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[54] LUBRICATING OIL COMPOSITIONS

[75] Inventors: **Eduard J. Van de Kraats; Johannes De Jong**, both of Amsterdam, Netherlands

[73] Assignee: **Shell Oil Company**, Houston, Tex.

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Primary Examiner—W. Cannon

Attorney, Agent, or Firm—Henry C. Geller

[57]

ABSTRACT

Pour points of lubricating oils are depressed by adding thereto small amounts of oil-soluble copolymer of polyalkyl methacrylates having (a) a molar percentage of alkyl methacrylates with branched alkyl chains from 5 to 25 percent, (b) at least six alkyl chains with a different number of carbon atoms, and (c) a number average molecular weight of 2,000 to 2,000,000, wherein the alkyl groups in said alkyl methacrylates contain 9 to 18 carbon atoms with an average of from 12.4 to 13.7 carbon atoms.

3 Claims, No Drawings

LUBRICATING OIL COMPOSITIONS

BACKGROUND OF THE INVENTION

The viscosity of a lubricating oil (lubricating oil as used in this specification also includes lubricating oil compositions which comprise, besides a lubricating oil proper, additives which render improved properties to that lubricating oil) at different temperatures is considered a measure of the suitability for application of that lubricating oil. In general, lubricating oils were, until recently with relation to their viscosity properties, valued and classified according to their viscosity at 210°F (99°C) and 100°F (38°C). Of late, additional requirements have been set for the viscosity at 0°F (-18°C) since the viscosity at this temperature is a measure of the applicability of a lubricating oil at very low ambient temperatures, e.g., for cold starting of automotive vehicles. The viscosity at 0°F (-18°C) is determined with a standardized method (ASTM method D 2602) and in general the requirement set is that the viscosity determined in that way be for, e.g., a 10W oil at most 24 Stokes.

Base oils for the preparation of lubricating oils can be prepared from vacuum distillation fractions or residues of the vacuum distillation of crude mineral oils. In general, the vacuum distillation fractions and the deasphalted residue (or mixtures of one or more of the vacuum distillation fractions and/or the residue) are treated with a solvent, e.g., sulphur dioxide, furfural and phenol, for the removal of aromatic compounds.

Base oils for the preparation of lubricating oils can also be prepared by hydrocracking, which is understood to be a treatment of a mineral oil-based material with hydrogen at elevated temperature and pressure in the presence of a bifunctional catalyst comprising a metal-containing hydrogenating component on a carrier possessing cracking activity, with the object of, inter alia, increasing the viscosity index (as determined according to ASTM method D-2270) of the mineral-oil-based material; deasphalted residual fractions of the vacuum distillation of a crude mineral oil are very suitable to be hydrocracked.

The base oils for the preparation of lubricating oils may contain considerable quantities of wax. This wax separates if the base oil for the preparation of a lubricating oil is cooled below a certain temperature. As cooling proceeds, more wax is separated until the mixture of wax and oil almost or entirely ceases to flow. The lowest temperature observed in a standard laboratory test at which the waxy mixture still flows is called the pour point. The pour point of a lubricating oil is of great practical importance. To prevent difficulties in the use of the lubricating oils their pour points should lie below the minimum temperature at which the oil is stored, transported and used.

In order to prepare lubricating oils with a desired pour point from waxy base oils for the preparation of lubricating oils, two measures are in general applied in combination to decrease the pour point of the said base oil, namely (1) removal of part of the wax (dewaxing) and (2) addition of compounds which reduce the pour point (pour-point depressants).

Dewaxing may be carried out with the aid of urea; in most cases dewaxing comprises diluting the waxy base oil for the preparation of a lubricating oil with a suitable solvent, cooling the mixture and filtering off the wax precipitated. The mixture is cooled to such a tem-

perature that the dewaxed lubricating oil obtained after removal of the solvent has a pour point of about 16°F (-9°C). To the lubricating oil so obtained there are added pour-point depressants and, if desired, other additives (such as viscosity-index improvers, detergent additives, antioxidants, extreme-pressure additives) in order to prepare a lubricating oil composition. It has been found that several types of waxy base oils for the preparation of lubricating oils, after dewaxing to a pour point of about 16°F and addition of a pour-point depressant and of the desired additives, yield lubricating oil compositions which do not comply with the requirements set for the viscosity at 0°F discussed above. This can be overcome by carrying out the dewaxing at lower temperatures in order to obtain a lubricating oil with a pour point of about 0°F; more wax is removed and the viscosity at 0°F of the lubricating oil proper obtained (or the lubricating oil compositions prepared therefrom by addition of a pour-point depressant and, if desired, other additives) is below 24 Stokes.

However, in a number of cases the presence of conventional pour-point depressants in conventional amounts in the lubricating oil compositions obtained in this way does not give rise to so great a decrease of the pour point as in lubricating oil compositions in the preparation of which the dewaxing had been carried out to a pour point of the lubricating oil of about 16°F. This is in particular the case with lubricating oils which have a relatively low viscosity at 210°F, e.g., below about 10cS.

SUMMARY OF THE INVENTION

A class of novel compounds of particular structure and composition has now been found which effect a great reduction in pour point not only of lubricating oils the base oil of which has been dewaxed to a pour point of that lubricating oil of about 16°F, but also of lubricating oils in the preparation of which the dewaxing of the waxy base oil has been carried out in such a way that the pour point of the lubricating oil obtained is about 0°F. These compounds are oil-soluble polyalkyl methacrylates wherein the alkyl group has from 9-18 carbon atoms and meets the following requirements (a) the average number of carbon atoms of the alkyl chains in the methacrylates is from 12.4 to 13.7, (b) the molar percentage of the alkyl methacrylates with branched alkyl chains is from 5 to 25 percent, and (c) there are present among the alkyl chains in the methacrylates at least six alkyl chains with a different number of carbon atoms.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Alkyl chains are considered to be present in the oil-soluble polyalkyl methacrylates if the number of those alkyl chains is at least 1 percent of the total number of alkyl chains of 9-18 carbon atoms present in the polyalkyl methacrylates. Preference is given to polyalkyl methacrylates in which the average number of carbon atoms in the alkyl chains is from 12.8 to 13.5. Oil-soluble polyalkyl methacrylates in which some of the alkyl chains contain nine carbon atoms are very suitable; polyalkyl methacrylates wherein the number of alkyl chains of nine carbon atoms is from 2 to 10 percent of the total number of alkyl chains are in particular preferred.

In order to be particularly suited to effect an appreciable pour-point depression in a great variety of lubricating oils the polyalkyl methacrylates according to the invention must have at least six, and preferably at least eight, alkyl chains with a different number of carbon atoms present among the alkyl chains containing 9-18 carbon atoms.

Although the polyalkyl methacrylates may have some alkyl chains which contain fewer than nine (e.g., 1, 2 or 4) carbon atoms and/or more than 18 (e.g., 20, 22) carbon atoms, it is preferred that all alkyl chains present in the polyalkyl methacrylates of the invention contain from 9-18 carbon atoms.

In the polyalkyl methacrylates of the invention containing alkyl chains of 9-18 carbon atoms, at least 5 to 25 percent of which alkyl chains are branched alkyl chains. The term "branched alkyl chains" denotes alkyl chains which contain at least one tertiary or quaternary carbon atom. Polyalkyl methacrylates in which 5-15 percent of the alkyl chains are branched are particularly preferred.

The novel polyalkyl methacrylates are obtained by polymerization, e.g., radical polymerization, of a mixture of alkyl methacrylates at least part of which consists of alkyl methacrylates with 9-18 carbon atoms in the alkyl group. By the correct choice of the nature of the alkyl chains in the alkyl methacrylates with 9-18 carbon atoms in the alkyl group and of the mutual ratio by weight of these alkyl methacrylates in the mixture to be polymerized, a simple process yields polymers meeting the three aforementioned criteria.

Very suitable polyalkyl methacrylates are prepared by polymerization of a mixture of alkyl methacrylates part of which are derived from unbranched natural and/or synthetic alcohols with 16 and/or 18 carbon atoms and the remaining part from a mixture of branched and unbranched synthetic alcohols with 9-15 carbon atoms. The latter alcohol mixture can be obtained, for example, by the oxo process or by reacting a mixture of olefins with 8-14 carbon atoms (or several mixtures of olefins in this range, e.g., a mixture of olefins with 8-10 carbon atoms and a mixture of olefins with 11-14 carbon atoms), with carbon monoxide and hydrogen in the presence of a complex catalyst consisting of cobalt, carbon monoxide and a phosphorus compound.

The molecular weight of the polymers of the invention can vary within wide limits. Polymers used as lubricating oil additives should have a number average molecular weight of between 2,000 and 2,000,000, in particular between 5,000 and 500,000. The molecular weight was determined by an ebullioscopic method.

When the polyalkyl methacrylates are used as additives for lubricating oils they can be added directly to the oil or in the form of a concentrate obtained by mixing the polymers with a small quantity of oil.

The concentration in which the polyalkyl methacrylates can be used may also vary within wide limits, dependent on the structure and the molecular weight of the polymer to be used, the nature and the quantity of the waxes present in the lubricating oil and the pour-point depressing effect to be achieved. In some cases a quantity of 0.01 percent w calculated on the lubricating oil composition is sufficient to reach the desired pour point. In most cases a quantity of 2.0 percent w is ample. One preferably incorporates 0.05 to 0.5 percent w of the polymers in the lubricating oil. If the application

of the polymers in question is directed to VI improvement as well as to pour-point depression it may be desirable to incorporate quantities of the polymers greater than the afore-mentioned 2.0 percent w.

When the polymers concerned are used as additives in lubricating oils the lubricating oil compositions so obtained may also comprise other additives such as antioxidants, additives with a detergent action, viscosity-increasing compounds, anti-corrosives, anti-foaming agents, agents to improve the lubricating effect and other compounds which are usually added to lubricating oils.

EXAMPLE

Base Oils

Oil A: A lubricating oil with a viscosity of 4.87 cS at 99°C (210°F) and 29.6 cS at 38°C (100°F) obtained from a Middle East crude by distillation and extraction of aromatic compounds, followed by solvent dewaxing to a pour point of -18°C (0°F).

Oil B: A lubricating oil with a viscosity of 4.36 cS at 99°C (210°F) and 23.7 cS at 38°C (100°F) obtained from a Middle East crude as described for oil A, dewaxed to a pour point of -24°C (-11°F).

Oil C: A lubricating oil with a viscosity of 7.03 cS at 99°C (210°F) and 44.30 cS at 38°C (100°F) prepared from a deasphalted distillation residue of a Middle East crude by hydrocracking. The oil was dewaxed to a pour point of -18°C (0°F).

Oil D: A lubricating oil with a viscosity of 9.41 cS at 99°C (210°F) and 26.7 cS at 38°C (100°F) prepared from a deasphalted distillation residue of a Middle East crude by hydrocracking. The oil was dewaxed to a pour point of -18°C (0°F).

Oil E: A lubricating oil with a viscosity of 11.87 cS at 99°C (210°F) and 113.5 cS at 38°C (100°F) obtained from a Middle East crude by blending of solvent-extracted distillate fractions and a solvent-extracted deasphalted residue. The oil was dewaxed to a pour point of -9°C (16°F).

Oil F: A lubricating oil with a viscosity of 10.18 cS at 99°C (210°F) and 78.92 cS at 38°C (100°F) obtained by hydrocracking of a deasphalted distillation residue of a Middle East crude. The oil was dewaxed to a pour point of -21°C (-6°F).

Oil G: A lubricating oil with a viscosity of 5.37 cS at 99°C (210°F) and 33.9 cS at 38°C (100°F) obtained from a Middle East crude by distillation and extraction of aromatic compounds, followed by solvent dewaxing to a pour point of -9°C (16°F).

Polymers

Five polymers were prepared by copolymerization of a mixture of alkyl methacrylates partly derived from unbranched natural stearyl alcohol and for the remaining part from a mixture of branched and unbranched alcohols with 9 to 11 carbon atoms (alcohol I) and a mixture of branched and unbranched alcohols with 12-15 carbon atoms (alcohol II). The alcohols I and II had been obtained by reaction of a mixture of olefins with 8-10 and 11-14 carbon atoms, respectively, with carbon monoxide and hydrogen in the presence of a complex catalyst consisting of cobalt, carbon monoxide and a phosphorus compound.

The composition of alcohols I and II determined with the aid of gas chromatography and their apparent mo-

molecular weight according to their hydroxyl number are given in Tables I and II.

Table I

Composition of "Alcohol I"	
	%w
alcohols with < 9 carbon atoms	0.3
n-nonyl alcohol	17.5
iso-nonyl alcohol	1.9
n-decyl alcohol	41.8
iso-decyl alcohol	6.9
n-undecyl alcohol	26.0
iso-undecyl alcohol	5.3
alcohols with > 11 carbon atoms	0.3
average molecular weight	161

Table II

Composition of "Alcohol II"	
	%w
n-dodecyl alcohol	15.0
iso-dodecylalcohol	4.7
n-tridecyl alcohol	26.4
iso-tridecyl alcohol	7.3
n-tetradecyl alcohol	23.3
iso-tetradecyl alcohol	6.0
n-pentadecyl alcohol	14.0
iso-pentadecyl alcohol	2.3
average molecular weight	207

since it contains fewer than six alkyl chains with a different number of carbon atoms; they were prepared for comparative reasons. Polymer 5, also prepared for comparative reasons, did not contain alkyl chains with 9 carbon atoms and the average number of carbon atoms in the side chain is 14.2.

Table III shows the composition of the polymers and their activity as pour-point depressants in oils A-G.

Polymers 1 and 2 are more active than the comparative polymers 3, 4 and 5 in oils which have a viscosity of less than about 10 cS at 99°C (210°F) which have been dewaxed to a pour point of about -18°C (0°F), i.e., oils A-D. When polymers according to the invention are incorporated into an oil with a viscosity below about 10 cS at 99°C (210°F) which has been dewaxed to a pour point of -9°C (16°F) its pour point is on a par with the pour points of the same oil containing the comparative polymers (oil G). The same applies to oils which have a viscosity higher than about 10 cS at 99°C (210°F) irrespective of the pour point to which they have been dewaxed (oils E and F).

Table III

polymer	average number of carbon atoms in alkyl chains	composition,%w methacrylate ester in polymerization mixture derived from			pour point (°C) after incorporation of 0.5% of polymers in oils						
		alcohol I	alcohol II	stearyl alcohol	A -18*	B -24*	C -18*	D -18*	E -9*	F -21*	G -9*
1	13.5	23.8	50.5	25.7	-33	≤-36	-39	-30	-24	-33	-30
2	13.0	29.6	51.6	18.8	≤-36	≤-36	-39	-30	-24	-33	-30
3	14.0	13.5	56.5	30.0	-30	-30	-36	-27	-24	-33	-30
4	13.0	54.6	—	45.4	-27	-33	—	—	—	—	-30
5	14.2	—	85.0	15.0	-21	-30	-33	-24	-24	-27	-30

*The figures denote the pour point of the oil per se (°C).

In the preparation of the polymers the following conditions were adhered to:

Monomer concentration: 42.5%w, leading to the formation of copolymers with a number average molecular weight of about 50,000.
Solvent: toluene
Initiator: benzoyl peroxide
Initiator concentration: 0.30%w
Temperature: 80°C
Polymerization: 24 hours

Polymers 1 and 2 come within the scope of the invention. Polymer 3 is not according to the invention since the average number of carbon atoms in the side chains is 14, and polymer 4 is not according to the invention

We claim as our invention:

1. A lubricating oil composition consisting essentially of a wax-containing hydrocarbon lubricating oil having a viscosity of less than about 10 cS at 210°F and dewaxed to a pour point of about 0°F or less and from about 0.01 to 2 percent by weight of oil-soluble copolymer of polyalkyl methacrylates having (a) a molar percentage of alkyl methacrylates with branched alkyl chains from 5 to 25 percent, (b) at least eight alkyl chains with a different number of carbon atoms in which the number of alkyl chains of 9 carbon atoms is from 2 to 10 percent of the total number of alkyl chains, and (c) a number average molecular weight between 5,000 and 500,000, wherein the alkyl groups in said alkyl methacrylates contain 9 to 18 carbon atoms with an average of from 12.8 to 13.5 carbon atoms.

2. The composition of claim 1 in which the percentage of oil-soluble copolymer of polyalkyl methacrylates is about 0.05 to 0.5 percent by weight.

3. The composition of claim 1 in which the molar percentage of alkyl methacrylates with branched alkyl chains is 5 to 15 percent.

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