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PROCESS FOR LOWERING THE POUR  
POINTS OF MINERAL OILS

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9 Claims. (Cl. 196—1)

The invention relates to a process for reducing the pour points of mineral oils or mixtures containing mineral oils, or for the manufacture of such oils having relatively low pour points.

Some hydrocarbon oils, as for instance those originating from paraffin base materials and those obtained by hydrogenation, may show a large increase of viscosity upon the temperature being lowered. The viscosity may even be increased to the extent of rendering the oil entirely unpourable. This so-called "congelation" of the lubricating oil is to be ascribed to the crystallizable paraffin wax present therein. At a low temperature this paraffin wax forms a needle-like structure in the oil, with the result that the latter loses its fluidity. It is evident that lubricants having this property cannot be used in engines operating at low temperatures.

Various methods have already been proposed to separate the crystallizable paraffin wax from the oil. It is known to freeze the oil, sometimes after the addition of solvents, and subsequently to filter off the crystallized paraffin wax by means of filter-presses or centrifuges. It is further known to prevent the crystallization of paraffin wax at low temperatures by the addition of small or large quantities of special substances, known as pour point reducers.

It is already known to reduce the pour point of lubricating oils by adding thereto small quantities of a product obtained by coupling highly molecular paraffinic hydrocarbons to aromatic hydrocarbons, such as naphthalene, anthracene, or benzene.

It has now been found that pour point reducing agents of greater power than those formerly known can be obtained by using for their manufacture highly condensed cyclic hydrocarbons of compound cyclic structures instead of the simple aromatic hydrocarbons mentioned above. These highly condensed cyclic hydrocarbons may be found as naturally present in certain materials, in which case such mixtures may be used, if desired, as initial stock material for the coupling reaction with high molecular paraffinic hydrocarbons. The following are examples of materials containing highly condensed cyclic hydrocarbons, viz. high boiling Edeleanu extracts or polymers thereof, cracked high boiling distillates or residues. The latter materials contain, inter alia, crackene, a highly condensed aromatic hydrocarbon, which when coupled to one of the higher paraffinic hydrocarbons yields a product with a strong pour point reducing action. Liquid materials of the type of Edeleanu extracts and

cracked residues may be regarded as solutions of aromatic hydrocarbons.

The highly condensed cyclic hydrocarbons can also be obtained by subjecting cyclic and particularly aromatic hydrocarbons with or without side chains (partly or completely hydrogenated, if desired), substituted or not, or derivatives thereof, such as alkyl-aryl, oxy-aryl, or other similar compounds, their homologues and/or analogues, or solid or liquid mixtures containing these substances, to a heat treatment in the presence or absence of condensing agents. A few examples of substances which can be worked up into the desired highly condensed cyclic hydrocarbons are: benzene, naphthalene, anthracene, phenanthrene, tetraline, dihydroanthracene, methyl-naphthalene, fluoranthene, chrysene, retene, their homologues and hydrogenation products. It is, however, also possible to start with mixtures or solutions containing these or similar substances, such as Edeleanu extracts, obtained by the treatment with liquid SO<sub>2</sub> or kerosene or heavier petroleum distillates, such as lubricating oil distillates, or corresponding cracked fractions, or heavier residues; also certain tar-oil fractions may be used.

If necessary, metal halides, such as aluminium chloride, zinc chloride, ferric chloride, boron fluoride and the like, may be used as condensing agents.

In general not much is known with certainty as regards the constitution of the products obtained by condensing the above types of cyclic organic compounds. The product obtained, for example, by heating naphthalene with aluminium chloride, according to Homer and Purvis, is tetramethylpicene (vide J. Chem. Soc. 93, 1325, 1928).

The highly condensed cyclic organic compounds may be coupled, or condensed, with a paraffinic hydrocarbon, or a mixture of such hydrocarbons, by any known method, such, for example, as one of those described by Sabatier in his *Catalysis in Organic Chemistry*, Chapter XX.

The products obtained by condensation of highly condensed cyclic compounds with high molecular paraffinic hydrocarbons can be subjected to an extraction treatment with selective solvents whereby a separation into active and inactive constituents is effected.

For the purpose of illustrating the manner in which the invention can be carried out in practice, the following examples are set forth:

1. An Edeleanu extract with S. F. viscosity of 36 seconds at 25° C., obtained by treating spindle oil, was heated with about 10% anhydrous

ZnCl<sub>2</sub> at about 250° C. for about 4 hours at atmospheric pressure. The condensation product, rich in highly condensed aromatics, was separated from settled sludge, washed with water and then dried.

Chlorinated paraffin wax prepared in a conventional manner and containing 14.8% Cl was used as a source of paraffinic radicles to be coupled onto the condensed aromatic nuclei. This coupling was carried out by heating 15 grams of the above condensation product with 40 grams of the chlorinated paraffin wax, at 50°-60° C. for about 24 hours in the presence of anhydrous AlCl<sub>3</sub> and about 50 cm<sup>3</sup> of carbon bisulphide. Thereafter the product was separated from the sludge, washed with water and lye and then the constituents boiling below 300° C. were removed by steam distillation. The product thus obtained, when added in a quantity of 0.3% by weight to a Pennsylvania oil having a pour point of 0° C., lowered the pour point by 15° C.

2. Picene was prepared by heating 3 parts by weight of naphthalene with 1 part by weight of aluminium chloride during 10 hours at 100° C., diluting the resulting product with benzene, washing with iced water and eliminating the benzene and non-converted naphthalene by steam distillation and small quantities of formed dinaphthyl by distillation in vacuo until the temperature of the liquid is about 270° C. at a pressure of 10 mm.

A condensation product of picene with 3 mol. of chlorinated paraffin wax was obtained by stirring 20 grams of picene with 60 grams of chlorinated paraffin wax and 20 grams of AlCl<sub>3</sub> in 150 cm<sup>3</sup> of kerosene during 24 hours at room temperature, allowing the temperature to rise slowly to about 90° C., washing out with water in order to eliminate the AlCl<sub>3</sub> and removing the excess of kerosene and paraffin wax by distillation in a current of nitrogen (in order to exclude the influence of oxygen). When adding 0.5% of the resulting product to a Pennsylvania turbine oil, having a pour point of 0° C., a pour point reduction of 5° C. is obtained. When adding 2% the reduction amounts to more than 15° C.

A product prepared in exactly the same manner by condensation of 1 mol. of naphthalene with 3 mol. of chlorinated paraffin wax, when added in a quantity of 0.5% to the same Pennsylvania oil did practically not lower the pour point; 2% gave a pour point reduction of 1° C.

3. A condensation product of picene with 2 mol. of chlorinated paraffin wax was prepared by heating 20 grams of picene with 40 grams of chlorinated paraffin wax and 20 grams of AlCl<sub>3</sub> in 50 cm<sup>3</sup> CS<sub>2</sub> during 15 hours at 50°-60° C. whilst using a reflux condensor. 0.5% of the resulting product, when added to a Pennsylvania turbine oil, gave a pour point reduction of 9° C. After removing the excess of paraffin wax by distillation, as described in Example 2, 0.5% gave a reduction of 21° C. By extraction with butanone 15 grams of the product was separated into 9 grams insoluble in butanone and 6 grams soluble in butanone. 0.5% of the insoluble part gave a pour point reduction of more than 20° C., whilst the soluble part was inactive with regard to Pennsylvania turbine oil.

A product prepared in exactly the same manner by condensation of 1 mol. of naphthalene and 2 mol. of chlorinated paraffin wax, when added in a quantity of 0.5% to the same Pennsylvania oil, did practically not reduce the pour

point. After eliminating the excess of paraffin in a nitrogen current at 250° C. and a pressure of 10 mm., 0.5% gave a pour point reduction of 2° C. 15 grams of the product was separated by means of butanone into 8 grams soluble in butanone and 7 grams insoluble in butanone. The soluble part proved to be inactive with regard to Pennsylvania oil, whilst 1.5% of the insoluble part gave a pour point reduction of 3° C.

Instead of using the Friedel-Crafts reaction, the condensation products of highly condensed aromatics and high molecular paraffinic hydrocarbons can also be obtained in a different manner, as is shown by the following example.

4. 17 grams of picene were stirred during about 12 hours at room temperature with 32 grams of cetene sulphuric acid (obtained by mixing 67 grams of cetene with 30 grams of H<sub>2</sub>SO<sub>4</sub> of 96% while cooling with ice). Then the product was poured into iced water and extracted with benzene. The benzene extract was subsequently washed until neutral and then the benzene was evaporated. 0.5% of the resulting product reduced the pour point of Pennsylvania turbine oil by 5° C.

A product obtained in exactly the same manner from 13 grams of naphthalene and 65 grams of cetene sulphuric acid was inactive with regard to the same Pennsylvania turbine oil.

The examples given above clearly show that the products obtained by condensation of highly condensed aromatic hydrocarbons with high molecular paraffinic hydrocarbons are far more active pour point reducers than those obtained by condensation of the simple aromatic hydrocarbons with high molecular paraffinic hydrocarbons.

Results similar to those described above were also obtained when using instead of Edeleanu extract or naphthalene either substituted highly condensed cyclic hydrocarbons, or untreated cracked residues or the residues polymerized by reheating at cracking temperatures (above 700° F.), and, in some cases, in the presence of known catalysts. It was found advantageous, when using black oils of the type of fuel oils, to treat them with an asphalt precipitating solvent, such as a liquid low boiling aliphatic hydrocarbon, or a mixture of such hydrocarbons, or light naphtha, etc., in order to improve their color by removing asphaltic components. The asphalt-free oil was then subjected to a condensation treatment, and the resulting oil containing highly condensed aromatics was condensed with chlorinated paraffin wax, or other source of paraffinic group to be attached to the highly condensed aromatic nuclei, such as chlorinated products of the refined high boiling petroleum distillates, like paraffin base lubricating oils; it is to be understood, that any petroleum fraction with appreciable content of higher paraffinic hydrocarbons, can be chlorinated and used in preparing the pour point reducing agents of this invention; paraffinic hydrocarbons may be concentrated in such fractions by one of the known methods, such as sulphuric acid treatments, extraction with selective solvents, etc., and, preferably, should boil above 250° C. (A. S. T. M.), have an average molecular formula  $C_nH_{2n+1.5-1.0}$  and should leave at least 97% unsulfonatable residue after being treated with an excess of 98% H<sub>2</sub>SO<sub>4</sub>.

A few tenths per cent of the products manufactured by coupling highly condensed aromatic hydrocarbons with higher paraffinic hydrocar-

bons added to, say lubricating oils, is, as a rule, already sufficient to obtain a pour point reduction of 10-30° C. dependent on the pour point of the oil to be treated. The products are generally applicable to various kinds of hydrocarbon oils, e. g. natural as well as synthetic lubricating oils (manufactured from mineral or tar oils), fuel oils, oil residues, etc. Furthermore the compounds in question can be used in drilling wells, in order to prevent the deposition of well-wax.

I claim as my invention:

1. A process for lowering the pour point of mineral oil, which comprises incorporating therein a small quantity of an alkylated, highly condensed cyclic hydrocarbon having high molecular paraffinic side chains, and having nuclei containing more than three aromatic or hydrogenated rings.

2. The process according to claim 1 wherein the alkylated, highly condensed hydrocarbons are incorporated in pour point reducing proportions only.

3. A process for lowering the pour point of mineral oil, which comprises incorporating therein less than 1% of the product obtained by the condensation of halogenated high molecular paraffinic hydrocarbons with highly condensed cyclic hydrocarbons selected from the group consisting of cyclic hydrocarbons having more than three aromatic or hydrogenated rings in their molecules, and concentrated solutions of such polycyclic hydrocarbons obtained by the condensation of extracts obtained in refining mineral oils containing cyclic hydrocarbons with selective solvents for non-paraffinic hydrocarbons.

4. A process for lowering the pour point of mineral oil, which comprises incorporating therein less than 1% of the product obtained by the condensation of halogenated high molecular paraffinic hydrocarbons with a mixture of pre-condensed cyclic hydrocarbons selected from the group consisting of cyclic hydrocarbons having more than three aromatic or hydrogenated rings in their molecules, and concentrated solutions of such polycyclic hydrocarbons obtained by the condensation of extracts obtained in refining

mineral oils containing cyclic hydrocarbons with selective solvents for non-paraffinic hydrocarbons.

5. The process according to claim 4 wherein the mixture of pre-condensed cyclic hydrocarbons was formed by the condensation treatment of naphthalene in the presence of a catalyst.

6. As a new article of manufacture, a mineral oil containing a small quantity sufficient to reduce the pour point of said mineral oil of an alkylated, highly condensed cyclic hydrocarbon having high molecular paraffinic side chains, and having nuclei containing more than three aromatic or hydrogenated rings.

7. An improved lubricating oil comprising a blend of a viscous hydrocarbon fraction containing a waxy constituent in proportion sufficient to give an undesirably high pour point and a quantity less than 1% out sufficient to reduce said pour point of an alkylated highly condensed cyclic hydrocarbon having high molecular paraffinic side chains, and having nuclei having more than three aromatic or hydrogenated rings.

8. An improved lubricating oil comprising a blend of a viscous hydrocarbon fraction containing a solid waxy constituent in proportion sufficient to give an undesirably high pour point, and a quantity less than 1% but sufficient to reduce said pour point of alkylated picene having high molecular paraffinic side chains of the size of normally solid paraffinic hydrocarbons.

9. An improved lubricating oil comprising a blend of a viscous hydrocarbon fraction containing a solid waxy constituent in proportion sufficient to give an undesirably high pour point, and a quantity less than 1% but sufficient to reduce said pour point of an alkylated, highly condensed cyclic hydrocarbon having high molecular paraffinic side chains of the size of normally solid paraffinic hydrocarbons, and having nuclei of more than three aromatic or hydrogenated rings obtained by condensing liquid SO<sub>2</sub>-soluble portion of a mineral oil containing cyclic hydrocarbons in the presence of a catalyst.

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