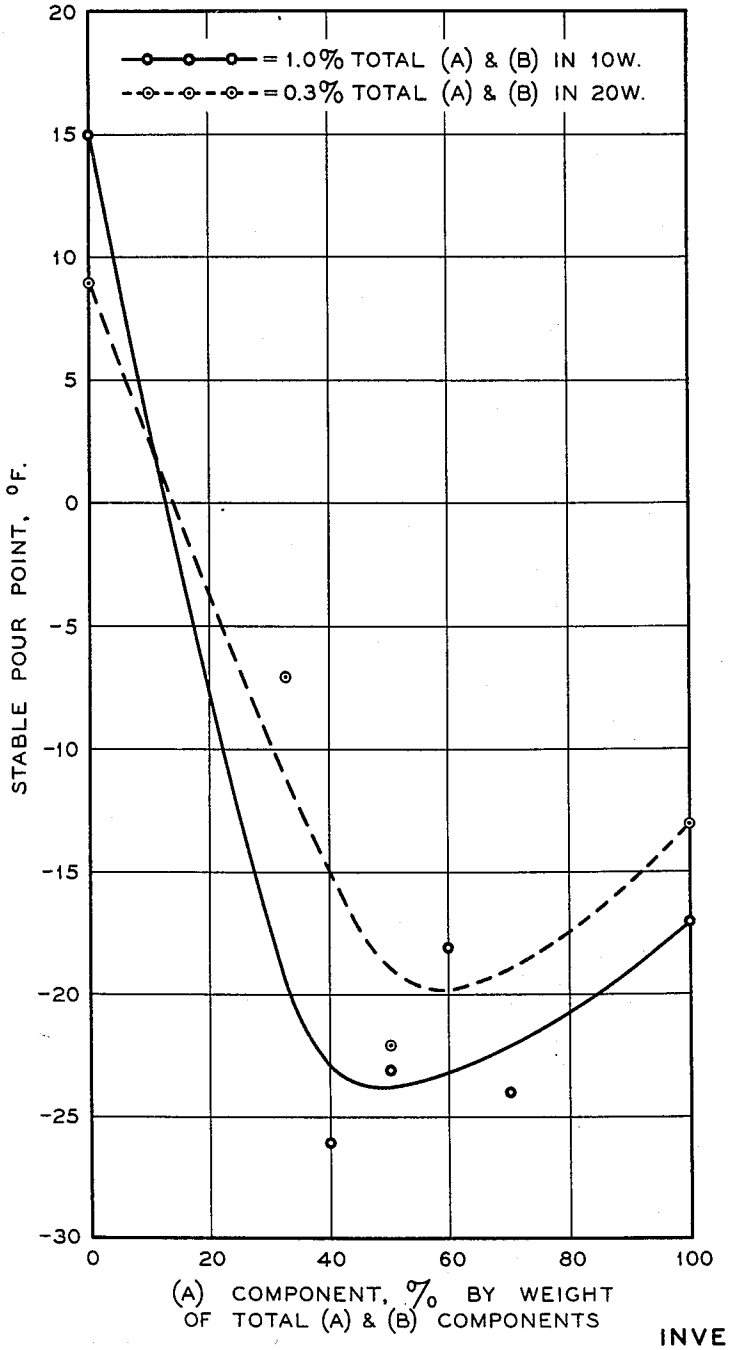
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LUBRICANT COMPOSITION

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LUBRICANT COMPOSITION

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This invention relates to a superior new lubricant composition. More particularly, the invention is concerned with a novel lubricating oil composition possessing outstanding flowing characteristics.

For proper use, it is essential that lubricant compositions be able to flow and circulate under all conditions which they are likely to encounter. Without these essential flowing characteristics, a lubricating oil composition is of little or no use, no matter how effective it may be otherwise.

When lubricating oils are cooled to sufficiently low temperatures they naturally become stiff and solid and incapable of flowing. This may be due to either congealing of hydrocarbons in the oil or crystallization of paraffin waxes in paraffinic type mineral oil. As an estimate of the approximate lowest temperature to which an oil of lubricating viscosity may be cooled and still flow and circulate during its life, the "pour point" of the oil is determined. This is usually taken as the lowest temperature at which a sample of the oil will flow or "pour" under certain generally accepted specific test conditions.

Although a lubricating oil composition may have originally had an apparently satisfactory pour point, that is, one that indicates the oil should be able to flow and circulate under expected conditions of use, it often happens that the pour point of the oil will rise during storage due to fluctuations of temperature until the oil is no longer satisfactory for use. Thus, it is seen that a lubricating oil composition desirably possesses not only a low pour point as such, but also a low pour point that is stable under the normal fluctuation of temperature during storage which may be encountered in the life of the oil.

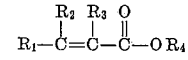
It has now been found that a lubricant composition comprising a mineral lubricating oil and the combination of (A) a polymeric alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid with (B) an aromatic-petroleum wax condensate pour depressant, said combination being present in amounts sufficient to depress the pour point of the mineral lubricating oil, surprisingly possesses a stable pour point which is substantially lower than that obtainable by the use of either component of the combination alone.

The superior new lubricant composition of the invention possesses outstanding low temperature flowing characteristics which make it particularly useful under any temperature conditions which it is likely to be subjected to during its normal life. Not only does the lubricant composition have a very low pour point, but the pour point is remarkably stable to temperature fluctuations that are usually encountered by lubricating oil compositions following their manufacture.

Any mineral lubricating oil is suitable for the compositions of this invention. The mineral lubricating oil, which is the sole oil constituent of the composition, may be either naphthenic or paraffinic in nature. It may be prepared by any of the standard refining methods known to the art. However, it is in the use of paraffinic base oils, more particularly the lighter weight SAE 10W and/or

20W oils, that the combination of polymeric alkyl ester of lower aliphatic α,β-unsaturated monocarboxylic acid and aromatic-petroleum wax condensate pour point depressant according to the invention provides its most outstanding desirable effect. These oils are also commonly described in the art as waxy mineral lubricating oils.

The polymeric alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid may be further described as one having monomer units of the type illustrated by the following general formula:



in which R_1, R_2 and R_3, which may be the same or different, are members of the group consisting of hydrogen and alkyl radicals of from 1 to 4 carbon atoms and R_4 is an alkyl group.

The polymer of the monomeric alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid of the type described above desirably possesses an average molecular weight above about 2000, as determined by standard light scattering methods. For best results, the average molecular weight is preferably in the range of from about 10,000 to about 30,000.

Illustrative lower aliphatic α,β-unsaturated monocarboxylic acids from which the alkyl esters may be derived include acrylic acid, methacrylic acid, crotonic acid, tiglic acid, angelic acid, α-methyl crotonic acid, β-ethyl crotonic acid, hydrosorbic acid and the like. Preferred for present purposes are acrylic acid and methacrylic acid. The term "lower" used in the description of these acids is employed in its commonly accepted sense and includes those acids of 7 carbon atoms or less.

The alkyl group of the alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid in accordance with the invention may be any of the type obtained with alcohols having up to 30 carbon atoms. The group may be branched chain, straight chain or cyclic in nature. Higher alkyl groups are particularly suitable. Preferably, the alkyl groups contain from 8 to 24 carbon atoms, since they provide the desired degree of oil solubility. For present purposes most preferred alkyl groups within this range are the decyl, dodecyl or lauryl, tridecyl, tetradecyl and hexadecyl or cetyl groups. In this description of the alkyl groups the term "higher" is used in the sense in which it is commonly employed and denotes those groups containing eight or more carbon atoms which are obtained from higher aliphatic alcohols.

The aromatic-petroleum wax condensate pour depressant of the compositions according to this invention may also be described as an alkyl aromatic pour depressant. Included within this terminology is a wide variety of known pour point depressants. The preferred compounds of this type are made by Friedel-Crafts condensation of long chain aliphatic compound with a low molecular weight aromatic compound. Suitable long chain aliphatic compounds include halogenated petroleum waxes, higher aliphatic alcohols, and the like, of up to 20 to 30 carbon atoms or more. Aromatic compounds which may be employed include toluene, xylene, naphthalene, phenol, cresol, amino phenols, thiophenols and the like. Of these examples, the chlorinated petroleum waxes and hydrocarbon aromatics such as naphthalene are preferred.

The naphthalene petroleum wax condensate pour point depressant considered to be the most suitable for present purposes is of a well-known type characterized by alkyl groups of 10 to 18 carbon atoms each and a total molecular weight of from about 1500 to about 3000. Such condensates are conveniently prepared by standard methods. As an example, paraffin wax is chlorinated to

a chlorine content of about 10 to 15% or more. About 100 parts by weight of the chlorinated paraffin wax is then condensed with from about 10 to 20 parts by weight naphthalene in the presence of aluminum chloride catalyst. Solvents such as petroleum naphthas, tetrachlorethane and the like may be employed, and temperatures in the range of from about room temperature up to about 500° F. may be employed. After the reaction is complete, ordinarily within ten hours or less, the reaction mixture is hydrolyzed with water and caustic, and the solvent may then be evaporated by distillation or other means to give the desired naphthalene petroleum wax condensate pour point depressant.

As already stated, the combination of polymeric alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid with an aromatic petroleum wax condensate pour point depressant is employed in the lubricant compositions of the invention in amounts sufficient to depress the pour point thereof. The amount of the combination required in any particular case will depend on the particular grade of mineral lubricating oil base. The necessary proportions to lower or depress the pour point are simply and readily determined by a visual inspection of the flowing or "pouring" characteristics of the composition. Usually from about 0.01% by weight to about 10% by weight of the combination based on the lubricant composition is sufficient. For present purposes, when the preferred combination of higher alkyl methacrylate and alkyl acrylate polymers with aromatic-petroleum wax condensate pour point depressants in the regular grades of mineral lubricating oils are concerned, preferred proportions are in the range of from about 0.1% by weight to about 2.0% by weight. By the "regular grades of mineral lubricating oils" are meant the usual SAE viscosity classes of 10, 10W, 20W, 20, 30, 40 etc.

The relative proportions of (A) polymeric alkyl ester of lower aliphatic α,β-unsaturated monocarboxylic acid and (B) aromatic-petroleum wax condensate type pour point depressant cover a wide range, since the addition of small proportions of either component to the other appears to improve its pour point stability. Preferably, the ratio of (A) component to (B) component on a parts basis will be in the range of from about 0.1 to about 5 parts of (A) to 1 part of (B) on a weight basis. The most suitable ratios for the regular grades of mineral lubricating oil are from about 0.5 to about 3 parts of (A) for each part of (B). Expressed in the nearest round percentages, this means that the (A) component preferably constitutes from about 10 to about 85 percent and preferably from about 35 to about 75 percent by weight of the total (A) and (B) components in the lubricant composition.

The lubricant compositions of the invention are particularly useful in the form of lubricating oil concentrates for the production of stable low pour point blends. Since the combination of (A) and (B) components results in unusually stable pour point depressing properties, regardless of temperature fluctuations which might be encountered by the concentrates during storage, there is a great demand for lubricant compositions of this type in the manufacture of lubricating oils. In accordance with the present invention, stable lubricating oil pour point additive concentrates containing up to from about 20 to about 30 percent by weight or more of the active components are poduced which do not deteriorate under normal storage conditions, as have compositions of the type employed heretofore.

Suitable lubricant compositions according to the invention also contain certain conventional additives. Such additives include lubricating oil detergents and stabilizing agents as illustrated by calcium petroleum sulfonate and calcium alkyl phenate. Oxidation and corrosion inhibitors of the type such as zinc thiophosphate and diparaffin sulfide are also employed. The additives are present in the compositions in minor proportions sufficient to enhance the detergency and stability of the oil or to inhibit oxidation and corrosion characteristics of the oil. Ordinarily, amounts of additive in the range of from about 0.1 to about 5% by weight based on the lubricant composition are suitable for these purposes.

Various blends of the polymeric alkyl ester of lower aliphatic α,β-unsaturated monocarboxylic acid and aromatic-petroleum wax condensate pour point depressant in mineral lubricating oil according to the present invention as described above were prepared. The oil was a solvent refined SAE 10W waxy mineral lubricating oil containing 6.9% by weight based on the total composition of a typical additive concentrate consisting of about 12% a calcium alkyl phenate, namely, calcium dodecyl phenate, 12% calcium petroleum sulfonate, 10% a zinc thiophosphate, namely, zinc didodecylphenyl dithiophosphate, 3% diparaffin sulfide and 63% solvent refined mineral lubricating oil, said percentages being on a weight basis. The aromatic-petroleum wax condensate pour point depressants in these blends included:

(1) The condensate of chlorinated petroleum wax with phenol and phthalic anhydride in which the alkyl groups contain from 10 to 18 carbon atoms each;

(2) The condensation product of chlorinated petroleum wax and naphthalene having an average molecular weight of from 1500 to 3000 and alkyl groups of from 10 to 18 carbon atoms each; and

(3) A mixture of:

(*a*) The condensate of chlorinated petroleum wax and naphthalene of 1500 to 3000 average molecular weight and 10 to 18 carbon atoms in each alkyl group, and

(*b*) Polymerized C_{12}–C_{14} alkyl fumarate of 3000 to 8000 molecular weight in the ratio of 0.5–2.0 to 1.0.

The (A) component employed in combination with the aromatic-petroleum wax condensate (B) components described above was a polymeric lauryl methacrylate having an average molecular weight of about 20,000. In these blends the proportions as set out in the tables which follow are given on a weight basis unless otherwise expressed.

The stable pour points of a variety of the above blends as well as a lubricating base oil alone were determined by a series of tests. These stable pour point tests were designed to find the maximum solidification temperature, which is the highest temperature at which a given blend becomes solid during the test. The regular ASTM pour points of the blends were also obtained for the purpose of further comparison. In both the stable pour point test and the ASTM pour point test, method D–97–47 for determining pour points was followed. In the stable pour point test, however, the results were derived by daily observations of a large number of samples in the field undergoing temperature fluctuations due to actual climatic conditions.

In the ASTM pour point method, a glass test jar 1¼" in diameter and 4½ to 5" high is filled to a depth of 2" with the oil to be tested. The test jar is then closed with a cork carrying a test thermometer in such a position that the bulb of the thermometer is located in the oil. The oil sample in the test jar is then gradually cooled in a low temperature cooling bath. The test jar is removed at each thermometer reading, which is a multiple of 5° F., and is tilted to ascertain whether or not the oil in the jar will still move. As soon as the oil in the test jar does not flow when tilted, the jar is held in a horizontal position for five seconds. When there is no movement in five seconds, the temperature is recorded as the solid point of the oil and the pour point is taken as the temperature 5° F. above this solid point.

In the stable pour point test employed here, the ASTM pour point test jars containing the oil were exposed to ambient temperatures existing in the field. The test jars were observed daily during the five winter months to determine if the oil flowed or was solid, in accordance with

the ASTM procedure outlined above. During the period the oils were observed, the temperature varied between +35° F. and −60° F. The tests show the highest degree of pour point reversion of each blend, since the "stable pour point" is the maximum solidification temperature to which the pour point depressant combination reverted due to the effect of temperature cycling.

The recorded results of a series of tests on the various blends as described above are set forth in the following table.

Table I

Total Combination Pour Depressant, Percent	(A) Component, Percent	(B) Component, Percent			Stable Pour Point, ° F.	ASTM Pour Point, ° F.
		Pour Depressant (1)	Pour Depressant (2)	Pour Depressant (3)		
0.8	0.8				−25	−25
		0.8			−4	−5
			0.8		+5	−10
				0.8	−11	−15
	0.2		0.6		−34	−15
	0.2			0.6	−15	−15
	0.2	0.6			−34	−10
1.2	1.2				−27	−30
		1.2			−2	−15
			1.2		0	−20
				1.2	+2	−20
	0.6	0.6			−40	−20
	0.6		0.6		−40	−25
	0.6			0.6	−35	−25

From the above table of test results it will be readily seen that the lubricant compositions of this invention containing (A) a polymeric alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid with (B) an aromatic-petroleum wax condensate pour point depressant give surprisingly low stable pour points, up to 13° F. lower than those obtained with single pour point depressants. Blends of aromatic-petroleum wax condensate pour point depressants with polymeric pour depressants as in (3) above which provide fairly low stable pour points are also substantially improved in lubricant compositions according to this invention.

The above results are particularly surprising in view of the fact that other combinations of pour point depressants such as the polymerized alkyl fumarate and chlorinated petroleum wax-naphthalene condensate of pour depressant (3) noted above, when employed in similar proportions alone, are found to give much poorer stable pour points than the combination of the present invention. Although the composition of the invention had a stable pour point of −35° F. within the range tested, the polyfumarate and wax-naphthalene condensate of composition (3) gave a stable pour point as high as +2° F.

The outstanding flowing characteristics of the compositions according to this invention were further studied with respect to different proportions of the (A) component and the (B) component in representative lubricating oil compositions. In addition to the SAE 10W base oil and concentrate referred to above in connection with the blends of Table I, there were employed two different solvent refined SAE 20/20W oils, one containing 6.9% by weight lubricating oil additive concentrate and the other containing 8.0% by weight lubricating oil additive concentrate, the concentrate in these cases being the same as that described in connection with the 10W oil already referred to. In the oil tested, the (A) component was a polylauryl methacrylate of the previously described type, and the (B) component was a petroleum wax-naphthalene condensate referred to as (2) above. The results of pour point tests performed on these blends are given in the following table:

Table II

Oil	Total Combination Pour Depressant, Percent	(A) Component, Percent	(B) Component, Percent	Stable Pour Point, ° F.	ASTM Pour Point, ° F.
SAE 10W (6.9 wt. Percent Conc.)	0.8	0.8	0.0	−13	−15
		0.7	0.1	−18	−20
		0.6	0.2	−18	−30
		0.5	0.3	−24	−30
		0.4	0.4	−16	
		0.2	0.6	−8	−10
		0.0	0.8	+13	−10
	0.9	0.9	0.0	−16	−20
		0.7	0.2	−24	−25
		0.6	0.3	−18	−30
		0.5	0.4	−23	−30
		0.4	0.5	−29	−30
		0.0	0.9	+15	−20
	1.0	1.0	0.0	−17	−20
		0.7	0.3	−24	−30
		0.6	0.4	−18	−30
		0.5	0.5	−23	−30
		0.4	0.6	−26	−35
		0.0	1.0	+15	−20
SAE 20/20W (6.9 wt. Percent Conc.)	0.3	0.3	0.0	−13	−10
		0.15	0.15	−22	−10
		0.1	0.2	−7	0
		0.0	0.3	+9	0
SAE 20/20W (8.0 wt. Percent Conc.)	0.25	0.25	0.0	−20	−10
		0.167	0.083	−23	−10
		0.125	0.125	−18	+10
		0.10	0.15	−18	+10
		0.0	0.25	+11	+5
	0.35	0.35	0.0	−20	−15
		0.233	0.117	−24	−10
		0.175	0.175	−23	−10
		0.14	0.21	−23	+5
		0.0	0.35	+8	0

The data of the above table shows that the combination of (A) and (B) components in the lubricant compositions of the invention provides remarkable improvements in the solidification temperatures as previously described in all proportions. Whenever a certain amount of (A) component is combined with a certain amount of (B) component, an enhancement of the flowing characteristics is noted.

As a graphical illustration of the outstanding flowing characteristics of the lubricant compositions of the invention, the data outlined in Table II above was plotted to give the curves of the accompanying drawing. These curves show the effect of variations in the proportions of (A) and (B) components on the maximum solidification temperatures. Reference to the drawing shows at a glance that the pour point reversion tendencies of a lubricant composition are effectively counteracted when components (A) and (B) are employed together in all proportions. However, it is further apparent from the drawing that the greatest benefits are obtained when the preferred proportions of 0.5 to 3 parts by weight of component (A) are employed for each part of component (B), said parts being on a weight basis.

This application is a continuation-in-part of Foehr and Furby patent application Serial No. 509,749, filed May 20, 1955, and now abandoned.

We claim:

1. A lubricant composition consisting essentially of a waxy mineral lubricating oil as its sole oil constituent, minor proportions of calcium petroleum sulfonate and calcium dodecyl phenate sufficient to enhance the detergency and stability of the oil, minor proportions of zinc didodecylphenyl dithiophosphate and diparaffin sulfide sufficient to inhibit oxidation and corrosion characteristics of the oil and the combination of (A) a polymeric higher alkyl ester of a lower aliphatic α,β-unsaturated monocarboxylic acid of not more than 7 carbon atoms having an average molecular weight above about 2000 and from 8 to 24 carbon atoms in each of the alkyl groups with (B) a naphthalene-petroleum wax condensate pour depressant, said combination being present in amounts sufficient to depress the pour point of the mineral lubricating oil and the (A) component constituting from about 35 to about 75% by weight of the total (A) and (B) components.

2. A lubricant composition consisting essentially of a waxy mineral lubricating oil as its sole oil constituent, minor proportions of calcium petroleum sulfonate and calcium dodecyl phenate sufficient to enhance the detergency and stability of the oil, minor proportions of zinc didodecylphenyl dithiophosphate and diparaffin sulfide sufficient to inhibit oxidation and corrosion characteristics of the oil and the combination of (A) a polymeric lauryl methacrylate having an average molecular weight of about 20,000 with (B) a naphthalene-petroleum wax condensate pour depressant having an average molecular weight of from about 1500 to 3000 and alkyl groups of from about 10 to 18 carbon atoms each, said combination being present in amounts sufficient to depress the pour point of the mineral lubricating oil and the (A) component constituting from about 35 to about 75% by weight of the total (A) and (B) components.

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