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GREASES

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The present invention relates to improvements in greases and more particularly to relatively low soap-content greases of the type of ball bearing greases, mine loader greases and other anti-friction bearing greases and to the method of preparing the same.

An object of the invention is to provide a relatively low soap-content grease of the type of ball bearing grease, mine loader grease, etc., which has a smooth, short fibre structure, and which shows little or no change in consistency on working or in service. Another object of the invention is to provide a relatively low soap-content grease which is adapted for service at high and low temperatures which will not leak oil or lose consistency at elevated temperatures and which does not become hard at low temperatures. A further object of the invention is to provide a grease of the type of ball bearing grease which is stable against oxidation. Other objects and advantages of the invention will become apparent from the following description thereof.

I have discovered that the foregoing objects can be attained by incorporating in relatively low soap-content greases, of the type of ball bearing greases and similar anti-friction bearing greases, relatively small amounts of sulfonic soaps, preferably the soaps of preferentially oil-soluble sulfonic acids obtained in the treatment of mineral oils with strong sulfuric acid. Greases of the type herein referred to contain from about 2% to about 25% of an alkali metal soap or mixtures of alkali metal soaps and an alkaline earth soap of fatty materials such as fats or fatty acids. Thus, the grease may be prepared, for example, with sodium, potassium or lithium soaps of fats or fatty acids, preferably the sodium soap, or mixtures of such soaps and an alkaline earth soap, such as for example soda-lime soaps. Fats or fatty acids such as tallow, Standard Fatty Acids, stearic acid, animal fatty acids and the like are suitable materials from which to prepare the aforementioned soaps, although I prefer to employ saturated fatty acids such as stearic acid.

In order to obtain the above-mentioned objects it is essential to incorporate in the grease a small amount namely from about 0.25% to about 5% of a sulfonic acid soap. The sulfonic acid soaps which are particularly well adapted for this particular grease are the soaps of preferentially oil-soluble sulfonic acids obtained in the process of treating petroleum oils, particularly viscous petroleum oil stocks, with concentrated or fuming sulfuric acid. In the treatment of petroleum

oils with concentrated or fuming sulfuric acid there are obtained two layers, an acid sludge layer containing preferentially water-soluble sulfonic acids which because of their characteristic greenish color are known in the art as green acids, and an upper oil layer which contains the preferentially oil-soluble sulfonic acids which have a reddish brown color and are referred to in the petroleum refining art as mahogany acids. After the acid sludge is removed the acid treated oil layer is then treated with a neutralizing agent such as an alkali metal hydroxide, for example sodium hydroxide or potassium hydroxide, preferably the former, whereby the sulfonic acids in said oil layer are converted to the corresponding soaps which are then separated from the oil by means of suitable solvents such as for example alcohol. Alkaline earth soaps such as for example calcium, barium, magnesium soaps and the heavy metal soaps of these sulfonic acids can be obtained by reacting the mahogany acids with an hydroxide or oxide of the desired alkaline earth metal. The metal soap can also be obtained by double decomposition using alkali metal soap and an alkaline earth salt.

While the soaps of preferentially oil-soluble sulfonic acids derived from treatment of viscous petroleum oils with fuming sulfuric acid can be suitably employed, I have obtained especially good results by employing the soaps of preferentially oil-soluble sulfonic acids derived from a particular sulfuric acid treatment of petroleum oil distillates, namely the soaps of the preferentially oil-soluble sulfonic acids derived by treating petroleum distillates of from about 70 seconds to about 500 seconds or higher and preferably from about 200 seconds to about 400 seconds Saybolt Universal at 100° F. with from about 6 pounds to about 9 pounds and preferably from about 7 pounds to about 8 pounds of concentrated sulfuric acid, particularly fuming sulfuric acid per gallon of oil.

The method of obtaining these desirable soaps of preferentially oil-soluble sulfonic acids derived from petroleum oils is illustrated by the following example:

The petroleum oil distillate having Saybolt Universal viscosity at 100° F. of from about 200 seconds to about 400 seconds is treated with from about 7 to about 8 pounds of fuming sulfuric acid per gallon of oil in one-half pound increments or "dumps." After the acid sludge from each one-half pound acid "dump" is settled and withdrawn, the next one-half pound of fuming sul-

sulfuric acid is added to the oil. The temperature of the oil before the fuming acid is added thereto is maintained at a temperature below about 60° F. but due to the heat of reaction upon the addition of the sulfuric acid, the temperature of the oil may rise to from about 90° F. to about 100° F. After the required total amount of fuming sulfuric acid has been added to the oil and the oil freed of acid sludge, the acid treated oil containing oil-soluble sulfonic acids dissolved therein, is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is then separated from the oil solution containing dissolved therein sodium soap of sulfonic acids and the latter then separated from the oil by extraction with alcohol of about 60% strength. The alcohol layer containing dissolved sodium sulfonates is then separated from the oil and subsequently distilled to recover the alcohol and water. The sulfonic soap obtained in this manner contains from about 30% to about 60% sodium sulfonate, from about 30% to about 60% oil, from about 1% to about 10% water, and up to 10% of inorganic salts which may be removed by the procedure hereinafter described.

The above procedure may be modified after the acid sludge is removed from the acid treated oil. The oil containing dissolved sulfonic acids is extracted with about 60% alcohol to remove the sulfonic acids which may then be neutralized with sodium hydroxide and subsequently freed of the alcohol by distillation.

The crude soaps of these preferentially oil-soluble sulfonic acids obtained by the procedure described above may be freed of inorganic salts by purification. This purification is preferably accomplished by dilution of the crude soap with from about 1/2 to about 10 parts, preferably 1 to 2 parts of 50% or higher strength alcohol, preferably alcohol of 60 to 70% strength, and allowing the salts to settle while maintaining the mixture within the temperature range of 130 to 175° F., preferably 155 to 165° F. When the salts have settled the supernatant alcohol-soap layer is separated and the alcohol is recovered by conventional distillation procedure. The crude soaps can also be purified by extraction with mixtures of a petroleum solvent such as naphtha and alcohol of from about 10% to about 45%, preferably 40% concentration.

Sulfonates can also be obtained by treating petroleum oils with SO₂, SO₂Cl₂, or with a mixture of gaseous SO₂ and Cl₂.

Greases of the present invention are suitably

designed. Thus, while I prefer to use a mineral oil having a viscosity of about 300 seconds Saybolt Universal at 100° F., mineral oils of 60 seconds to 1500 seconds Saybolt Universal viscosity at 100° F. can be used. The oil employed can be a single fraction of desired viscosity or it can be blends of various fractions required to obtain any desirable viscosity.

The following examples are illustrative of greases made in accordance with the present invention.

Example I

A soft smooth mine loader grease was prepared having the following formula:

	Pounds
Single pressed stearic acid.....	3.1
Soda mahogany soap.....	0.9
Dry caustic soda.....	0.52
SAE 50 oil.....	16.3
SAE 10 oil stock.....	79.5
The finished grease had the following composition:	

	Per cent
Soda soap of stearic acid.....	3.3
Soda mahogany soap (oil-free basis).....	.4
Mineral oil.....	96.3

Example II

A ball bearing grease having the following formula:

	Pounds
Single pressed stearic acid.....	13.6
Soda mahogany soap.....	4.0
Dry caustic soda.....	2.25
SAE 50 oil.....	13.8
SAE 10 oil stock.....	67.5

This grease which has the following composition:

	Per cent
Soda soap of stearic acid.....	14.6
Soda mahogany soap (oil-free basis).....	1.6
Oil.....	83.8

has a low penetration differential, a smooth structure, good resistance to oil leakage at elevated temperatures, good dispensability at low temperatures, a high melting point and excellent oxidation stability.

The improvement effected by the use of the oil-soluble sulfonic soap in greases of the above type is illustrated by the following data obtained with the above grease and conventional soda stearate anti-friction bearing greases, identified in the table below as grease No. 1, a sulfonic soap grease and grease No. 2 and grease No. 3, conventional soda stearate greases.

Grease	Structure	Penetration at 77° F.		Differential	Drop point, °F.	T. C. C. °F. ¹				
		Unworked	Worked			0	77	150	200	250
No. 1.....	Smooth.....	251	280	19	382	660	400	290	260	240
No. 2.....	Short fibre.....	151	283	132	363	(²)	700	580	400	204
No. 3.....	do.....	213	334	121	342	(²)	500	388	290	166

¹ Torsion cone consistometer test described in the Oil & Gas Journal, 37, 46 (March 30, 1939), page 83.

² Too hard.

those coming within the following general formula:

	Per cent
Soap of fatty material.....	2-25
Soap of oil-soluble sulfonic acid.....	0.25-5
Oil.....	70-97.75

The choice of oil used will be largely determined by the nature of the service for which the grease

The above data show that greases of the present invention are superior to conventional anti-friction greases in that the former have a smoother structure, have lower differentials between the unworked and worked penetration, have higher drop points, and flatter temperature-consistency curves.

Example III

A mixed soda-lime soap grease having a composition of

	Per cent
Soda-lime stearic acid soap	11.2
Soda mahogany soap (oil-free basis)	1.4
Oil	87.4

was prepared from the following formula:

	Pounds
Single pressed stearic acid	10.4
Hydrated lime	0.2
Dry caustic soda	1.6
Soda mahogany soap	3.4
SAE 50 oil	16.80
SAE 10 oil stock	69.60

The soda mahogany soap in the above formulas was 40% soda mahogany soap and 60% oil. The greases of Examples II and III before filling were stirred cold in the mixer to give a very smooth grease without any substantial loss in consistency. The low soap content grease of Example I was filled hot without working in the mixer.

In preparing greases of the hereindescribed type the desired amount of fatty material and the sulfonic soap are charged to the grease mixer and sufficient oil added to make a base containing from about 40% to about 50% oil and from about 50% to about 60% soap. The mix is then heated to 225-235° F. and a saponifying agent, for example caustic soda, in a 48° Baumé solution, is then gradually added in an amount sufficient to react with all of the fatty material and leave approximately 1% excess caustic in the base. The temperature is maintained at about 225° F. to 240° F. until the base becomes heavy, and the temperature then gradually increased to about 280° F. to 300° F. and maintained at this temperature until the base becomes very short, heavy and plastic. Heating of the mix is then stopped and additional oil graded in the mixture while the temperature drops to about 250° F., which temperature is maintained during the remainder of the grading-in step. When the grease has been adjusted to the desired consistency heating is discontinued and water introduced into the kettle jacket to cool the mixture as rapidly as possible, and stirring continued until the mixture becomes smooth and of the desired texture. In the case of mixed soap greases such as soda lime soap grease, the lime, for example, is added in the early stages and allowed to react with the fatty material before the caustic soda is added.

In the case of greases having a relatively low soap content such as the greases described in Example I, which are filled hot, the temperature of the mixture is gradually lowered from 250° F. to about 160° F. while the oil is being graded in.

If desired the sulfonic acid soap can be formed in situ by using sulfonic acid and neutralizing in the mixer simultaneously with the preparation of the fatty soap base.

Greases made in accordance with the present invention may have added to them small amounts, namely from about 0.01% to about 2.0% of various addition agents to impart thereto certain desired properties. For example the grease may contain a pour point depressor, oxidation inhibitor, oiliness agent and/or other types of additives. Oxidation inhibitors especially well adapted for use in the hereindescribed greases are polyamines, such as triethylene tetramine, and the neutralized reaction products

of a phosphorus sulfide and a hydrocarbon, preferably an olefin polymer, particularly a mono-olefin polymer having a molecular weight within the range of from about 150 to about 50,000 or more and preferably from about 500 to about 10,000, such as isobutylene polymer.

The phosphorus sulfide-olefin polymer reaction product may be obtained by reacting a phosphorus sulfide such as P_2S_3 , P_2S_5 , P_4S_7 , P_4S_8 , etc., preferably P_2S_5 , with an olefin polymer of the type herein described at a temperature of from about 200° F. to about 500° F., and preferably from about 200° F. to about 400° F. It is advantageous to maintain a non-oxidizing atmosphere, such as, for example, an atmosphere of nitrogen, above the reaction mixture. From about 1% to about 50%, and preferably from about 5% to about 25% of the phosphorus sulfide may be used. Usually it is preferable to use an amount of phosphorus sulfide that will completely react with the polymer, for example, 10%, so that no purification is necessary. However, excess phosphorus sulfide may be used and separated from the product after the reaction is completed, by filtering or by diluting with a solvent such as hexane, filtering, and distilling off the solvent. The reaction mixture may be further treated by blowing with steam or nitrogen at an elevated temperature to improve the odor thereof.

The above described phosphorus sulfide-mono-olefin polymer reaction product is then neutralized with a suitable alkali such as a hydroxide, an oxide, or a carbonate of an alkali or of an alkaline earth metal or with ammonia, and preferably with potassium hydroxide. This neutralization may be carried out by contracting the phosphorus sulfide-polymer reaction product, either as such or dissolved in a suitable solvent, such as naphtha, with a solution of the neutralizing agent, for example, potassium hydroxide dissolved in alcohol. The neutralization may also be accomplished by adding the dry neutralizing agent, such as KOH, NaOH, Na_2CO_3 , $KHCO_3$, CaO, or dry ammonia to the phosphorus sulfide-polymer reaction product, preferably at an elevated temperature of from about 100° F. to about 400° F., preferably in a non-oxidizing atmosphere.

The neutralized product, as aforesaid, may be further treated with a salt of a heavy metal to obtain a heavy metal derivative thereof.

The effectiveness of the above additive in grease is demonstrated by the following data obtained in the Norma-Hoffman Bomb Test, which is described in Product Engineering for June, 1936. The tests were made with 20 gram samples at 210° F. for 100 hours with an initial pressure of 110 pounds.

Sample	Soap	Additive	Pressure drop, lbs.	Increase acidity Mg. KOH/g. sample
60				
65 1	Na stearate	Percent	7.2	1.8
2	Na stearate	None	8.7	1.6
3	Na sulfonate	None	5.2	
4	Na stearate	10.25	1.4	0.3
4	Na sulfonate	10.5	1.0	0.5
70 5	Na stearate	11.0		
	Na sulfonate			

¹ Additive used was a neutralized reaction product of phosphorus pentasulfide and an isobutylene polymer.

At the completion of the tests Sample No. 1 was darker and heavier than the original test sample

and had an oxidized odor, Sample No. 3 was only slightly heavier and darker than the original and Samples 4 and 5 showed substantially no change.

Although the invention has been described in connection with certain specific examples and embodiments thereof, it is to be understood that these are by way of example and not by way of limitation, and the invention is not to be limited thereby except insofar as defined by the scope of the appended claims.

I claim:

1. A low soap-content grease of the type suitable for ball bearing grease comprising from about 2% to about 25% of a soap selected from the class consisting of an alkali metal soap of a saturated fatty material and an alkali metal-alkaline earth mixed soap of a saturated fatty material, a major portion of which is the alkali metal soap, a small amount, not greater than about 5%, sufficient to produce a smooth consistency-stable grease, of an oil soluble soap of a sulphonc acid of the type derived from petroleum oils, and mineral oil.

2. A soft, smooth, low soap-content grease of the type suitable for ball bearing grease comprising from about 2% to about 25% of an alkali metal soap of a saturated fatty material, from about .25% to about 5% of a preferentially oil-soluble soda soap of sulfonic acid of the type derived from petroleum oils and mineral oil.

3. A low soap-content grease of the type suitable for ball bearing grease comprising from about 2% to about 25% of an alkali metal soap of a saturated fatty material, from about .25% to about 5% of an alkali metal soap of sulfonic acid of the type derived from petroleum oils and mineral oil.

4. A grease as described in claim 3 in which the alkali metal soap of the fatty material is the soda soap and the alkali metal soap of sulfonic acid is the soda soap of sulfonic acid.

5. A low soap-content grease of the type suitable for ball bearing grease comprising from about 2% to about 25% of an alkali metal soap of a saturated fatty material, from about 0.25% to about 5.0% of a preferentially oil-soluble alkaline earth soap of a petroleum sulfonic acid and mineral oil.

6. A low soap-content grease of the type suitable for ball bearing greases comprising from about 2% to about 25% of an alkali metal-alkaline earth mixed soap of saturated fatty material, a major proportion of which is the alkali metal soap, a small amount, not greater than about 5%, sufficient to produce a smooth consistency-stable grease, of a petroleum sulphonc acid soap, and mineral oil.

7. A grease as described in claim 6 in which the mixed soap of the fatty material is the soda-lime soap of stearic acid and the sulfonic acid soap is the soda soap of sulfonic acid.

8. A grease of the type suitable for ball bearing grease comprising from about 2% to about 25% of a soda soap of stearic acid, from about .25% to about 5% of a soda soap of sulfonic acid of the type derived from petroleum oil and mineral oil.

9. A stable low soap-content grease of the type suitable for ball bearing grease comprising from about 2% to about 25% of a soap of a saturated fatty material selected from the group consisting of an alkali metal soap of a saturated fatty material and an alkali metal-alkaline earth mixed soap of a fatty saturated material, the major proportion of which is the alkali metal soap, from about 0.25% to about 5.0% of a preferentially oil-soluble soap of a sulfonic acid of the type derived from petroleum oil, from about 0.01% to about 2.0% of an oxidation inhibitor and a mineral oil.

10. A stable grease as described in claim 9 in which the oxidation inhibitor is the neutralized reaction product of a phosphorus sulfide and a hydrocarbon.

11. A grease as described in claim 9 in which the oxidation inhibitor is the neutralized reaction product of a phosphorus sulfide and an olefin polymer.

12. A grease as described in claim 9 in which the oxidation inhibitor is the neutralized reaction product of phosphorus pentasulfide and an isobutylene polymer.

13. A grease as described in claim 9 in which the oxidation inhibitor is a polyamine.

14. A grease as described in claim 9 in which the oxidation inhibitor is triethylene tetramine.

15. The method of preparing a low soap-content grease having a low penetration differential, a smooth structure, resistance to oil leakage at elevated temperatures and stable against oxidation, comprising mixing a saturated fatty material, an oil soluble soap of sulfonic acid of the type derived from petroleum oil and sufficient mineral oil to make a base containing from about 40% to about 50% oil and from about 50% to about 60% soap, heating the mixture to a temperature of about 225° F. to 235° F., adding a saponifying agent selected from the group consisting of an alkali metal basic compound and a mixture of an alkali metal basic compound and an alkaline earth basic compound, the major quantity of which is the alkali metal basic compound, in an amount sufficient to react with all of the fatty material and leave approximately 1% excess alkaline material in the base, maintaining the temperature at about 225° F. to 240° F. until the base becomes heavy and gradually increasing the temperature to about 280° F. to about 300° F. and maintaining the mixture at said last mentioned temperature until the base becomes short, heavy and plastic, grading in a mineral oil in an amount sufficient to reduce the soap content of the grease to not less than about 2% and not more than about 25% while the temperature is gradually lowered to about 250° F. at which temperature grading in of the oil is continued until the mixture acquires the desired consistency, rapidly cooling the mixture by suitable means and stirring the mixture until the same is worked smooth.

16. The method of preparing a low soap-content soda-lime soap grease comprising mixing together stearic acid, soda mahogany soap and sufficient oil to make a soap base containing from about 40% to about 50% mineral oil and from about 50% to about 60% soap, heating the mixture to a temperature of from about 225° F. to about 235° F., adding the required amount of hydrated lime to the mixture to react with the stearic acid, gradually adding a 48° Baumé solution of caustic soda to the mixture in an amount sufficient to react with all of the remaining stearic acid and leave approximately 1% excess caustic soda in the base, maintaining the temperature at about 225° F. to about 240° F. until the base becomes heavy and gradually increasing the temperature to about 280° F. to about 300° F. and maintaining the base at said last named temperature until the base is short, heavy and plastic, adding a mineral oil in an amount sufficient to reduce the soap content of the grease to not less than about 2% and not more than about 25% to the mixture and gradually reducing the temperature to about 250° F. at which temperature the remainder of the oil is graded in, rapidly cooling the graded mixture and stirring

the cooled mixture until the same is worked smooth.

17. The method of preparing a low soap-content grease comprising mixing together a saturated fatty material, an oil soluble soap of sulfonic acid of the type derived from petroleum oil and sufficient mineral oil to make a base containing from about 40% to about 50% oil and from about 50% to about 60% soap, heating the mixture to a temperature of about 225° F.-235° F., adding caustic soda in a 48° Baumé solution, in an amount sufficient to react with all of the fatty material and leave approximately 1% excess alkaline material

in the base, maintaining the temperature at about 225° F. to 240° F. until the base becomes heavy and gradually increasing the temperature to about 280° F.-300° F. and maintaining the mixture at said temperature until the base becomes short, heavy and plastic, gradually lowering the temperature to about 160° F. while grading in the oil in an amount sufficient to reduce the soap content of the grease to not less than about 2% and not more than about 25% required to obtain the desired consistency and filling said grease while at said last mentioned temperature.

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