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HYDROCARBON OIL

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This invention relates to hydrocarbon oils and particularly to mineral oil compositions having low pour points and high stability against breakdown under oxidizing conditions.

Hydrocarbon oils, derived from paraffin and mixed base crude oils, contain an appreciable amount of paraffin wax which causes the oil to solidify at low temperatures and, in the case of lubricating oils, prevent efficient flow of the lubricants to moving parts. In the low viscosity mineral oils, such as those boiling above the kerosene range and used as fuels in compression-ignition engines, the presence of wax may cause congelation of the oil in storage tanks at low temperatures. Such wax may be removed by cold settling or by dilution with a low boiling naphtha followed by chilling and centrifuging or filtration. These processes of removing the wax are expensive and may, if complete removal of the wax is effected, result in a lubricant with a reduced viscosity index or a fuel with unsatisfactory combustion characteristics. Accordingly, it is generally desirable to reduce the pour point of the oil and improve its flow characteristics at low temperature while retaining a substantial amount of wax in the oil.

Many materials have been proposed for addition to lubricating oils to reduce their pour points and to improve their flow characteristics at low temperatures. Such materials include condensation products of aromatic hydrocarbons with chlorinated paraffin wax, mixed aryl alkyl ketones, and fatty acids and their salts and esters. Such materials act with varying degrees of efficiency in depressing the pour points of the oils, but generally have no beneficial effect on any of the other properties of the lubricants. Under conditions of service which are found in modern automobile engines, oils tend to oxidize and form sludge which deposits on engine parts or to form corrosive products which seriously attack alloy bearings. Many materials have been added to oils to reduce their tendency toward deterioration, but such materials generally have no beneficial effect on other properties of the oils.

It is an object of the present invention to provide hydrocarbon oils with reduced pour points and improved flow characteristics at low temperatures. Another object of my invention is to provide lubricants which will have improved stability, as well as improved pour point characteristics. A further object is to provide new and improved pour point depressant compositions for addition to petroleum oils. A more particular

object of my invention is to provide hydrocarbon lubricating oils of reduced pour point which is maintained to a high degree under conditions of service in an engine and which have had their tendency toward the formation of engine deposits substantially reduced. A still further object is to provide a method for reducing the pour points and improving the stability of hydrocarbon oils. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with my invention which comprises incorporating in a hydrocarbon oil a small proportion of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-aliphatic-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by an aromatic or aromatic ether radical and the N-aliphatic group contains at least 12 carbon atoms. I have found that such polymeric materials are very effective to reduce the pour points and improve the flow characteristics of mineral oils at low temperatures. At the same time, the polymeric materials improve the stability of the oils and particularly reduce the tendency of the oils to form objectionable deposits in engines under conditions of service. Furthermore, the oils, containing such polymeric materials, show high resistance to corrosion of alloy bearing metals.

The polymeric materials, to be added to the hydrocarbon oils in accordance with my invention, may be described alternatively as polymeric imides, having a molecular weight of at least 1000, formed by reacting a copolymer of an olefin, having linked thereto an aromatic radical either directly or through an ether linkage, and a maleic anhydride, with a primary aliphatic amine containing at least 12 carbon atoms in the aliphatic group. The polymeric material may also be characterized as a polymeric material having a molecular weight of 1000 or more and having, as its monomeric unit, the hypothetical addition product of an N-substituted imide of an alpha-beta unsaturated dicarboxylic acid, in which the substituent on the nitrogen atom is an aliphatic group containing at least 12 carbon atoms, with a compound having the general formula



wherein X is an aromatic group joined to the carbon residue, either directly or through an oxygen or sulfur atom, by a single bond and Y is a hydrogen atom or an alkyl or aryl group joined directly to the carbon residue.

The aliphatic groups, in the N-aliphatic-2,5-pyrrolidinedione nucleus, include cyclo aliphatic and branched chain aliphatic, as well as straight chain aliphatic groups. Also, the aliphatic group may be saturated or unsaturated. Generally, it will be preferred that the aliphatic group be a hydrocarbon group, that is, one which consists of carbon and hydrogen. However, the aliphatic group may be substituted by other elements or groups, such as chlorine, fluorine, divalent sulfur-containing, and oxygen-containing groups, particularly in the form of ether or thioether linkages. The primary amines, from which the N-aliphatic groups are derived, may be derived from vegetable, animal or fish oils or by the oxidation of paraffin or other petroleum fractions or from naphthenes. I have found that the best results are obtained when the N-aliphatic group is an alkyl group and particularly an octadecyl group. By an "alkyl" group, I mean a saturated aliphatic hydrocarbon group.

Each of the dimethylene groups, which forms a chain member in the polymeric compounds, must have at least one hydrogen replaced by an aromatic or an aromatic ether radical and preferably by an aromatic radical. By an "aromatic radical," I mean one in which the free valence belongs to a ring carbon atom of a benzene ring. By an "aromatic ether radical," I mean that a ring carbon atom of a benzene ring is joined to a carbon of the dimethylene group by an ether linkage or, in other words, through oxygen or sulfur. The aromatic and aromatic ether radicals, attached to the dimethylene group, may be substituted by elements and groups other than carbon and hydrogen, such as chlorine, fluorine, nitro, ethoxy, isobutyloxy, ethylthiopropylthio, benzylthio, ethyl carboxy, hydroxy, methyl, ethyl, allyl, benzyl, cyclohexyl and the like. Preferably, the aromatic radicals are aryl radicals, that is, radicals which consist of carbon and hydrogen, and particularly aryl radicals of the benzene series. By an "aryl radical of the benzene series," I mean one which contains one and only one benzene ring.

The preferred polymeric materials of my invention are the styrene/N-octadecyl-maleimide and the indene/N-octadecyl-maleimide products.

The polymeric materials, which are to be employed in accordance with my invention, may be prepared by the copolymerization of an olefinic compound, containing an aromatic nucleus, with the anhydride of an alpha-beta unsaturated acid, in a manner similar to the process described in Patent 2,047,398 to Voss et al., and then reacting such copolymer with an aliphatic primary amine containing at least 12 carbon atoms. The polymeric materials may be obtained also by copolymerization of the imide of the unsaturated dibasic acid with the aromatic ring-containing olefin in a manner similar to the process described in British Patent 505,120, complete accepted May 5, 1939. The preferred polymeric materials are derived from styrene, indene or coumarone/maleic anhydride copolymers and long chain aliphatic primary amines.

Preferably, the aromatic ring-containing olefin, the anhydride and the aliphatic amine are reacted together in substantially molar ratios. However,

the relative proportions of anhydride and olefin may be varied within wide limits. For example, one mole of the dicarboxylic acid anhydride may be polymerized with 3 moles of the aromatic substituted olefin or vice versa and the resulting polymers heated with the aliphatic amine in the proportion of one mole of the amine to each mole of the anhydride. The polymerization may be brought about by heating, generally at temperatures of from about 50° C. to about 150° C. The polymerization may be carried out without the use of a solvent or other diluent or may be carried out in a suitable inert solvent, such as benzene, xylene, toluene, methylene chloride and the like at reflux temperatures. It will generally be desired to employ catalysts, such as barium peroxide, benzoyl peroxide and acetyl peroxide, to speed up the polymerization, although this is not always necessary. When employed, the catalysts will generally be used in concentrations ranging from about 0.1% to about 2% by weight. The reaction of the amine with the anhydride to form the imide will generally require higher temperatures on the order of about 170° C. to about 220° C.

By a hydrocarbon "oil," I mean one which has a viscosity of at least 35 seconds Saybolt at 100° F., and intend to include therein oils in the fuel oil range, including Diesel fuels and furnace oils, as well as the higher viscosity oils, employed as lubricating oils and greases. The oils may be solvent extracted oils or conventionally refined oils, obtained from various base crude oils. They may be specially compounded oils, such as those containing lard oil, fish oil, castor oil or the like. When the oils are fuel oils, designed for use in high speed Diesel engines, they may contain ignition primers, such as ethyl nitrate. The polymeric materials may be added to refined oils or may be added to the oils during any suitable stage in the refining process.

The proportion of the polymeric material to be added to the oil will depend upon the effect desired, but will generally lie between 0.02% and 5.0%. They may be employed in concentrations as high as 50%, whereupon grease-like products are obtained. Preferably, for my purpose, the polymeric materials will be employed within the range of from 0.02% to about 2.0%. Generally, the desired effect will be obtained when the polymeric material is employed in the oil in a concentration of from about 0.1% to about 0.5%.

In order to more clearly illustrate my invention, the preparation of representative polymeric materials and the results which are obtainable by the practice of my invention, the following examples are given, in which all quantities are given as parts by weight, except where otherwise specifically stated:

Example I

Twenty-six and nine-tenths parts of octadecylamine and 9.8 parts of maleic anhydride were mixed and heated to 170° C. in an oil bath until bubbling and evolution of water vapor stopped. The resulting product was mixed with 10 parts of styrene, 0.3 part of benzoyl peroxide was added, and the mixture thoroughly stirred and then placed on a steam bath for 2 hours, heating in this period to about 80° C. The resulting product, weight 32 parts, was somewhat gummy and resinous and could be pulled out into threads. It was dissolved in benzene, filtered, and the solvent removed by evaporation on a steam bath. The product was readily dissolved in oil by warm-

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ing and stirring and showed excellent pour point depressing action when tested in a paraffin base oil of S. A. E. 30 grade, as follows:

Concentration, percent by weight	Pour point, °F.
None (control).....	30
0.2.....	0
0.5.....	0

Example II

Styrene and maleic anhydride were mixed in equimolar proportions and dissolved in xylene in sufficient quantity to form a 15% solution. This solution, to which 1% of benzoyl peroxide (based on reaction ingredients in xylene solution) had been added, was heated to 100° C. and allowed to stand at this temperature until polymerization was complete. The resulting polymer was removed from the xylene by filtration, washed, and dried. Its molecular weight, on the basis of viscosity measurements, was in excess of 1000. Fifty and five-tenths parts of this polymer and 67.5 parts of octadecylamine were mixed thoroughly and heated for three hours at 210-220° C. The reaction mass was dissolved in benzene, filtered, and the solvent removed by evaporation. Two batches of material, prepared in the above fashion, yielded 230 parts of product. This material was dissolved in a Mid-Continent S. A. E. 20 oil to form a 33½% solution which was fluid when warm and grease-like when cool. The solution, tested in an S. A. E. 30 paraffin base oil, yielded the following data:

Per cent by weight of solution	Per cent by weight of active ingredient	Pour point, °F.
0.0	0.0	30
0.1	0.033	20
0.3	0.1	10
0.4	0.133	-10
0.5	0.166	-10
0.6	0.2	-10
0.7	0.233	-5
0.8	0.266	-10
1.0	0.333	-5

Example III

In this example, a styrene-maleic anhydride polymer was used whose molecular weight, on the basis of viscosity measurements, was 2½ to 3 times that of the polymer used in the preceding example. The polymer was heated with octadecylamine in the same ratios and using the same procedure as given in Example II. The final product, when tested in oil, yielded the following pour point data:

Concentration of polymer, percent by weight	Pour point, °F.
0.....	30
0.1.....	0
0.2.....	+5
0.3.....	0
0.5.....	-5

Example IV

Using a styrene-maleic anhydride polymer similar to that in Example III, 5.34 parts of polymer were heated with 7.23 parts of hexadecylamine and worked up as in Example II, yielding 11 parts of a resinous-like, stringy product. When tested in a paraffin base S. A. E. 30 oil, this prod-

uct, in 0.5% concentration, lowered the pour point from 30° F. to 10° F.

Example V

Twenty-two parts of indene (80% pure) and 14.7 parts of maleic anhydride were mixed, 0.5% by weight of benzoyl peroxide was added, and the mixture heated carefully on a steam bath for ½ hour. Forty and four-tenths parts of octadecylamine were added and the components thoroughly mixed. They were heated to 190° C. until bubbling ceased (about 2 hours), dissolved in benzene, and filtered. After evaporation of the solvent, 55 parts of a reddish resin was obtained which was fluid when warm. This material yielded the following results when tested for pour point depressant action in a wax-containing oil of S. A. E. 30 grade.

Concentration, percent by weight	Pour point, °F.
0.....	30
0.1.....	25
0.2.....	10
0.3.....	0
0.5.....	-5

Example VI

Ninety-three and six-tenths parts of a crude coumarone-indene fraction and 39.2 parts of maleic anhydride were mixed and 2 parts of benzoyl peroxide added. The temperature rose rapidly and the material became quite thick. After an hour, the product was scraped into cold methanol and the insoluble portion was filtered and dried, yielding 73 parts by weight of a resinous product. Forty-seven parts of this resin were heated with 59 parts of octadecylamine to 200° C. until bubbling ceased (about 2 hours), dissolved in benzene, filtered, and the solvent removed on the steam bath, yielding 81 parts of a tough reddish resin-like material. This material, when tested in a wax-containing oil of S. A. E. 30 grade, gave the following results.

Concentration, per cent by weight	Pour point, °F.
0.....	30
0.2.....	10
0.3.....	-5

The effect of the product from Example V, on viscosity and viscosity index, was also determined, using the polymer in 2% concentration. The data are:

	Control oil	Oil containing polymer
Saybolt Universal viscosity at 100° F. seconds.....	322	353
Saybolt Universal viscosity at 200° F. do.....	53	55
Viscosity index.....	92.5	96

These data indicate that this type of product does not affect the viscosity index adversely and, in fact, has a small beneficial action on this characteristic property.

The effectiveness of this type of product, in reducing the quantity of deposits formed by an oil, was determined in a manner similar to that described in U. S. Patent 2,236,168, page 2, lines 66 to page 3, line 7. In this case, a Mid-Continent S. A. E. 20 oil, containing 60 P. P. M. of dissolved iron (as oleate), was dropped onto the cylinder

and the following data obtained on the quantity of deposit formed.

	Mg. deposit per 30 cc. oil
Oil alone-control	231.5
Oil with 0.5% styrene/N-octadecyl-maleimide polymer	173.6
Per cent reduction in deposit	25

The merit of this type of polymer was also established in full scale engine tests. Styrene/N-octadecyl-maleimide polymer, in concentrations as low as 0.033%, yielded a good engine score, particularly with respect to formation of engine deposits, showed high corrosion resistance to alloy bearing metals, and maintained a high degree of pour point depressant activity.

It will be understood that the preceding examples and specific embodiments are given for illustrative purposes only and that many variations and modifications may be made therein particularly in the polymeric materials, the proportions, the preparation of the polymeric materials and in the other ingredients in the oils without departing from the spirit or scope of my invention. For example, effective products may also be prepared from phenyl vinyl ether, α -naphthyl vinyl ether, phenyl vinyl thioether, and β -naphthyl vinyl ether, by reaction with an N-octadecyl-maleimide or N-hexadecyl-maleimide. Styrene/maleic anhydride polymer, heated with dodecylamine and a mixture of octadecylamine and oleylamine, yielded products which also showed effectiveness in reducing pour point and engine deposits, although not to as great a degree as those given in the examples. Still other polymeric materials, which come within the scope of this invention, are as follows, all being polymers with molecular weights of at least 1000:

Coumarone/N-octadecyl-maleimide
Mixed coumarone-indene/N-octadecyl-maleimide
Phenyl vinyl ether/(N-octadecyl)-ethylmaleimide
 α -Naphthyl vinyl ether/N-heptadecyl-maleimide
Styrene/N-(2-ethylhexadecyl) maleimide
Indene/N-(2-hexadecyleicosanyl) maleimide
Phenyl vinyl thioether/N-octadecyl-maleimide
 β -Naphthyl vinyl thioether/N-hexadecyl-maleimide
Indene/N-naphthenyl-maleimide
Styrene/N-naphthenyl-maleimide
Stillbene/N-octadecyl-maleimide
 β -methylstyrene/N-naphthenyl-maleimide
Ethyl cinnamate/N-octadecyl-maleimide
p-Hydroxystyrene/N-hexadecyl-citraconimide
Stillbene/(N-octadecyl) chloromaleimide
Styrene/(N-octadecyl) phenylmaleimide

The polymeric materials of my invention may be employed in oils containing other additives, such as organic phosphates or phosphites, for example, tricresyl phosphate or tributyl phosphite; metal soaps or additives, for example, copper naphthenate, tin oleate, copper derivatives of terpene mercaptans; sulfur-containing stabilizers, such as sulfurized sperm oil, S-alkylated 2-mercapto-thiazolines, S-alkylated-2-mercaptobenzothiazole, tetra-alkyl thiuram disulfides; with anti-ring sticking agents or with viscosity index improving agents, such as polymerized isobutylene. Mineral oil compositions of the type described herein may be used in lubrication of internal combustion engines, for bearings sub-

jected to high speeds and high pressures, for gear lubrication of the hypoid, spiral, or bevel types, for railroad rolling stock, for marine engines, and for protective coatings on metallic surfaces subject to corrosion. They may be used as bases for greases and as components of fuel oils. The pour point depressants may be used as dewaxing assistants in refinery operations in connection with dewaxing solvents wherein higher oil yields and products of lower pour point are obtained. They are of particular importance in fuel oils for high speed Diesel engines since they permit the manufacture and use of fuel oils of higher paraffin content and improved ignition qualities.

I claim:

1. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-aliphatic-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by a member of the group consisting of aromatic and aromatic ether radicals and the N-aliphatic group contains at least 12 carbon atoms.

2. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-aliphatic-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by a member of the group consisting of aromatic and aromatic ether radicals and the N-aliphatic group contains at least 12 carbon atoms and consists of carbon and hydrogen.

3. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-alkyl-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by a member of the group consisting of aromatic and aromatic ether radicals and the N-alkyl group contains at least 12 carbon atoms.

4. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-aliphatic-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by an aromatic radical and the N-aliphatic group contains at least 12 carbon atoms.

5. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are di-

methylene groups and N-alkyl-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by an aromatic radical and the N-alkyl group contains at least 12 carbon atoms.

6. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-aliphatic-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by an aryl radical and the N-aliphatic group contains at least 12 carbon atoms and consists of carbon and hydrogen.

7. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-alkyl-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and

4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by an aryl radical of the benzene series and the N-alkyl group contains at least 12 carbon atoms.

8. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear polymeric material having a molecular weight of at least 1000 whose chain units are dimethylene groups and N-octadecyl-2,5-pyrrolidinedione nuclei which form chain members with the dimethylene groups by linking through the 3 and 4 carbon atoms of the pyrrolidinedione nucleus, in which each dimethylene group has a hydrogen replaced by an aryl radical of the benzene series.

9. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear styrene/N-octadecyl-maleimide polymer having a molecular weight of at least 1000.

10. A paraffin wax-containing hydrocarbon oil having incorporated therein a small proportion, sufficient to reduce the pour point of the oil, of a linear indene/N-octadecyl-maleimide polymer having a molecular weight of at least 1000

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