment and in general be at least 50 lbs./sq. in. although lower pressure can sometimes be used with high boiling fractions of the cracked product. The upper limit of pressure is not generally critical. However, there is little advantage in using pressures exceeding the bubble point pressure of the feed at the temperature of the treatment.

Preferably the distillation of the heat treated cracked hydrocarbon fraction, wherein a resinous polymer fraction is recovered, is effected with separate recovery of a gasoline fraction, a distillate polymer fraction and a resinous polymer fraction.

It is particularly preferred that the heat treated product is distilled at atmospheric pressure to remove a gasoline fraction overhead, and to recover a polymer fraction under reduced pressure, preferably below 300 mm. Hg, or is distilled in the presence of steam to recover a distillate polymer fraction overhead and a fraction containing resinous polymers as bottoms.

It has been found that by distillation under reduced pressure or in the presence of steam, it is possible to avoid or reduce deterioration in the color and physical properties of the resinous polymers.

In general, it is preferred to recover a distillate polymer fraction which has an initial boiling point at least 10° C. above the final boiling point of the cracked hydrocarbon fraction subjected to heat treatment and a final boiling point in the range 200–300° C.

Thus, for example, the distillation of the heat-treated product may be carried out continuously or batchwise to remove a stabilized gasoline fraction boiling up to 140°–170° C., a distillate polymer fraction boiling in the range 170° to 250° C. and a residue polymer fraction boiling above about 250° C. (all distillation temperatures being reduced to atmospheric pressure) when employing a feed-

stock of final boiling point in the range 140–170° C.

It is desirable that air or oxygen-containing gases be excluded during the process and, in particular, during the heat treatment and distillation stages in order to obtain products of good color.

The distillate polymer fraction obtained according to this invention has been found to be suitable material for use as a component in a drying oil mixture. Thus this fraction may be used as a turpentine substitute. It may also be used as an additive to vegetable drying oils (for example linseed, tung and tall oils) to improve their film forming properties, and may be incorporated into natural or synthetic resins used in the surface coating industry. Preferably this distillate polymer fraction has an initial boiling point in the range 130° to 200° C. and a final boiling point in the range 200°–300° C.

Furthermore, it has been found that the resinous polymers produced according to this invention are of good color and will dry to hard films, with or without the addition of drying agents such as cobalt salts. They also form hard elastic films when baked on to surfaces either alone or with the addition of small amounts of vegetable drying oils or semi-drying oils or other plasticizers. Thus the residual polymers prepared in the examples described hereinafter gave hard films free from tack when painted on to steel sheet and baked at 100°–150° C. for 1–4 hours.

It is believed that the good qualities of the polymers which are obtainable by the process of the invention are attributable to the formation of novel polymer mixtures obtained by interpolymerization of constituents of the wide boiling range feedstock to the heat treatment.

It has also been ascertained that the recovered gasoline fraction is much superior to the feedstock, particularly in respect of stability and gum forming characteristics.

The invention is illustrated but in no way limited by the following examples.

EXAMPLE 1

The feedstock treated was a 35°–145° C. fraction of gasoline prepared by steam cracking a naphtha fraction from Middle East crude oil, the cracker coil exit temperature being 1325° F. The fraction was heated for six hours at a temperature of 150° C. under its own vapour pressure (250 lbs./sq. in. gauge). After this treatment the product was distilled at 9 mm. of mercury pressure. Distillation of the residue was continued at 12 mm. of mercury pressure. Bromine numbers quoted were determined by the Kauffman method. The results obtained are shown in the following Table 1.

Table 1

Product	Wt. percent of 35–145° C. fraction (feed)	Bromine Number	Refractive Index n_D^{20}
Gasoline Fraction (Feed)	100	77	1.4520
Gasoline Fraction recovered	86	70	1.4503
Distillate Polymer Fractions:			
33–44°/9 mm	3.9	50	1.4786
44–52°/9 mm	3.8	67	1.4803
52–80°/12 mm	2.1	117	1.4930
80–85°/12 mm	0.4	128	1.4968
Residual polymer	3.8	125	

The ratio of residual polymer to distillate polymer increased steadily during the six hours' heat treatment. The total amount of residual polymer and distillate polymer also increased during the six hours. The experiment was repeated with a heat treatment time of 12 hours. It was found that during the second 6 hours' period there was only a slow increase in the total of

residual polymer and distillate polymer product formed and in the ratio of residual polymer to distillate polymer, using the same cut point between residual polymer and distillate polymer in the distillation of both products.

EXAMPLE 2

The experiment was repeated using a 40–142° C. cut of cracked gasoline produced as described in Example 1. Heating was continued for six hours at a temperature of 155° C. and the product distilled as before. The experiment was repeated with a heat treatment time of 12 hours. The results are summarized in Table 2.

Table 2

	Wt. percent of feed (42°–142° C. cut)	Bromine Number (Kauffman)	Refractive Index n_D^{20}
Feed	100	80	1.4541
After 6 hours heating:			
Gasoline fraction	85	71	1.4497
33°–50° C./10 mm	4.1	39	1.4755
50°–60° C./10 mm	3.0	57	1.4813
60–82° C./10 mm	3.7	114	1.4920
Residual polymer	4.2	135	
After 12 hours heating:			
Gasoline fraction	83	73	1.4457
30–57° C./3.5 mm	6.7	43	1.4773
57–80° C./7 mm	4.9	93	1.4873
80–97° C./3.5 mm	1.4	151	1.5016
Residual polymer	4.0	100	

EXAMPLE 3

A crude gasoline distillate obtained by steam cracking a naphtha cut from Middle East crude with a cracker coil exit temperature of 719° C. was heated under autogenous pressure in an agitated steel autoclave at 150–160° C. for 6 hours. The run was repeated using heart cuts of the gasoline. The boiling ranges of the feeds to the thermal treatment and the autogenous pressures generated were as follows:

Table 3

Boiling Range of Feed to Thermal treatment	Pressure, lb./sq. in. gauge
40–150° C.	250
65–145° C.	200
(15–200° C.) (Crude Gasoline)	180

The products were separately distilled to recover unchanged gasoline redistilled and under reduced pressure to separate distillate polymer and residual polymer.

The yields of distillate polymer and residual polymer obtained are shown in Table 4:

Table 4

Boiling Range of feed to Thermal Treatment	Polymer Distillate			Residual Polymer	
	Boiling Range	Yield, wt. percent of cut processed	Bromine No.	Yield, wt. percent of cut processed	Bromine No.
40°–150° C.	44°/9 mm.–82°/3.2 mm.	7.9	92	4.6	60
65°–145° C.	76°/63 mm.–123°/25 mm.	5.4	137	4.8	96
15°–200° C.				2.0	71

When the crude gasoline was employed as feedstock to the thermal treatment, a distillate polymer fraction was not isolated, the components thereof being mainly recovered with the overhead fraction. However, the residual polymer obtained from the crude gasoline was of good quality, comparable with that made from the 40–150° C. cut although of slightly darker color.

EXAMPLE 4

This example illustrates the batchwise operation of the process on a wide boiling feed, and also shows the effect of polymerization temperature on the product yields. A cracked distillate of boiling range 15–200° C. from the steam cracking of naphtha under substantially the same conditions as these used in preparing the feedstock of Example 3 was thermally polymerized under various conditions. The product was distilled to separate recovered gasoline boiling up to 200° C.

The bottoms were redistilled at a pressure of 5–50 mm. of mercury to recover distillate polymer boiling over the range 200–300° C. (corrected to 760 mm.). The polymerization conditions and product yields are shown in Table 5. All yields are as weights percent of the cracked distillate feed.

The yield of residual polymer increased continuously with rise in polymerization temperature, the yield of distillate polymer varying relatively little. At polymerization temperatures over about 270° C. darker colored residual polymers were obtained. The product obtained at 300° C. had a distinct color, and the odor of the gasoline recovered at this temperature was also inferior. For this reason polymerization temperatures below about 275° C. are preferred, although higher temperatures may be used in conjunction with shorter residence times, especially when the color of the residual polymer is not critical.

Table 5

Run No	88	93	105	94	99
Polymerization Conditions:					
Pressure lbs./sq. in. gauge	150	180	180	280	500
Temp., °C.	156	200	200	250	300
Time, hours	6	6	6	6	6
Recovered Gasoline (up to 200° C./760 mm.):					
Yield, wt. percent	89.1	84.1	84.6	79.8	73.1
Bromine No.	------	56	57	48	36
Distillate Polymer (200-300° C./760 mm.):					
Yield, wt. percent	8.3	8.9	9.0	8.6	7.8
Residual Polymer:					
Yield, wt. percent	2.6	7.0	6.4	11.6	19.1
Bromine No	------	80	83	69	82

EXAMPLE 5

The results obtained by thermal polymerization of a cracked distillate prepared by steam cracking a primary flash distillate are shown in Table 6. This cracked distillate contained much more lower boiling (C_5–C_7) hydrocarbon, and only small quantities of material boiling over 120° C./760 mm. The products were recovered in the same way as in Example 4, except that two fractions of distillate polymer were collected, and the recovered gasoline was collected up to 135° C.

The yields of residual polymer in this case were considerably less than from the naphtha cracking product of 15–200° C. boiling range, the products being very similar to those obtained from the 40–150° C. cut of the cracked distillate from naphtha.

Table 6

Run No	118	119	122	123
Steam Cracking (coil exit) Temp. in feed production °C.	719	719	732	732
Polymerization Conditions:				
Pressure, lbs./sq. in. gauge	380	1,330	400	1,480
Temp., °C.	200	250	200	250
Time, hours	6	6	6	6
Recovered Gasoline (up to 135° C.):				
Yield, wt. percent	86.6	83.8	83.0	81.0
Bromine No	45	51	58	52
Distillate polymer (135°–200° C.):				
Yield, wt. percent	8.7	9.6	11.1	11.1
Bromine No	154	146	164	163
Distillate Polymer (200-300° C.):				
Yield, wt. percent	3.2	3.5	3.7	3.7
Bromine	186	186	185	180
Residual Polymer:				
Yield, wt. percent	1.5	3.1	2.2	4.2
Bromine No	131	133	132	137

The residual polymers produced by distillation to an end point of 300° C./760 mm. are viscous liquids or semi-solid resins. Further distillation, preferably under reduced pressure to avoid darkening of the resins by excessive still-bottom temperatures results in the removal of further volatile products leaving solid resins as residual products. This is illustrated by the following example.

EXAMPLE 6

Residual polymers boiling over 300° C. produced from steam-cracked naphtha as described in Example 4 were further distilled under a pressure of about 5 mm. of mercury. Solid products were obtained on which softening points (ring and ball) were determined. The results are summarized in Table 7.

It appears from these results that somewhat higher melting resins are obtained at a polymerization temperature of 200° C. than at 250° C. for the same end point in the distillation of the residual polymer, although higher yields are obtained at 250° C.

Table 7

Polymerization Run No	108			111		
Polymerization Temp., °C.	200			250		
Overhead Temperature in Product Distillation (corre. to 760 mm.)	300	350	400	300	350	400
Softening point of Residual Resin (Ring and Ball) °C.	14.5	37.5	65.5	15	31	47
Yield of Residual Resin wt. percent on Cracked Distillate	5.9	4.7	3.4	11.7	10.3	8.6

EXAMPLE 7

Continuous tests have been carried out in a stainless steel tubular reactor 15" long and 1.6" internal diameter, the liquid feed being pumped up flow through this reactor. The products were separated by distillation in the same way as in the batch tests described above. Illustrative results obtained are shown in Table 8, which gives the product yields and reaction conditions for a number of these tests. The feed was a cracked distillate obtained by the steam cracking of naphtha at 719° C., as used in Examples 3 and 4.

Products made by heat treatment at temperatures in excess of about 275° C. tended to be darker in color than products produced at lower temperatures, and temperatures in the range 200–275° C. are therefore preferable when it is desired to produce resins of pale color.

Table 8

Run No	1	3	4	7	8	12	16	18	21
Conditions of Polymerization:									
Temperature, °C	200	230	230	300	299	275	250	275	250
Pressure, p. s. i. g	300	300	300	330	330	330	330	330	300
Residence, hours	1.0	0.5	1.0	1.0	0.5	2.0	3.0	4.0	4.0
Product data:									
Recovered Gasoline, 200° C. end point—									
Wt. percent on feed	87.9	89.85	88.7	82.75	84.1	83.6	83.7	82.2	84.2
Bromine No	63	80	61	61	60	50	62	55	61
Distillate Polymer, 200-300° C., 760 mm.—									
Wt. percent on feed	9.85	7.35	8.05	6.5	7.6	6.95	8.85	7.05	8.2
Residual Polymer, Over 300° C.—									
Wt. percent on feed	2.25	2.8	3.25	10.75	8.35	9.45	7.45	10.75	7.6
Bromine No	94	106	71	91	101	70	60	61	65

EXAMPLE 8

A naphtha cut from Middle East crude was steam-cracked with a cracker coil exit temperature of 719° C., a crude gasoline boiling over the range 15–200° C. being obtained from the product by distillation.

A 20–58° C. cut was obtained from this crude gasoline by further distillation and subjected to a preliminary heat treatment at 100° C. for 8 hours to dimerize the cyclopentadiene contained therein. The product was distilled to remove dicyclopentadiene as bottoms, the overhead product being subjected to further heat treatment in an agitated steel autoclave at 150–160° C. for 6 hours, the pressure generated being 290 lbs./sq. in. gauge. The product was distilled at atmospheric pressure to recover overhead, unchanged gasoline, the bottoms being further distilled under reduced pressure to separate distillate polymer and resinous polymer fractions. The yields obtained are shown in Table 9.

Table 9

Boiling Range of feed to Thermal Treatment, °C./760 mm.	Polymer Distillate		Residual Polymer		
	Boiling Range	Yield wt. percent of cut processed	Bromine No.	Yield wt. percent of cut processed	Bromine No.
20–58° C (Cyclopentadiene free)	38°/20 mm.-66°/10 mm.	5.3	228	310	118

We claim:

1. A process for the production of hydrocarbon polymers which comprises subjecting a cracked hydrocarbon fraction of petroleum origin having an initial boiling point in the range 15°–120° C. and a final boiling point in the range of 140°–200° C., to a heat treatment in the liquid phase at a temperature in the range 150°–300° C. and at a pressure in the range 50–2000 lbs./sq. in. gauge for a period of at least 30 mins. and thereafter distilling the product to recover a hydrocarbon polymer fraction.

2. A process as specified in claim 1 in which the cracked hydrocarbon fraction is a cracked naphtha fraction having an initial boiling point in the range 35° to 50° C., and a final boiling point in the range 140° to 170° C. obtained by steam cracking a 90° to 210° naphtha cut at a cracking coil exit temperature of 670° to 730° C.

3. A process for the production of hydrocarbon polymers which comprises subjecting a cracked hydrocarbon fraction of petroleum origin having an initial boiling point in the range 15°–120° C. and a final boiling point in the range 140° C.–200° C., to a heat treatment in the liquid phase at a temperature in the range 150°–300° C. and at a pressure in the range 50–2000 lbs./sq. in. gauge for a period of at least 30 mins. and thereafter distilling the product to recover a gasoline fraction, a distillate polymer fraction and a residual polymer fraction.

4. A process as specified in claim 3 in which the heat treated product is distilled at atmospheric pressure to remove said gasoline fraction as overhead, and to recover a polymer fraction as bottoms, thereafter distilling said polymer fraction under reduced pressure to recover a distillate polymer fraction as overhead and said residual polymer fraction containing resinous polymers as bottoms.

5. A process as specified in claim 3 in which the heat treated product is distilled at atmospheric pressure to remove a gasoline fraction overhead, and to recover a polymer fraction as bottoms, thereafter distilling said polymer fraction in the presence of steam to recover said distillate polymer fraction overhead and said residual polymer fraction containing resinous polymers as bottoms.

6. A process as specified in claim 4 in which the fraction containing resinous polymers is further distilled while maintaining the partial pressure of the overhead product below 300 mm. of mercury, with recovery of resinous polymers as bottoms.

7. A process as specified in claim 3 in which the distillate polymer fraction has an initial boiling point in the range 130–200° C. and a final boiling point in the range 200°–300° C.

8. A process for the production of hydrocarbon polymers which comprises subjecting a cracked hydrocarbon fraction having an initial boiling point in the range 15°–120° C. and a final boiling point in the range 140°–200° C., and obtained by steam cracking a petroleum naphtha fraction boiling in the range 90–250° C., to a heat treatment in the liquid phase at a temperature in the range 150°–300° C. and at a pressure in the range 50–2000 lbs./sq. in. gauge for a period of at least 60 mins. and thereafter distilling the product to recover a gasoline fraction, a distillate polymer fraction and a residual polymer fraction.

9. A process as specified in claim 12 in which the second heat treatment, wherein hydrocarbon polymers are produced, is carried out at a temperature in the range 100°–275° C.

10. A process as specified in claim 9 in which the second heat treatment, wherein hydrocarbon polymers are produced, is carried out at a pressure in the range 100–2000 lbs./sq. in. gauge.

11. A process as specified in claim 10 in which the heat treatment, wherein hydrocarbon polymers are produced, is carried out for a period of 3–6 hours.

12. A process for the production of hydrocarbon polymers which comprises subjecting a cyclopentadiene-containing cracked hydrocarbon fraction of petroleum origin having an initial boiling point in the approximate range 15° to 30° C. and a final boiling point in the range 50°

to 70° C. to a preliminary heat treatment at a temperature in the range 70°–120° C., whereby cyclopentadiene contained in the fraction is converted to its dimer, thereafter distilling the product to remove said dimer, subjecting the cyclopentadiene free cracked hydrocarbon fraction obtained overhead to a heat treatment at a temperature above the temperature of said preliminary heat treatment and at a superatmospheric pressure, and distilling the product to recover a hydrocarbon polymer fraction.

13. A process for the production of hydrocarbon polymers which comprises subjecting a cyclopentadiene-containing cracked hydrocarbon fraction of petroleum origin having an initial boiling point in the approximate range 15° to 30° C. and a final boiling point in the range 50° to 70° C. to a preliminary heat treatment at a temperature in the range 70°–120° C., whereby cyclopentadiene contained in the fraction is converted to its dimer, thereafter distilling the product to remove said dimer, subjecting the cyclopentadiene free cracked hydrocarbon fraction obtained overhead to a heat treatment for a period of at least 60 minutes at a temperature above the temperature of said preliminary heat treatment and at a superatmospheric pressure, and distilling the product to recover a gasoline fraction, a distillate polymer fraction and a residual polymer fraction.

14. A process as specified in claim 13 in which the distillate polymer fraction has an initial boiling point in the range 130°–200° C. and a final boiling point in the range 200°–300° C.

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