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SULFONATE BASE LUBRICATING GREASE

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The present invention relates to a sulfonate base lubricating grease and more particularly to a lubricating grease containing metallic sulfonates of a character designed to impart high melting point characteristics to lubricating grease compositions.

It is well known in the prior art that certain types of lubricating greases, for example the lime soap base greases, have good lubricating characteristics at low temperatures but are not suitable for use at elevated temperatures, for example temperatures above 150° or 175° F. The lime soap greases prepared from fats or fatty acids which have long been used for thickening lubricating oils in the preparation of grease type lubricants, normally require the presence of a small amount of water to insure mechanical stability. In the absence of such water, the soap and the lubricating oil separate at higher temperatures, for example 150° to 175° F., or more. This oil separation appears to be due to the evaporation of the water content at the higher temperature, the water normally serving to bond the soap into the oil in some manner and prevent separation in ordinary storage or low temperature use.

The deficiencies in calcium base greases mentioned above have long been known and numerous attempts have been made in the prior art to replace the water with higher boiling compounds. For example, calcium salts of certain saturated carboxylic acids, such as acetic acid, have been added in minor proportions to calcium soap greases to prevent the separation of oil from the soap and also to raise the melting point of the composition. Such a composition is disclosed in U. S. Patent No. 2,197,263.

Conventional greases of the types mentioned above consist largely of lubricating oil of appropriate grade thickened to a grease consistency with a fatty acid soap of a suitable metal, usually calcium, although the soaps of other metals are frequently employed. It has also been known in the prior art that certain of the so-called "mahogany" soaps, that is the metal salts of high molecular weight alkyl-aryl sulfonic acids derived from the manufacture of white oils in petroleum refining, are useful in the manufacture of certain lubricating greases. Such materials, however, are generally oil soluble and thus have little thickening effect. As a result, they are ordinarily used in minor proportions along with conventional fatty acid soap type thickeners.

The present invention is based on the discovery that a very suitable lubricating grease may be prepared by using an appropriate quantity of a relatively high molecular weight metal sulfonate in combination with a relatively small amount of

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a lower molecular weight and relatively oil-insoluble metal sulfonate. The lower metal sulfonates and to some extent some of the higher sulfonates also, are quite water-soluble but the lower sulfonates are not appreciably soluble in mineral oil. The present invention depends on the fact that a combination of high molecular weight and low molecular weight sulfonates dispersed in mineral oil produces a smooth, homogeneous, high melting point lubricating grease which cannot be obtained by the use of either type of sulfonate alone.

It has been found that a grease employing a combination of high and low molecular weight sulfonates as a thickening agent has a dropping point very substantially higher than in the case of grease which is thickened with the calcium soaps of fatty acids. The following examples show the relative characteristics and properties of various samples exemplifying the present invention.

EXAMPLE 1

A lubricating grease was prepared by combining 20 parts by weight on a dry soap basis of oil-soluble calcium petroleum sulfonate having a molecular weight of about 740, 8 parts by weight of calcium ethane sulfonate with a molecular weight of about 258, and 72 parts of mineral lubricating oil of appropriate viscosity, for example 100 S. S. U. at 100° F. or 40 S. S. U. at 210° F. The high molecular weight calcium sulfonate was prepared by calcium chloride treatment of sodium sulfonates recovered in the manufacture of white oils.

These sulfonates, as is well-known in the art, are commonly obtained by treating the lubricating oil and heavier fractions of petroleum with strong, preferably fuming, sulfuric acid to form alkyl-aryl sulfonic acids. The acids so formed are neutralized with an alkaline material, such as sodium hydroxide, to form the sulfonates. The acids and the monovalent metal sulfonates of molecular weight substantially above 300 are generally oil-soluble. They may be recovered from the oil in which they are formed by selective solvent extraction, for example by extraction with isopropyl alcohol.

The particular high molecular weight sulfonate used was prepared from an emulsion consisting of a 55% concentrate in oil and water of a sodium salt of sulfonic acid of molecular weight varying between 300 and 400. This emulsion was treated with calcium chloride and the sodium chloride resulting from double decomposition was washed out. The high molecular weight calcium sulfonate thus obtained was dissolved in part of the mineral oil and the low molecular weight sulfonate (calcium ethane sulfonate obtained by direct lime

treatment of ethane sulfonic acid) was dissolved in water. The two solutions were then mixed and heated to a temperature of about 300° F. with continued agitation until all water had been removed. Thereupon the remainder of the mineral oil was added with stirring and the grease composition was then cooled with continued stirring to a temperature of 200° F. At that temperature the grease was poured into containers.

EXAMPLE 2

Another example of a grease comprising higher and lower calcium sulfonates was prepared by combining 11 parts by weight of a calcium petroleum sulfonate of relatively high molecular weight with 6 parts of ethane sulfonic acid (molecular weight 110) and 2.4 parts of lime in 80.6 parts of mineral oil. The mineral oil used in this example had a viscosity of 320 S. S. U. at 100° F. and a viscosity index of 40. The alkyl-aryl sulfonic acid used in preparing the higher sulfonate had a molecular weight of approximately 350. In this example the mol ratio of high molecular weight sulfonic acid to low molecular weight sulfonic acid was 1 to 2 as indicated below in the table. This composition had a good firm consistency as evidenced by its worked penetration of 310, and a high dropping point of 400+°F.

EXAMPLE 3

Another sample was made by combining 16 parts by weight of the calcium petroleum sulfonate of Example 2 with 4.4 parts of ethane sulfonic acid, 1.8 parts of hydrated lime, and 77.8 parts of the same oil as was also used in Example 2. The grease of this example was prepared in substantially the same manner as that of Example 1. It will be noted that the mol ratio of the higher and lower sulfonates was approximately 1 to 1. The grease had a slightly softer penetration than that of Example 2, but was smooth and transparent in texture and had a dropping point in excess of 400° F.

EXAMPLE 4

A further example was prepared by using 16% by weight of calcium sulfonate prepared from a sulfonic acid having a molecular weight of about 450. To this were added in aqueous solution 3.8% by weight based on the final composition, of ethane sulfonic acid, and 1.6% of hydrated lime. The mineral oil content was 78.6%, the same oil being used as in Examples 2 and 3 above. In this composition the mol ratio of the higher and lower sulfonates was 1 to 1. The excess alkalinity was considerably lower than in Examples 2 and 3. The grease was somewhat softer, having a worked penetration of 360 but it was smooth and transparent in appearance and had a dropping point in excess of 400° F.

The compositions described above in Examples 2, 3 and 4, were prepared in the same general manner, that is by dissolving the high molecular weight sulfonates in part of the oil, adding the lower sulfonate in an aqueous solution, dehydrating by heating to a temperature in the neighborhood of 300° F. and thereafter adding the remainder of the mineral oil and cooling with stirring to temperature of around 200° F.

The comparative formulas and properties of the calcium sulfonate greases of Examples 2, 3 and 4 are shown in the following table:

TABLE 1

Formulae and properties of calcium sulfonate greases

	Ex. 2	Ex. 3	Ex. 4
Formula, percent by weight:			
Calcium Petroleum Sulfonate	11	16	16
Ethane Sulfonic Acid	6	4.4	3.8
Hydrated Lime	2.4	1.8	1.6
Mineral Oil [1]	80.6	77.8	78.6
Mol. Wt. of Petroleum Sulfonic Acid used in preparation of Calcium Sulfonate.	350	350	450
Approx. Mol. Ratio of H. M. W. Sulfonate to L. M. W. Sulfonate.	1:2	1:1	1:1
Inspections:			
Per Cent Total Free Alkali (as NaOH)	0.6	0.8	0.1
Worked Penetration, 77° F	310	340	360
A. S. T. M. Dropping Point, °F	+400	+400	+400
Appearance	(2)	(2)	(3)

[1] 320 S. S. U. at 100° F.; 40 V. I.
[2] Smooth, sl. opaque.
[3] Smooth, transparent.

Two further examples were prepared using the same mineral oil as in Examples 2, 3 and 4 by substituting other sulfonates for the calcium sulfonates.

EXAMPLE 5

The composition was prepared consisting of 16% by weight of oil-soluble barium petroleum sulfonate prepared from the same relatively high molecular weight sulfonic acids as the calcium sulfonates of Examples 2 and 3 above. 4.2% of ethane sulfonic acid and 6.4% of barium hydroxide octa-hydrate were added being combined with 73.4% of mineral oil of 320 S. S. U. at 100° F. and a viscosity index of 40.

The greases of Example 5 had a considerably harder consistency than those of Examples 1 and 4 above. The dropping point, however, was lower, being approximately 260° F. The product was smooth and transparent.

EXAMPLE 6

A soda base grease was prepared by using 25% of the oil soluble sodium sulfonate prepared from the same acids as Examples 2, 3 and 5 with 11% ethane sulfonic acid, 5% sodium hydroxide and 60% of the same mineral oil as in Example 5. The mol ratio of the low molecular weight sulfonate in this example was about twice that of Example 5. The grease was of hard consistency having a penetration number of 220 and it had a dropping point of 420° F. The grease was smooth and transparent, having a slight tackiness. Comparative properties of the greases of Examples 5 and 6 are listed in Table 2:

TABLE 2

Formulae and properties of barium sulfonate and sodium sulfonate greases

	Ex. 5	Ex. 6
Formula, per cent by weight:		
Barium Petroleum Sulfonate	16	------
Sodium Petroleum Sulfonate of high molecular weight	------	24
Ethane Sulfonic Acid	4.2	11
$Ba(OH)_2.8H_2O$	6.4	------
Sodium Hydroxide	------	5
Mineral Oil [1]	73.4	60
Approx. Mol. ratio of H. M. W. Sulfonate to L. M. W. Sulfonate	1:1	1:2
Inspections:		
Per cent Total Free Alkali (as NaOH)	0.3	1.0
Worked Penetration, 77° F	215	220
A. S. T. M. Dropping Point, °F	260	420
Appearance	(2)	(4)

[1] 320 S. S. U. at 100° F.; 40 V. I.
[2] Smooth, transparent.
[3] Smooth, sl. tacky, transparent.

In general, grease compositions prepared according to the present invention make use of the oil-soluble petroleum sulfonates of commerce. These usually contain petroleum sulfonic acids ranging in molecular weight from 300 to 500 or slightly more. They are usually soluble in mineral oil, becoming very tacky and viscous at high concentrations. On the other hand, the low molecular weight sulfonic acids, such as ethane sulfonic acid, which has a molecular weight of 110, form metallic salts which will not dissolve in oil. Methane sulfonic acid, with a molecular weight of about 96, may be used for preparing the lower molecular weight sulfonate, and other homologues such as propane and butane sulfonate may be used. Mixtures of these and related acids may be used also.

As indicated from the data above, by mixing the salts of high and low molecular weight sulfonic acids, the melting point of greases may be raised considerably and their structural stability is improved. The foregoing examples show the use of the calcium, barium, and sodium sulfonates, but it will be understood that other sulfonates, such as zinc, aluminum, lithium, and the like may also be employed. In general, it is preferred that equal or substantially equal molar proportions of the higher and lower sulfonates be used but the invention contemplates the use of various ratios, for example from 1 proportion of high molecular weight sulfonates to 3 of the lower composition on the one hand, to 3 proportions of the high molecular weight compound with 1 proportion of the lower compound.

The quantity of sulfonate employed depends somewhat upon the viscosity of the mineral oil chosen. For a very light mineral oil, it is necessary to use larger quantities of sulfonates to get a suitable grease consistency. On the other hand, when heavy oils are employed, the sulfonate concentrations may be much lower. Thus, for a very heavy oil as little as 5% of the oil soluble sulfonate and about 3% of the non-oil soluble sulfonate will make a grease of reasonable good consistency. For a very light oil, several times as much may be required.

In general, the sulfonate proportions will be between 5 and 25% of the high molecular weight compound and from about 3 to 20% of the low molecular weight compound. As suggested above the high molecular weight sulfonates are preferably derived from sulfonic acids having an average molecular weight within the general range of about 300 to about 500. Acids having molecular weight of around 400 are particularly preferred. The non-oil soluble sulfonates may be derived from the so-called black or green acids having an average molecular weight less than 300 and preferably between about 96 and 250. Ethane sulfonic acid is specifically preferred for preparation of the oil insoluble sulfonate ingredient. Mineral oils used in such greases should preferably have a viscosity of at least 60 S. S. U. at 100° F. and their viscosity may run as high as 1000 S. S. U. at 210° F.

It will be understood that conventional additives which are commonly used in lubricating greases may be added to the foregoing compositions as will be evident to those skilled in the art. Such additives may comprise the usual antioxidants, rust inhibitors, tackiness agents, viscosity index improvers, extreme pressure agents, and the like.

What is claimed is:

1. A grease composition consisting essentially of mineral lubricating oil containing 5 to 25% by weight, based on the total composition, of an oil soluble sulfonate having a sulfonate radical molecular weight of more than 300 and not substantially greater than about 500, and 3 to 20% of a non-oil soluble sulfonate of a sulfonic acid having a molecular weight between 96 and 250, the combined sulfonates being effective to impart a grease-like consistency to said oil.

2. A lubricating grease composition of high melting point consisting essentially of a mineral base lubricating oil of viscosity within the range of 60 S. S. U. at 100° F. to 1000 S. S. U. at 210° F., said oil containing 5 to 25%, by weight based on the final composition, of an oil soluble metal sulfonate having a sulfonate radical molecular weight of more than 300 and not substantially greater than about 500 and 3 to 20% of an oil insoluble metal alkyl sulfonate of a sulfonic acid having a molecular weight between 96 and 250.

3. Composition as in claim 2 wherein said oil soluble sulfonate is an alkaline earth metal salt of sulfonic acids having an average molecular weight between about 300 and about 500.

4. Composition as in claim 2 wherein said oil soluble sulfonate is the calcium salt of petroleum sulfonic acids having an average molecular weight between about 300 and about 500.

5. Composition as in claim 2 wherein said oil soluble sulfonate is the barium salt of sulfonic acids having an average molecular weight between about 300 and about 500.

6. Composition as in claim 2 wherein said oil soluble sulfonate is the sodium salt of sulfonic acids having an average molecular weight between about 300 and about 500.

7. Composition as in claim 2 wherein said oil insoluble sulfonate is the sodium salt of sulfonic acid having an average molecular weight between about 96 and 250.

8. A lubricating grease composition of high melting point consisting essentially of a mineral base lubricating oil of viscosity between 60 S. S. U. at 100° F. and 1000 S. S. U. at 210° F., 5 to 25% by weight, based on the final composition, of substantially equimolar of the calcium salt of sulfonic acid having an average molecular weight of between 300 and 400, and the calcium salt of ethane sulfonic acid, the combined quantities of sulfonates being sufficient to impart a grease like consistency to said oil.

9. Composition according to claim 1 containing an excess of metal base beyond that required to neutralize the acids of said sulfonates.

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