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HYDROCARBON OIL COMPOSITIONS

Jack Linsk and Clyde S. Scanley, Hammond, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to hydrocarbon oils, and more particularly to hydrocarbon oil compositions having improved pourpoint characteristics.

Hydrocarbon oils, particularly those derived from paraffin and mixed base crude oils, contain petroleum waxes, particularly paraffin waxes, which cause such oils to congeal or solidify at relatively high temperatures. Even when such oils are dewaxed by well known methods sufficient wax is retained in the oil so that such oils may congeal or solidify at temperatures of 0° F. to 32° F. To reduce the pourpoint of an oil by the complete removal of the wax contained therein is uneconomical, and undesirable for other reasons. Accordingly, it is generally preferred to reduce the pourpoint of an oil and improve its flow characteristics at low temperatures by other means.

It is an object of this invention to provide a hydrocarbon oil exhibiting a reduced pourpoint and improved flow characteristics at low temperatures. Another object of the invention is to provide a wax-containing hydrocarbon oil having a low pourpoint. Still another object of the invention is to provide a method of reducing the pourpoint of a hydrocarbon oil. Other objects and advantages of the invention will become apparent from the following description thereof.

In accordance with the present invention, the foregoing objects, among others, can be attained by incorporating in a hydrocarbon oil an esterified tripolymer, hereinafter described, in smali but sufficient quantities to impart improved pourpoint properties to the hydrocarbon oil. The substance employed in the present invention is an ester of a tripolymer of an unsaturated non-benzenoid hydrocarbon, an unsaturated polycarboxylic acid or anhydride thereof, and an alkyl vinyl ether of the type $CH_2=CH-O-R$, in which R is an alkyl group of 2 to about 18 carbon atoms, and preferably from about 4 to about 10 carbon atoms.

Examples of suitable unsaturated polycarboxylic acids and anhydrides are maleic acid, fumaric acid, aconitic acid, itaconic acid, citraconic acid, maleic anhydride, itaconic anhydride, citraconic anhydride, etc., although maleic anhydride is preferred.

Examples of suitable vinyl ethers are ethyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, 2-ethylhexyl vinyl ether, octyi vinyl ether, dodecyl vinyl ether, octadecyl vinyl ether, etc.

The unsaturated non-benzenoid hydrocarbons include the acyclic unsaturated hydrocarbons and the alicyclic unsaturated hydrocarbons of 2 to about 18 carbon atoms. Examples of suitable hydrocarbons are ethylene, n-butylene, diisobutylene, hexene, cyclohexene, octene-1, decene-1, tridecene-1, hexadecene-1, octyne-1, octadecene, etc. Individual non-benzenoid hydrocarbons or mixtures thereof can be used.

The tripolymer can be prepared by polymerizing a mixture of the unsaturated non-benzenoid hydrocarbon, for example an olefin, an unsaturated carboxylic acid or anhydride, and an alkyl vinyl ether in solution in a suitable solvent, such as toluene, benzene, acetone, etc., at a temperature of from about 70° F. to about the boiling point of the solvent. The reaction is initiated by a suitable catalyst, such as an organic peroxide, for example, benzoyl peroxide, acetyl peroxide, stearyl peroxide, chlorobenzoyl peroxide, dimethyl peroxide, etc., or an inorganic catalyst, such as for example, an alkali metal persulfate, hydrogen peroxide, etc. In the preparation of the tripolymer, the olefin, unsaturated carboxylic acid or anhydride, and the alkyl vinyl ether can be used in the molar ratio of 1:10:9 to 9:10:1, but preferably 1:2:1. The tripolymer precipitates from the reaction mixture and is then esterified by boiling with an excess of the selected alcohol in benzene or toluene solution, in the presence of a suitable catalyst, such as sulfuric acid, toluene sulfonic acid, etc. Any suitable aliphatic alcohol can be used in the esterification reaction, although aliphatic alcohols of at least about 6 carbon atoms, and preferably 8 to 20 carbon atoms, are preferred. Mixtures of such alcohols may also be used. When vinyl ethers containing particularly long alkyl groups, such as octadecyl vinyl ether, are used, alcohols having as low as four or even two atoms per molecule may be used to obtain hydrocarbon soluble polymer. Examples of suitable aliphatic alcohols are ethyl alcohol, hexyl alcohol, n-octyl alcohol, n-nonyl alcohol, oxononyl alcohol, n-dodecyl alcohol, n-tetra-decyl alcohol, n-hexadecyl alcohol, tridecyl alcohol, etc. When the esterification is judged complete the acid is removed by water washing and the solution dried, for example, with anhydrous sodium sulfate, or by distillation. The excess alcohol and solvent may be removed and recovered by suitable means, preferably by vacuum distillation. Alternatively, the alcohol and solvent may be recovered by steam distillation, in which case the polymer may be dissolved in a suitable mineral oil and the residual moisture removed by air blowing at 220°–250° F.

The tripolymers of this invention are moderately tacky and have softening points slightly above room temperature. They are easily handled, and dissolve readily in hydrocarbon oils. It will be apparent to those skilled in the art that a wide variety of compositions is possible. Thus, if it is desired to use a short chain alcohol to esterify the tripolymers of this invention, it will be desirable to use a vinyl ether having a longer alkyl group in the original tripolymer, although a vinyl ether having a short alkyl group will also be satisfactory. Tripolymers in the molecular weight range of 1000 to about 40,000, and preferably 2,000 to about 20,000 can be employed in the present invention.

The esterified tripolymer is suitably employed in hydrocarbon oils in amounts of from about 0.05% to about 15%, by weight, and preferably from about 0.1% to about 5%, by weight. The term "hydrocarbon oil" as used herein refers to oils having a Saybolt Universal viscosity at 100° F. of at least 35 seconds, and includes oils in the fuel oil range, such as diesel fuels, furnace oils and heater oils, as well as higher viscosity oils used as lubricating oils and in greases. The oils may be natural or synthetic oils and may be solvent-extracted hydrocarbon oils or conventionally refined oils obtained from various base crude oils. Furthermore, the oils may be petroleum distillates or residuums or mixtures thereof, or may be mixtures of natural hydrocarbon oils and synthetic oils. Additionally, the hydrocarbon oil may be compounded with animal, vegetable and/or marine oils and can contain additives, such as detergent-type additives, corrosion inhibitors, antioxidants, E. P. agents, etc.

In order to illustrate our invention, the following examples are given:

Example I

A mixture of 20 grams of decene-1, 10 grams of maleic anhydride and 16 grams of 2-ethylhexyl vinyl ether was polymerized in toluene solution at 100° C. for sixteen hours, using 250 milligrams of benzoyl peroxide as the catalyst. After concentration under vacuum, 35 grams of granular solid polymer was obtained. Six grams of the polymer was dissolved in 100 ml. of benzene and 35 g. of decanol-1. One gram of concentrated sulfuric acid was added as an esterification catalyst, and the solution was refluxed about 40 hours. At this time no more water was collecting in the water trap. The solution was cooled, washed with water, and concentrated in vacuum at 150° C. The residue was light amber in color and weighed 8.9 g.

Example II

Five grams of the tripolymer prepared in Example I was esterfield with 35 g. of dodecanol-1 in the manner described above. The solution was concentrated by distillation and poured into aqueous methanol containing enough dissolved NaOH to neutralize the sulfuric acid used in the esterification reaction. The polymer precipitated, and was washed twice with methanol, then with water, and dissolved in naphtha. The naphtha solution was dried over anhydrous sodium sulfate and concentrated in vacuum. The yield of polymer was 6.5 g.

Various amounts of the esterified polymers obtained in Examples I and II were added to a zero pourpoint hydrocarbon oil and the pourpoints determined. The results obtained are tabulated in the following table:

Polymer Ester	Percent By Weight	Hydrocarbon Oil	Pourpoint, ° F.
n-Decyl	0.3	SAE 5 W Base Oil	—30.
Do	1.2	do	—50—pouring.
n-Dodecyl	1.0	do	Do.

Example III

A tripolymer was prepared by copolymerization of octadecene-1 with maleic anhydride and 2-ethylhexyl vinyl ether in the manner demonstrated in Example I. Portions of the solid tripolymer obtained were then esterified with n-dodecyl and n-tetradecyl alcohols as in Example II. Various amounts of the resultant esterified tripolymers were added to various base oils and pourpoint determinations made. The results obtained are tabulated in the following table:

Base Oil	Polymer Ester	Percent (weight)	Pourpoint, ° F.
SAE 5 W Base Oil	None		0
Do	Dodecyl	0.1	—45
Do	do	0.2	—50
Do	Tetradecyl	0.1	—30
Do	do	0.2	—35
SAE 10 Base Oil	None		+5
Do	Dodecyl	0.1	—10
Do	do	0.4	—40
Do	Tetradecyl	0.1	—20
Do	do	0.2	—30

Example IV

A tripolymer was prepared by copolymerizing octene-1 with maleic anhydride and 2-ethylhexyl vinyl ether in the manner described in Example I, and portions of this polymer were esterified with n-decyl alcohol, n-dodecyl alcohol, and n-tetradecyl alcohol. The resultant esterified compositions were dissolved in various base hydrocarbon oils and the pourpoints determined. The results obtained are tabulated in the following table:

Base Oil	Polymer Ester	Percent (weight)	Pourpoint, ° F.
SAE 5 W Base Oil	None		0
Do	n-decyl	0.1	—15
Do	do	0.2	—20
Do	do	0.4	—25
SAE 10 Base Oil	None		0
Do	n-decyl	0.4	—10
SAE 5 W Base Oil	n-dodecyl	0.1	—40
Do	do	0.4	—55
SAE 10 Base Oil	do	0.2	—5
Do	do	0.4	—40
SAE 40 Base Oil	None		0
Do	n-dodecyl	0.2	—5
SAE 5 W Base Oil	n-tetradecyl	0.1	—40
SAE 10 Base Oil	do	0.2	—45
SAE 40 Base Oil	do	0.2	—15

Example V

A tripolymer was prepared from 22.4 grams disobutylene, 9.8 grams maleic anhydride, and 15.6 grams 2-ethylhexyl vinyl ether in the manner described in Example I. The solid polymer weighed 27 g. Samples of the polymer were esterified with tetradecanol-1 in the manner described in Example I. The esterified polymer was isolated as follows: Benzene and excess alcohol were recovered by steam distillation. The polymer was then dissolved in naphtha, the solution washed with water, dried over anhydrous sodium sulfate, and concentrated in vacuum. For commercial operation the polymer could be dissolved in a suitable base oil, the concentrate washed with water, and dried by air or nitrogen blowing at 220° F.—300° F.

The tetradecanol ester lowered the pourpoint of an SAE 5 W Base Oil from 0° F. to about —50° F. in 0.1% concentration.

The base oils used in the above tests were solvent-extracted lubricating oil base stocks of the following Saybolt Universal viscosities:

Oil	Viscosity (secs.)	Temperature, ° F.
SAE 5 W	90	100
SAE10	85	130
SAE 20	170	130
SAE 40	75	210

The ester tripolymers of the present invention, while exhibiting good pourpoint depressing properties, have little effect on the viscosity index of the oil. Comparison of the products illustrated in the examples demonstrate that the non-benzenoid hydrocarbon, e. g., olefin, has a marked effect on the pour depressing properties of the resulting composition.

Percentages given herein and in the appended claims are weight percentages, unless otherwise stated.

While we have described our invention by reference to certain specific examples, these have been given by way of illustration only, and not by way of limiting the invention, which includes within its scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. A hydrocarbon oil composition comprising a major proportion of a hydrocarbon oil and a small proportion, sufficient to improve the pourpoint properties of said oil, of an ester of an aliphatic alcohol with a tripolymer, having a molecular weight of from about 1000 to about 40,000, of an unsaturated hydrocarbon selected from the group consisting of an acyclic unsaturated hydrocarbon, an alicyclic unsaturated hydrocarbon and mixtures thereof, an unsaturated polybasic compound selected from the group consisting of maleic acid, fumaric acid, aconitic acid, itaconic acid, citraconic acid and anhydrides thereof, and an alkyl vinyl ether having 2 to about 18 carbon atoms in the alkyl group, said unsaturated hydrocarbon, said unsaturated polybasic compound, and said alkyl vinyl

ether being employed in the molar ratio of from about 1:10:9 to 9:10:1.

2. A lubricant composition as described in claim 1 in which the unsaturated hydrocarbon is decene-1.

3. A hydrocarbon composition described in claim 1 in which the unsaturated hydrocarbon is octadecene-1.

4. A hydrocarbon composition as described in claim 1 in which the unsaturated hydrocarbon is octene-1.

5. A hydrocarbon oil composition as described in claim 1 in which the unsaturated hydrocarbon is diisobutylene.

6. A hydrocarbon oil composition as described in claim 1 in which the unsaturated hydrocarbon is octyne-1.

7. A hydrocarbon oil composition as described in claim 1 in which the unsaturated polybasic compound is maleic anhydride.

8. A hydrocarbon oil composition as described in claim 1 in which the unsaturated polybasic compound is citraconic acid.

9. A hydrocarbon oil composition as described in claim 1 in which the unsaturated polybasic compound is itaconic anhydride.

10. A hydrocarbon oil composition as described in claim 1 in which the alkyl vinyl ether is 2-ethyl hexyl vinyl ether.

11. A hydrocarbon oil composition as described in claim 1 in which the alkyl vinyl ether is butyl vinyl ether.

12. A hydrocarbon oil composition as described in claim 1 in which the alkyl vinyl ether is octadecyl vinyl ether.

13. A hydrocarbon oil composition as described in claim 1 in which the aliphatic alcohol is ethyl alcohol.

14. A hydrocarbon oil composition as described in claim 1 in which the aliphatic alcohol is n-decyl alcohol.

15. A hydrocarbon oil composition as described in claim 1 in which the aliphatic alcohol is n-dodecyl alcohol.

16. A hydrocarbon oil composition as described in claim 1 in which the aliphatic alcohol is n-tetradecyl alcohol.

17. A lubricant composition comprising a major proportion of a wax-containing lubricating oil and from about 0.05% to about 10% of an ester of an aliphatic alcohol having at least 6 carbon atoms with a tripolymer of an acyclic unsaturated hydrocarbon having 2 to about 18 carbon atoms, maleic anhydride, and an alkyl vinyl ether having 2 to about 18 carbon atoms in the alkyl group, said tripolymer having a molecular weight of from about 1000 to about 40,000 said unsaturated hydrocarbon, said maleic anhydride, and said alkyl vinyl ether being employed in the molar ratio of from 1:10:9 to 9:10:1.

18. A method of improving the pourpoint of a lubricant composition comprising a major proportion of a hydrocarbon lubricating oil normally containing wax, comprising adding to said wax-containing hydrocarbon lubricating oil from about 0.05% to about 10% of an ester of an aliphatic alcohol with a tripolymer, having a molecular weight of from about 1000 to about 40,000, of an unsaturated hydrocarbon selected from the group consisting of an acyclic unsaturated hydrocarbon, an alicyclic unsaturated hydrocarbon and mixtures thereof, an unsaturated polybasic compound selected from the group consisting of maleic acid, fumaric acid, aconitic acid, itaconic acid, citraconic acid, and anhydrides thereof, and an alkyl vinyl ether having 2 to about 18 carbon atoms in the alkyl group, said unsaturated hydrocarbon, said unsaturated polybasic compound, and said alkyl vinyl ether being employed in the molar ratio of from about 1:10:9 to 9:10:1.

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