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**MIXED SALT LUBRICANT COMPOSITIONS
HAVING IMPROVED BASE OILS**

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This invention relates to lubricating oil compositions containing mixed-salt thickeners and having an improved base oil. Particularly, the invention relates to mixed-salt lubricants in which the base oil comprises a mixture of a naphthenic lubricating oil, a solvent extract obtained by solvent extraction of a mineral lubricating oil, and propane precipitated resin. This base oil gives good adhesiveness and improves the water and fire resistance of the lubricant.

Recently, lubricating compositions thickened with the calcium salts of low molecular weight fatty acid in combination with calcium salts of higher molecular weight fatty acid have found widespread use in commercial applications. These mixed-salt lubricants have good antiwear and load-carrying ability, which properties made them commercially successful. The commercial versions of these lubricants have been previously prepared with naphthenic mineral lubricating oil having a low viscosity index, which is a common base oil in the lubricants industry. It has now been found that by preparing mixed-salt lubricants with a high viscosity base stock comprising a naphthenic distillate, a solvent extract from a paraffinic or a mixed base lubricating oil, and a viscous propane extracted resin, the resulting lubricant is improved with regard to water resistance (including both water repellancy and structural stability when water is worked into the product), fire resistance and is more transparent. In addition, the lubricants have a fibrous structure and improved adhesiveness to metal. These improved properties are quite important from a commercial standpoint. Thus, certain semi-fluid versions of the mixed-salt thickened lubricants are commercially used in forced feed lubricating systems. In many such systems the lubricant flows upward through a sight glass containing water and glycerine. In this manner, the rate of lubricant flow can be visually observed as the drops of lubricant pass upward through the water-glycerine mixture and the flow adjusted by a regulating valve. In this application, prior mixed-salt lubricants prepared with the conventional naphthenic lubricating oils would displace water from the sight glass and/or fog it so as to necessitate frequent cleaning. However, the water-resistant compositions of the present invention greatly alleviate this difficulty. Water resistance and adhesiveness are also important qualities in the case of solid greases thickened with mixed-salt systems. Thus, these properties further extend the usefulness of the grease into applications, such as automotive chassis lubrication, where the need for these properties is obvious. Fire resistance is also important in certain applications such as lubricant of ladle cars in steel mills where high temperatures are encountered. And of course, for a general purpose lubricant, all of the above qualities are desirable.

Surprisingly, it has been found that the above noted properties are not all obtained by using any combination of any two of the three base stock materials noted above. For example, the naphthenic distillate with the propane extracted resins actually increases the water absorption ability of the lubricant rather than decreases it. This is somewhat surprising since propane precipitated resins have been generally thought of as water-proofing agents. Combinations of the naphthenic distillate with the solvent extract in grease, while improving the fiber and adhesive qualities of the lubricant, result in such a low viscosity in-

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dex that the greases tend to thin excessively at higher temperatures or to excessively harden at low temperatures. However, in the fluid lubricants where V.I. is not so important, a combination of naphthenic distillate and solvent extract may be used.

The base oil of the invention will comprise about 60 to 80 wt. percent of naphthenic oil, about 30 to 10 wt. percent of solvent extract and about 15 to 3 wt. percent of propane precipitated resin. Preferred proportions are 70 to 80 wt. percent of naphthenic oil, 20 to 15 wt. percent of solvent extract oil and 3 to 10 wt. percent of propane precipitated resins, all of said weight percentages being based upon the total amount of base oil. The base oil composition will have a viscosity of 45 to 100, preferably 50 to 75 SUS at 210° F., and a V.I. (Dean and Davis viscosity index) of 10 to 70, preferably 30 to 60.

The naphthenic lubricating oil used above is a neutral distillate oil prepared from a naphthenic crude oil. It will have a viscosity of 50 to 80 SUS at 210° F., and a V.I. of 30 to 60. A commercial oil of this type used in several of the examples is available under the trade-name of Diol 55.

The solvent extract will have a viscosity of 100 to 175 SUS at 210° F., and a V.I. of below 0, e.g. -100 to 0. It can be prepared by solvent extraction of paraffinic or mixed base lubricating oil with phenol, furfural, nitrobenzene, etc. as is known in the art. A commercial oil of this type used in several of the examples is commercially available under the trade-name of Nuso 125.

The propane precipitated resin will have a viscosity of 1,000 to 10,000, preferably 1,500 to 3,000 SUS at 210° F., and a V.I. of 100 to 150. These resins are obtained by treating a non-asphaltic crude oil, e.g. Pennsylvania or Mid-Continent crude, with liquid propane and then recovering the precipitated resins.

The above types of oils and resins are well known in the art and the exact method of their manufacture forms no part of this invention. Rather they are described herein only to the extent necessary to identify the oils contemplated by the invention.

The lubricating compositions of the invention comprise a major amount of the lubricating base oil described above and about 5 to 30, e.g. 8 to 20 wt. percent of the mixed salt-thickener. This thickener, in turn, comprises a co-neutralized mixture of the alkaline earth metal salts of a low molecular weight acid such as acetic acid and C₇ to C₁₂ fatty acids. Usually about 4 to 20, preferably 4 to 12 moles of low molecular weight acid, e.g. acetic acid, per mole of C₇ to C₁₂ fatty acid will be used. There may also be present about 0.1 to 3.0 mole of a C₁₄ to C₃₀ fatty acid or hydroxy fatty acid such as 12-hydroxy stearic acid per mole of the C₇ to C₁₂ fatty acid.

The co-neutralization is carried out by reacting an alkaline earth metal base such as the hydroxides or carbonates of calcium, barium, strontium or magnesium with the mixture of acetic and higher fatty acids. Calcium is the preferred metal, being generally used in the form of a lime slurry. While acetic acid is usually used as the low molecular weight acid, its anhydride may be used instead.

The intermediate molecular weight fatty acids, i.e. the C₇ to C₁₂ acids, will include those straight chain, saturated acids such as capric, caprylic, pelargonic acid, lauric acid, etc.

As mentioned above C₁₄ to C₃₀ fatty acids may also be used, such as stearic, 12-hydroxy stearic, oleic, tallow, hydrogenated fish oil acids, etc.

If desired, various inorganic acids may be used to replace part or all of the acetic acid component in the preparation of the thickener. Thus, strong mineral acids such as hydrochloric acid, nitric acid, sulfuric acid, orthophosphoric acid and spent acids from sulfonation process

may also be incorporated. Also dithiodialkyl phosphoric acid wherein the alkyl groups contain 3 to 10 carbon atoms can be used to advantage. An especially preferred inorganic acid is orthophosphoric acid, which is economical, and less corrosive to the manufacturing equipment than acetic acid. Furthermore, by using the phosphoric acid to replace a portion of the low mol. wt. fatty acid, the resulting grease is made more resistant to color and oxidation degradation than if no phosphoric acid was used. This acid is not volatilized during the heating process. Also various inorganic salts such as alkaline earth metal or alkali metal (e.g. sodium and lithium) nitrites, phosphates, chromates, and carbonates may be added to the lubricant.

Various other additives may also be added to the lubricating composition (e.g. 0.1 to 10.0 weight percent based on the total weight of the composition), for example, oxidation inhibitors such as phenyl- α -naphthylamine; corrosion inhibitors, such as sorbitan monooleate; supplemental grease thickeners such as polyethylene and polypropylene; stabilizers such as aluminum hydroxy stearate, and the like.

The compositions of the invention may be prepared in several ways. In one method, all the acids are dispersed in the base oil and neutralized with the metal base. The resulting product can then be heated to about 225° to 400° F., preferably 250° to 350° F., to dehydrate the mixture. The resulting composition will be in the form of a physical mixture of the salts. This technique is advantageously used in making semi-fluids or soft greases. If the same composition is heated above 400° F., say about 430 to 600° F., a pronounced thickening effect occurs. This high temperature technique is used to advantage when a more solid or a harder product is desired. Still another technique forms a solid or harder grease but avoids the high temperatures. This last technique involves partially neutralizing the acids dispersed in oil, i.e. neutralizing only 90 to 98% of the available acidity, heating at 300° to 350° F. for 1 to 8 hours, during which heating the acidity further decreases to about 0.5 to 5.0% calculated as oleic acid of the original available acidity, and then adding more metal base sufficient to attain a slight degree of alkalinity. In each of the above cases, the mixture may then be next cooled to about 200° to 210° F., where conventional additives, if any, may be added. The grease is then cooled to below 150° F. where it may be homogenized, as by passing through a Gaulin

homogenizer or a Charlotte mill, followed by subsequent cooling to room temperature. If desired, grease concentrates can be made by the above techniques and then diluted with additional lubricating oil to form the final composition.

The invention will be further understood by the following examples:

EXAMPLE I

(All parts by weight)

Grease A.—A base oil was prepared by simple mixing 36.7 parts of Diol 55, a naphthenic neutral distillate lubricating oil having a viscosity of 55 SUS at 210° F., and a V.I. of 35; 29.2 parts of Nuso 125, a lubricating oil having a viscosity of 160 SUS at 210° F., and a V.I. of below 0 prepared by phenol extraction of naphthenic type mineral oil; and 7.4 parts of Pennzoil resin, a resin obtained by propane extraction of a Mid-Continent crude. This resin had a viscosity at 210° F. of 2,600 SUS and a V.I. of over 100. The resulting base oil had a viscosity at 210° F. of 71 SUS and a V.I. of 45.

The above base oil and 9.2 parts of hydrated lime were added to a fire heated kettle and intimately mixed. To this slurry was added 11.0 parts of glacial acetic acid and 5.5 parts of Wecoline AAC acids (a commercial acid derived from coconut oil and consisting of about 26 wt. percent lauric acid, about 28 wt. percent caprylic acid and about 46 wt. percent capric acid).

The mixture was stirred for a half hour and then heating was begun. The heat was turned off after heating about 0.1 hour at a temperature of 440° F. The grease was cooled to 200° F. and 1 part of phenyl α -naphthylamine was added as an oxidation inhibitor. The product was then Gaulin homogenized at 3,000 p.s.i.

Grease B.—A grease was prepared in the same manner as grease A, except that the base oil consisted of 36.7 parts of the naphthenic distillate and 36.6 parts of the phenol extract, the naphthenic distillate and phenol extract being the same oils described in grease A.

Grease C.—This grease was prepared in the same manner as greases A and B, except that the base oil consisted of 63.8 parts of naphthenic distillate oil and 9.5 parts of the propane precipitated resin. The naphthenic distillate oil and the resin were the same used in preparing grease A.

Grease D.—A fourth grease was prepared in the same manner as greases A, B and C, except that the base oil was naphthenic distillate alone.

Table 1

	GREASE			
	A	B	C	D
Components (weight percent):				
Glacial acetic acid.....	11.0	11.0	11.0	11.0
Wecoline AAC acids.....	5.5	5.5	5.5	5.5
Hydrated lime.....	9.2	9.2	9.2	9.2
Phenyl α -naphthylamine.....	1.0	1.0	1.0	1.0
Naphthenic oil, 55 SUS at 210° F.....	36.7	36.7	63.8	73.3
Phenol extract oil.....	29.2	36.6		
High V.I. propane extracted resin.....	7.4		9.5	
Properties:				
Appearance.....	Very fibrous uniform	Very fibrous, uniform	Uniform, not fibrous	Uniform, not fibrous.
Dropping point ° F.....	500+	500+	500+	500+
Penetration 77° F. mm./10:				
Unworked.....	215	264	250	265
Worked 60 strokes.....	300	322	280	310
Worked 10,000 strokes (fine hole worker plate).....	340	377	350	340
Shell roller test (4 hours):				
Micro Pen. mm./10, before.....	144	166	160	163
Micro Pen. mm./10, after.....	183	200	235	210
4 ball wear scar, mm. (1800, r.p.m., 10 kg. load, 75° C., 1 hour).....	0.33	0.41	0.34	0.39
Water washing test (laboratory).....	(1)	(1)	(1)	(1)
Water absorption test, percent absorbed (Mil-G-16908).....	45	100	115	90
Almen test (wgt. carried):				
Gradual loading.....	15	15	15	15
Pin condition.....	Excellent	Excellent	Excellent	Excellent
Shock loading.....	15	15	15	15
Pin condition.....	Excellent	Excellent	Excellent	Excellent
Adhesiveness to metal surfaces.....	do	do	Good	Poor
Water washing—stream of water under pressure.....	None removed	None removed	Turns light brown and washes off.	Good.

1 No loss—grease insoluble.

As seen from the above examples, the combination of the base oils of the invention (grease A) resulted in a water absorption of 45 wt. percent as compared to absorptions of 90 to 115% for greases B to D. Water absorption up to about 50% wt. percent is desirable since it allows the grease to operate under damp conditions and prevents rusting and still does not adversely affect the grease. However, large amounts of water absorption, e.g. 90 to 115 wt. percent, excessively soften the grease so that it loses its structure and is easily removed from the bearings. It is also to be noted that grease prepared without the extracted oil (greases C and D) did not have a fibrous structure, which is a disadvantage in many instances due to lack of adhesiveness to metal surfaces and lack of ability to seal out water and dirt.

To further illustrate the invention a series of semi-fluid lubricants were prepared:

EXAMPLE II

(All parts by weight)

Lubricant A.—A base oil was prepared by mixing 51.2 parts of Diol 55, a naphthenic neutral distillate lubricating oil having a viscosity of 55 SUS at 210° F., and a V.I. of 35; 13.0 parts of Nuso 125, the extract having a viscosity of 160 SUS at 210° F., and a V.I. of below 0; prepared by phenol extraction of naphthenic type mineral oil; and 4.2 parts of a resin obtained by a propane extraction of a Mid-Continent crude. The resin had a viscosity at 210° F. of 2,600 SUS and a V.I. of over 100. The resultant base oil had a viscosity at 210° F. of 78 SUS and a V.I. of 45.

To the above base oil, in a steam heated kettle, was slowly added 10.6 parts of hydrated lime while stirring. Then a mixture of 16.0 parts of glacial acetic acid and 3.8 parts of Wecoline AAC acid was added to the kettle while stirring. The temperature was then raised to about 160° to 180° F., and a free acidity determination showed the free acidity to be 3.20 wt. percent calculated in terms of oleic acid. Additional lime was then added in order to neutralize the free acidity and give a product having 0.10 wt. percent free alkalinity calculated as NaOH. The temperature was then raised to 320° F., at which point heating was discontinued and cooling water was passed through the kettle jacket. On cooling to 200° F., 0.4 part of phenyl α -naphthylamine was added as an oxidation inhibitor. The composition was then allowed to cool to 100° F., where it was diluted with an equal amount of the oil blend described above and the final composition was then passed twice through a Charlotte mill having 0.004" clearance. The product was finished by adjusting the oil content to give a desired ash content, homogenizing a third time through the Charlotte mill, deaerating, filtering and packaging. All the above noted determinations of alkalinity and acidity were made in accordance with the method of ASTM D-664.

Lubricant B.—A second lubricant was prepared in the same manner as lubricant A described above except that the base oil consisted solely of a naphthenic neutral distillate lubricating oil having a viscosity of 80 SUS at 210° F., and a V.I. of 35 available under the trade-name of Diol 80.

The compositions prepared and their properties are summarized in the following table:

Table 2

	Lubricant A	Lubricant B
Base formulation (percent weight):		
Glacial acetic acid.....	16.00.....	16.00.....
Wecoline AAC acid.....	3.80.....	3.80.....
Hydrated lime.....	10.60.....	10.60.....
Phenyl α -naphthylamine.....	0.40.....	0.40.....
Diol 80.....		69.20.....
Diol 55.....	51.20.....	
Nuso 125 (phenol extract).....	13.80.....	
Pennzoll resins (2,600 SUS at 210° F.).....	4.20.....	

Table 2—Continued

	Lubricant A	Lubricant B
5 Properties:		
Appearance.....	Uniform, appears transparent. No great thixotropy.	Opaque, thixotropic but fluid.
Sulfated ash, percent.....	5.09.....	5.0.....
4-hour centrifuge test: 1500 r.p.m.—percent sediment.....	1.1.....	1.0.....
10 SSU vis./100° F.....	1,473.....	1,743.....
SSU vis./210° F.....	106.....	123.....
Filtration through 100 mesh screen.....	Excellent.....	Excellent.....
4 ball wear test—scar dia. mm., (1,800 r.p.m., 10 kg., 75° C., 1 hour).....	0.22.....	0.22.....
15 Lubricator life in days ¹	90+.....	35.....
Sight-glass fluid 50% water/50% glycerine, 1 qt./day rate through dispenser.....	Sight glass fluid clear.	Fluid in sight glass displaced.

20 ¹ Manzell lubricator.

As part of the above comparison, lubricant A gave a uniform transparent lubricant having a sight-glass life of over 90 days, while lubricant B gave an opaque, thixotropic material having a sight-glass life of 35 days. This sight-glass test was carried out by recycling 2 gals. of the lubricant through a sight-glass containing a 50/50 mixture of water and glycerine, at the rate of 1 qt. of lubricant per day. With lubricant A, the sight-glass fluid was perfectly clear after 90 days at which point the test was discontinued. However, with lubricant B, the sight-glass began fogging after 18 days and at the end of 35 days it was no longer possible to observe the flow of lubricant through the sight-glass.

What is claimed is:

1. A lubricating composition comprising a base oil and about 5 to 30 wt. percent of a mixed-salt thickener, said thickener comprising about 4 to 20 moles of calcium acetate per mole of calcium salt of a C₇ to C₁₂ fatty acid, said base oil consisting essentially of 60 to 80 wt. percent of a naphthenic oil having a viscosity of 50 to 80 SUS at 210° F. and a V.I. of 30 to 60, about 30 to 10 wt. percent of a solvent extract having a viscosity of 100 to 175 SUS at 210° F. and a V.I. of —100 to 0 and 15 to 3 wt. percent of propane precipitated resin having a viscosity of 1,000 to 10,000 SUS at 210° F. and a V.I. of 100 to 150.

2. A lubricating oil composition containing a base oil and about 8 to 20 wt. percent of a mixed-salt thickener, said thickener comprising a co-neutralized mixture of calcium salts of acetic acid and calcium salts of a C₇ to C₁₂ fatty acid in a molar proportion of about 4 to 12 moles of acetic acid per mole of said C₇ to C₁₂ fatty acid, said base oil consisting essentially of 70 to 80 wt. percent of naphthenic oil having a viscosity of 50 to 80 SUS at 210° F. and a V.I. of 30 to 60, about 20 to 15 wt. percent of solvent extract having a viscosity of 100 to 175 SUS at 210° F. and a V.I. of —100 to 0 and 3 to 10 wt. percent of propane precipitated resin having a viscosity of 1500 to 3,000 SUS at 210° F. and a V.I. of 100 to 150, said base oil having a viscosity of 45 to 100 SUS at 210° F. and a V.I. of 10 to 70.

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