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PROCESS OF SELECTIVELY POLYMERIZING DIOLEFINS IN AN UNSATURATED AND AROMATIC GASOLINE DISTILLATE

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2 Claims. (Cl. 196—78)

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This invention relates to a process of treating highly cracked gasoline distillates to obtain valuable high diene content polymers and stabilized motor fuel products.

Intensive cracking processes have been developed for producing large amounts of low boiling mono-olefins and diolefins needed for manufacture of synthetic rubber-like polymers. Also, in these processes are produced distillates boiling in the gasoline range, of about 100° F. to 450° F., containing considerable amounts of aromatic hydrocarbons mixed with unsaturated hydrocarbons that are very unstable. The complexity and high instability of these distillates created a problem of selectivity removing the unstable components and, in doing so, forming high diene number polymers that are particularly useful by virtue of their conjugated unsaturation.

An object of this invention is to provide a method of treating that results in the production of high diene number polymers having the property of reacting with relatively large proportions of maleic anhydride, and similarly being capable of combining with large proportions of sulfur or other substances that add particularly to conjugated double bonds.

A further object is to provide a method of treating which conserves valuable unsaturated fuel components that are stable and desirable in the fuel.

Further objects and advantages will be apparent.

Intensive cracking of petroleum cracking stocks occurs when the stocks are heated to temperatures in the range of 1000° F. to 1600° F. At these high temperatures, the cracking is beneficially carried out in the presence of steam or a gas that prevents excessive coke formation. Substantial quantities of unsaturated gaseous hydrocarbons, such as ethylene, propylene, butylenes, and butadiene, are produced. The gasoline distillates yielded contain large amounts of unstable hydrocarbons that readily form gums on oxidation. Among the unstable distillate components, compounds to be expected are typified by C_5 to C_{12} acyclic and cyclic diolefins, such as pentadienes, cyclopentadiene, hexadienes, cyclohexadiene, and the like.

Clay treating processes known to have been used successfully on gasoline distillates produced under mild conditions of cracking were found unsuitable for treating distillates produced under severe cracking conditions.

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The present invention is based primarily on the discovery that the presence of low boiling mono-olefins in a distillate interferes with selective polymerization of higher boiling diolefin components in the distillate, especially if the amount of low boiling diolefins is reduced, and the desired selectivity is obtained in a clay treatment of the distillate freed of low boiling olefins at temperatures in the range 250° F. to 350° F. for a controlled contact period.

In accordance with the present invention, the conditions of the treatment with the catalytic adsorbent have to be carefully controlled to obtain the desired products. The average optimum temperature of the adsorbent during the treatment is in the range 250° F. to 350° F. The optimum space velocity of the gasoline distillate feed is within the limits of 0.2 to 1 volume of the distillate oil per volume of the adsorbent per hour. The treating pressure is variable but should be sufficient to maintain the oil in liquid phase. Following the treatment, the stabilized distillate is separated from polymer and recovered by fractional distillation.

Isoprene (2-methyl-1,3-butadiene) is one of the low boiling C_5 diolefins formed in substantial quantities by intensive cracking, and is purposely separated from the gasoline distillates on account of its usefulness in the manufacture of synthetic rubber-like polymers. On clay treating the remainder of the gasoline distillates from which isoprene was removed, it was found that the polymer yield was high, but the diene number of the polymer was rather low, thus indicating that a considerable amount of the remaining diolefins interpolymerized with mono-olefins.

We then discovered that if the distillates are first processed to separate not only the isoprene but also low boiling mono-olefins, such as C_5 to C_6 olefins, in cuts boiling below 140° F., and the remainders of the distillates are clay treated under optimum conditions, the yield of high diene number polymer is more closely correlated to the diolefin contents of the feeds to the clay treatment, and the treated distillates show considerable improvement in stability, all of which indicate desired high selectivity in the polymerization of the diolefins.

Accordingly, it is now demonstrated to be advantageous to remove low boiling C_5 to C_6 olefins in removing a C_5 diolefin from the unsaturated and aromatic distillates produced by intense cracking before the distillates are subjected to

clay treatment under optimum conditions for selective polymerization of unstable diolefin components that remain in the distillates.

In the selective polymerization treatment, the distillates, freed of the low boiling unsaturates, are contacted in liquid phase with the polymerizing catalyst. They may be percolated through a bed of solid catalyst in granular or lump form, so that the distillate oil in filtering down through the bed washes away polymer from the catalyst.

Floridin, fuller's earth, Attapulgus clay, acid-treated clays, heat-treated clays, or other active siliceous adsorbents, such as zeolites, may be used as the polymerizing catalyst.

For the purpose of illustration, a mode of operation will be described with reference to gasoline distillates from a typical high-temperature steam-cracking process.

TABLE I

TYPICAL CRACKING OPERATION DATA

Fresh feed to cracking furnace, lbs./hr.	40,322
Total feed to cracking furnace, lbs./hr.	41,517
Steam feed to cracking furnace, lbs./hr.	8,025
Cracking temperature, coil outlet, °F.	1,212–1,246
Cracking pressure, lbs./sq. in. gauge	25
Products:	
Tar, lbs./hr.	7,110
°A. P. I.	8.2
Cycle gas oil, lbs/hr.	5,870
°A. P. I.	24.2
Unsaturated-aromatic naphtha distillate, lbs./hr.	9,980
°A. P. I.	49.4
Gas, lbs/hr.	18,000

The following tabulated data were obtained from treatments of the naphtha distillates under comparative conditions with the following alterations of the distillates treated:

A. C_5 diolefin (isoprene) removed, C_5 to C_6 olefins remaining in the naphtha.

B. C_5 diolefin (isoprene) left in with C_5 and C_6 olefins.

C. C_5 diolefin (isoprene) removed with C_5 and C_6 olefins.

TABLE II

NAPHTHA PRODUCTS FROM CLAY TREATING OF HIGH-TEMPERATURE CRACKING NAPHTHA DISTILLATES

Operating conditions of clay treatment

Temperature, °F.	300
Pressure, lbs./sq. in.	100
Feed rate, V./V./hr.	0.25
Clay	Attapulgus

Naphtha Inspections	A, Isoprene Removed, C_5 to C_6 Olefins Remaining in—		B, Isoprene Remaining in with C_5 to C_6 Olefins		C, Isoprene Removed with C_5 to C_6 Olefins	
	Feed	Product	Feed	Product	Feed	Product
Acid Heat (ASTM), ° F.	436	300	465	390	300	245
Aniline Point, ° F.	0	0	2	21	0	0
Peroxide No.	9	0.4	10	0.6	15	[0.3
ASTM Gum:						
Uninhibited	123	2	38	2	404	3
Inhibited	------	2	------	2	------	3
Gravity, ° A. P. I.	43.9	48.0	52.3	55.1	35.5	38.5
Distillation:						
I. B. P., ° F.	111	113	110	106	203	178
Per cent at—						
212° F.	40	41	25	21.5	22.0	17.5
257° F.	55	58.5	71.5	76.5	47.5	50.0
356° F.	81.5	85.0	86.5	93.5	94.5	86.0
F. B. P., ° F.	[1] 432	403	[1] 416	390	[1] 397	401
Loss, Per cent	------	3.0	------	1.7	------	1.1
Naphtha Yield, Per cent	------	82	------	83	------	81

[1] Pyrogallol added prior to distillation.

TABLE III

POLYMER PRODUCTS

Conditions and feeds the same as in Table II

Polymer Inspections [a]	A, Isoprene Removed, C_5 to C_6 Olefins Remaining in Feed	B, Isoprene Remaining in Feed with C_5 to C_6 Olefins	C, Isoprene Removed with C_5 to C_6 Olefins from Feed
Polymer Yield, Vol. per cent	18	17	19
Flash, Open Cup, °F.	240	275	245
Vis./100° F., S. S. U.	2,240	2,788	1,162
Vis./210° F., S. S. U.	78.5	87.3	64.8
Iodine No., cg./g.	249	296	275
Diene No., cg./g. [b]	2, 6[a]	17, 18[a]	20, 22[a]
Maleic Anhydride Value, mg./g.	65, 69[a]	76	102, 115[a]
Diene No. from Maleic Anhydride Value	11, 11[a]	12	17, 19[a]
Distillation:			
I. B. P., °F.	296	440	296
5%	484	487	436
10%	507	497	465
30%	568	569	544
50%	626	608	606

[a] Check Inspections.
[b] cg. Bromine adsorbed by components that react with maleic anhydride per gram of polymer sample.

The foregoing data, including check results, verify that removal of C_5 to C_6 olefins with the C_5 diolefin made the aromatic-unsaturated naphtha susceptible to a more selective polymerization of diolefins remaining in the naphtha on treatment under optimum conditions with the active adsorbent catalyst.

Typical gasoline distillates of intense cracking processes have aniline points of about 0° F. or lower. They generally contain 20 to 40 volume per cent aromatics, 50 to 70 volume per cent mono-olefins, and 10 to 20 volume per cent diolefins. A substantial part of these mono-olefins and diolefins are C_5 and C_6 unsaturated hydrocarbons, which boil at temperatures below 140° F.

The polymers of increased diene number obtained by the controlled selective polymerization of diolefins in the naphtha distillates following removal of low boiling olefins with low boiling diolefins are characterized by their ability to re-

act and combine with large quantities of sulfur supplied as elementary sulfur, sulfur halides, or other sulfurizing agents. The unsaturated polymers may be fully or partly sulfurized before being compounded with natural or synthetic rubbers. They may be co-vulcanized with the rubbers, in which they serve as plasticizers or extenders. They have been found to be particularly useful as plasticizers or softeners of rubber-like copolymers of diolefins, such as the copolymers of styrene with butadiene or isoprene.

After separation of diolefins from the low boiling cut of C_5 to C_6 olefins, e. g., by selective absorption of the diolefins with an ammoniacal cupreous salt solution, these C_5 to C_6 olefins are advantageously added to the stabilized aromatic naphtha product of the selectivity polymerization treatment to obtain a high quality gasoline motor fuel.

It is to be understood that various modifications are intended to come within the spirit and scope of this invention as defined in the appended claims.

We claim:

1. The process of selectively polymerizing diolefins in an unsaturated and aromatic gasoline distillate from a high-temperature cracking process, to obtain high diene number polymers and stabilized motor fuel, which comprises removing from the distillate an unsaturated hydrocarbon cut boiling below 140° F., passing the remainder of the distillate boiling above 140° F. into contact with catalytically active clay at an average temperature in the range of 250° F. to 350° F., said remainder of the distillate being in liquid phase and being contacted with the clay at a space velocity of 0.2 to 1 volume per volume of clay per hour, and recovering the thus clay-treated distillate freed of unstable diolefins and a polymer of high diene number.

2. The process as defined in claim 1, in which diolefins are removed from the unsaturated hydrocarbon cut boiling below 140° F., and monoolefins of the cut are added to the clay-treated distillate freed of diolefins.

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