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PROCESS FOR LOWERING THE POUR
POINTS OF MINERAL OILS

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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 when the temperature is 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 or otherwise precipitable 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 precipitable paraffin wax from the oil. It is known to freeze the oil, sometimes after the addition of solvents, and subsequently to filter off the solidified 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 was found that various hydrocarbons or hydrocarbon mixtures which have been subjected to polymerization or condensation treatment have the effect of lowering the pour point of oils containing waxy components. Examples of such hydrocarbon mixtures are, for instance, the residues obtained by cracking hydrocarbon oils or the products obtained by polymerizing Edeleanu extracts, either by heating alone or by heating in the presence of catalysts. It has been found that, in order to obtain hydrocarbon mixtures with such pour point-reducing properties, the heating must be carried out at at least a temperature where a cracking of the hydrocarbons begins to occur, e. g. at about 400° C.; cracked residues are obtained under conditions complying with this requirement. Now it has been discovered that in these pour point-reducing hydrocarbon mixtures, which may be further referred to as pyrogenic condensation products, the active pour point-reducing substances can be concentrated in certain parts or fractions, which must be considered to be the principal carriers of the pour point-reducing properties. These fractions, which can be separated in various ways from the inactive pyrogenic condensation prod-

ucts, may be best characterized by being insoluble in light hydrocarbon mixtures having a low aromatic content.

The process according to the invention consists in adding to a hydrocarbon oil, containing waxy components, a product which is obtained by separating from a hydrocarbon mixture, which already contains pour point-reducing substances, a fraction rich in such substances which are substantially insoluble in hydrocarbon mixtures having a low aromatic content. As is evident from its definition, this fraction may be separated by precipitating it with a low-boiling naphtha or gasoline, poor in aromatics, or by means of such other precipitants, as butane, pentane, alcohol-ether mixtures and in general those organic liquids which are or may be used to separate from asphalt and similar residual or tar-like materials the substances known in petroleum technology as asphaltenes, with which, however, the pour point-reducing substances need not by any means be identical. For instance various pour point-reducing substances according to the invention are insoluble in benzol, whereas, as it is known, asphaltenes are soluble therein to some extent.

In the claims the precipitants to be used according to the invention are referred to as aliphatic solvents, which expression includes all those solvents which are or may be used to separate asphaltenes from asphalt and similar residual or tar-like materials.

The separation of the active substances from mixtures containing them may be effected by fractionation, combined, if desired, with precipitation by above described means. Various fractions obtained by such combination treatment usually have different pour point-reducing activities; some fractions are far more active than others; they also may differ in their colours, some being black and others lighter. In many cases the latter will be chosen when it is a question of lowering the pour point of lubricating oil since in that case the colour is not adversely affected.

The pour point-reducing activity of substances precipitated by various diluents usually depends upon the precipitant (diluent) used; for instance, with kerosene, as diluent, less material is usually precipitated than with a light naphtha, but sometimes the precipitate appears to be more active.

Further it has been found that the activity of the pyrogenic condensation products can be increased by heating. This second heating may be carried out under practically non-cracking conditions, e. g. at 350° C., in contrast to the

first heating whereby the pyrogenic condensation products are formed. This heating may take place in a closed vessel. Also, the pyrogenic condensation products may be subjected to a distillation either with or without steam, vacuum and other known aids to distillation. This distillation results in the concentrating of the active components in the distillation residue (so that later less precipitant is required) and may also cause an increase in the activity of the pyrogenic condensation products, as a result of heating during the distillation. It is evident, that the heating treatment at or about 350° C. and the distillation, as described above, may be combined.

It has been found, that by properly regulating the time and temperatures of cracking, either followed or not by heating the pyrogenous condensation products at non-cracking temperatures, the pour point reducing substances of maximum activity can be produced. As a general rule, commercial cracked residues, which are obtained under the conditions selected for a maximum production of gasoline, are not sufficiently cracked to yield the most active pour point reducers; it is advantageous to subject such residues to further polymerizing heat treatments, preferably without further cracking at temperatures about 350° C. The active substances formed during such treatments reach a certain maximum (either quantitative or qualitative in character) and then, if overheated, begin to decline in their effectiveness. By actually testing the materials obtained at various stages of the polymerizing treatment, the optimum conditions for production of the most active product can be readily ascertained for any cracked residue. Sometimes it is found suitable to add the pyrogenic condensation products, activated by heating and/or concentrated by distillation, directly, without previous precipitation of the active substances, to the hydrocarbon oil whose pour point is to be lowered.

The pour point-reducing substances may be added to the hydrocarbon oils either in the form in which they are obtained or after being dissolved in a solvent; as suitable solvents, hydrocarbon mixtures of aromatic character, such as Edeleanu extract or tar oil, may be used for making relatively concentrated solutions. If solutions of moderate concentration are desired, then, for instance, lubricating oils may be used as solvents.

In order to promote the dissolving of pour point-reducing substances in hydrocarbon oils, a moderate heating, say at a temperature of about 100° C., may be used.

The invention is applicable to various types of hydrocarbon oils; for instance, the product manufactured according to the invention may even be added to crude oils, in order to prevent a deposit of well wax in the well, or used in the pipelines carrying crude-oils, etc.

It has been found that isolation of active pour point reducers could be particularly readily attained by means of such light solvents as lower members of paraffinic series, like butane, pentane and hexane.

Examples

I. Edeleanu extract from a Venezuelan lubricating oil fraction was heated at 400° C. under pressure for 4 hours. The product obtained was evaporated with steam until a volume equal to one-fifth of the volume of the original Edeleanu extract was obtained. This latter was treated

with an excess of naphtha with boiling range 60–80° C. The separated insoluble fraction was found to be 20 times as active, as regards pour point-reducing effect, than the substances dissolved in the naphtha, which were found to constitute about 50% of the concentrate. 0.05% of the substances insoluble in the naphtha, calculated on the weight of a Pennsylvanian turbine oil, was added with moderate heating to the oil, which had a pour point of 0° C.; as a result, the pour point of the turbine oil was reduced to –12° C.

II. A residue obtained in the Dubbs cracking of Venezuelan crude oil, when added in a quantity of 1% to a Pennsylvanian lubricating oil with the original pour point of 0° C. reduced the pour point of the oil by 18° C. A quantity of 0.1% did not appreciably affect the pour point.

The fraction precipitated from this cracked residue with 100 times its volume of pentane, which fraction constituted 26.7% of the residue, caused, when added with moderate heating in a quantity of 0.1% to the same Pennsylvanian lubricating oil, a pour point reduction of 15° C.

The fraction soluble in pentane, when added in a quantity of 2% after evaporation of the pentane, had no effect on the pour point of the Pennsylvanian oil.

III. Edeleanu extract from a heavy engine oil fraction of Venezuelan origin was heated for 4 hours to 400° C. under a pressure of about 7 atm., when a residue was obtained which constituted about 80% of the initial product. 1% of this pyrogenic condensation product added to a Pennsylvanian lubricating oil with a pour point of 0° C. reduced the pour point to –21° C. The addition of .1% practically did not affect the pour point of the lubricating oil.

When this pyrogenic condensation product was treated with 100 times its volume of pentane, a precipitate separated out in a quantity of 11.6% calculated on the heated product; 0.05% of the precipitate was added to the above-mentioned Pennsylvanian lubricating oil with moderate heating, whereby the pour point of the oil was reduced to –12° C.

2% of the fraction soluble in pentane added after evaporation of the pentane had no effect.

The foregoing examples demonstrate some of the methods of isolating active substances from pyrogenous condensation products and the effects of such separated substances upon the pour points of oils containing waxy components and having, therefore, relatively high pour points.

While certain specific liquids were particularly mentioned in the above description as being suitable for treating residual products of cracking, it should be clearly understood that other liquid solvents for the inert portions of such residual products may be successfully used in separating active pour point reducers from pyrogenous condensation products. Such solvents, which may include various straight run naphthas, preferably boiling below 225° C., or light kerosenes, or alcohols, ethers, mixtures etc., may generally be characterized as being of aliphatic nature, i. e. not aromatic; it should be realized, of course, that small quantities of aromatic substances, which may occur in commercial aliphatic solvents in quantities not exceeding 15% by volume, are to be considered as permissible for the purpose of this invention.

When separating the active substances from the pyrogenous condensation products it was found very expedient in many cases to employ a series of precipitations of the active substances

from successively obtained precipitates. In other words, the inert substances were removed from the original mixture by a series of successive extracting steps with portions of the same solvent or with different solvents being used in each step.

Often it was found advantageous to filter the mixture of pyrogenous condensation products, particularly those, which contain granular carbonaceous materials, and then proceed with the concentration of the active pour point-reducing substances in the filtrate.

As a further feature of this invention, the separation of active pour point-reducing substances may be accomplished by a method, which permits concentration of such substances separately from a gritty or granular material often found in cracked residues. This method consists of precipitating such gritty material by diluting a cracked residue with a relatively heavy or high boiling diluent, such as distillates boiling above 225° C. and preferably about 300° C. or higher, like stove oil or gas oil, etc. Edeleanu extracts and other oils with similarly high contents of aromatics (15% or above) were found very suitable for separating said gritty material from residues without an extensive loss of active substances. Some of the active pour point reducing substances are usually carried down with the precipitate but the major portion of these substances remains in the diluted oil, or the filtrate, and is then recovered therefrom by precipitation with a light aliphatic precipitant, such as described hereinbefore; the first diluent (high boiling) may be partly or completely distilled out of the filtrate, or liquid portion of the diluted cracked residue, before the low boiling diluent is added thereto.

As an example, a cracked Dubbs residue from cracking a topped crude was diluted with two volumes of a high boiling (240-290° C.) kerosene distillate (about 20% aromatics) at a temperature below 65° C.; and a precipitate containing gritty particles was filtered off. The filtrate was then mixed with about five volumes of a "pentane" fraction of natural gasoline (boiling range 28-38° C.), with the result that a new precipitate separated out, which had a marked power of lowering the pour points of paraffin base oils; by adding as little as 2-5% by weight of this precipitate to an oil having pour point -7° C., this was lowered to -25° C.

The first precipitate, which contained said gritty material was also extracted with a light naphtha at about 20° C., and the resulting undissolved material was found to be active as a pour point reducer, lowering the pour point of some of the Pennsylvanian lubricating oils by about 8° C. when added in quantities of about 5% by weight.

As a modification of the described methods of concentrating active pour point reducing substances, the following process has proved to be quite useful:

A sample of the Dubbs residue was diluted with an untreated kerosene distillate, and a precipitate containing a gritty carbonaceous material was separated out from a liquid portion of the diluted cracked residue. A quantity of commercial paraffin wax (about 20% by weight) was dissolved then in this liquid portion of the cracked residue while heating it up to about 65° C. Upon cooling to about 20° C. a part of the dissolved wax separated out of the solution together with some dark-coloured components of the resi-

due; this precipitate was filtered off and then thoroughly washed with the pentane fraction (B. P. 28-38° C.) to remove waxy components. The remaining dark-coloured substances were found to possess considerable pour point-reducing power, e. g. when .5% by weight was added to a paraffin base lubricating oil, its pour point was lowered from -7° C. to -20° C.

The solution of the remaining wax in the diluted cracked residue was also found to contain the desired active substances. This solution was diluted with about five volumes of the pentane fraction at an ordinary room temperature of about 20° C.; this caused a precipitate to separate out, which, when it was added in quantity of .5% by weight to the paraffin base oil, caused lowering of its pour point from -7° C. to -20° C.

It was generally observed, that the addition of pour point-reducing substances to lubricating oils results in modifying their colours and causes the oils to acquire the desirable green overtone. If necessary a careful acid treatment of the oils to which the pour point reducing substances are added may take place. Too intensive an acid treatment or treatment with decolourizing powders cannot be recommended, as such treatment tends to neutralize partly or even wholly the pour point reduction.

While various quantities of pour point-reducing substances of this invention may be used, these never need to exceed 1% by weight of the oil being treated.

I claim as my invention:

1. The method of lowering the pour point of a viscous mineral oil containing waxy components, which comprises incorporating into said oil the active substances separated from pyrogenous condensation products from mineral oil by precipitation with an aliphatic solvent.

2. In a process of lowering the pour point of a mineral oil containing waxy components the steps of: diluting a mixture of pyrogenous condensation products from mineral oil with a relatively low boiling aliphatic solvent, thereby causing precipitation of pour point-reducing substances from the mixture, separating the formed precipitate from the diluted mixture, and incorporating a small quantity of the separated precipitate into the said oil.

3. In a process of concentrating active pour point-reducing substances from a mixture of pyrogenous condensation products from mineral oil the steps of: heating said mixture at elevated temperatures not exceeding 400° C., separating a portion of the mixture which may vaporize at these temperatures from the less volatile portion, and diluting the latter with a relatively low boiling aliphatic solvent thereby causing precipitation of pour point-reducing substances.

4. In a process of concentrating active pour point-reducing substances from a mixture of pyrogenous condensation products from mineral oil the steps of: diluting the mixture with an aliphatic solvent, heating the diluted mixture to an elevated temperature, thereby substantially dissolving the inert portion of the original mixture in the solvent, separating the undissolved portion from the mixture, and extracting said portion with an aliphatic solvent at a room temperature, thereby concentrating the desired active substances in a residue which is substantially insoluble in said solvents.

5. An improved lubricating oil comprising a blend of a viscous hydrocarbon oil containing

waxy components in proportion sufficient to give a relatively high pour point and a portion of the pyrogenous condensation products from mineral oil which has been separated therefrom by precipitation with an aliphatic solvent.

6. The method of treating a hydrocarbon oil containing waxy components to reduce its pour point which comprises heating a mineral oil to a cracking temperature to produce pyrogenous condensation products, removing said products from the rest of the cracked oil, diluting said products with a relatively low boiling aliphatic solvent, to separate soluble products from insoluble components, separating the insoluble components from the diluent, and then adding the separated insoluble components to the oil containing waxy components in proportion to cause a lowering of its pour point.

7. The method according to claim 6 in which the mineral oil is a liquid SO_2 -soluble portion of a mineral oil and the temperature is about 400°C .

8. The method of treating a hydrocarbon oil containing waxy components to reduce its pour point which comprises reducing a cracked mineral oil residue containing pyrogenous condensation products by distilling at temperatures which are below cracking temperatures, and adding the portion of the residue which has been precipitated therefrom by a low boiling aliphatic solvent to said oil containing waxy components in proportion to cause a lowering of its pour point.

9. The method of treating a hydrocarbon oil containing waxy components to reduce its pour point which comprises digesting a cracked mineral oil residue containing pyrogenous condensation products at an elevated temperature which is below its cracking temperature, and adding the portion of the digested products which has been precipitated therefrom by a low boiling aliphatic solvent to said oil containing waxy components in proportion to cause a lowering of its pour point.

10. The method according to claim 9 in which the digesting is conducted at a temperature of about 350°C .

11. The method of treating a hydrocarbon oil containing waxy components to reduce its pour point which comprises diluting a cracked mineral oil residue containing pyrogenous condensation products with a liquid hydrocarbon having a high aromatic content, filtering the mixture, mixing the filtrate with a relatively low boiling aliphatic solvent, separating the insoluble constituents from the diluent and then adding them to said

oil containing waxy components in proportion to cause a lowering of its pour point.

12. The method of treating a hydrocarbon oil containing waxy components to reduce its pour point which comprises diluting a cracked mineral oil residue containing pyrogenous condensation products with a liquid hydrocarbon having a high aromatic content, heating the resulting mixture and dissolving paraffin wax therein beyond the amount which is soluble at ordinary temperatures, chilling the mixture to precipitate wax and active pour point reducers, separating the precipitated products from the liquid mixture, adding a relatively low boiling aliphatic solvent to said precipitated products to dissolve the wax, separating the insoluble residue from the wax solution, and adding the insoluble residue to said oil containing waxy components in proportion to cause a lowering of its pour point.

13. A process for the production of pour point depression agents from petroleum pitch which comprises commingling said pitch with naphtha, separating the naphtha and dissolved fractions from the insoluble residue, commingling the insoluble residue with a lubricating oil fraction and separating the lubricating oil solution of pour point depression agents from the remaining insoluble residue.

14. A process for the production of pour point depression agents from petroleum residue which comprises extracting said residue with naphtha, so as to obtain an insoluble portion, and admixing the insoluble portion to a lubricating oil to dissolve active pour point depression agents from said insoluble portion.

15. A process for the production of pour point depression agents from a pitch produced from cracked petroleum which comprises commingling said pitch with naphtha, separating the naphtha and dissolved fractions from the insoluble residue, commingling the insoluble residue with a lubricating oil fraction and separating the lubricating oil solution of pour point depression agents from the remaining insoluble residue.

16. A process for the production of pour point depression agents from a residue produced from cracked petroleum which comprises extracting said residue with naphtha, so as to obtain an insoluble portion, and admixing the insoluble portion to a lubricating oil to dissolve active pour point depression agents from said insoluble portion.

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