Patented June 2, 1953

2,640,811

UNITED STATES PATENT OFFICE

2,640,811

DEMULSIFIABLE LUBRICANT COMPOSITIONS

Helen Sellei Beretvas, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Application March 26, 1951, Serial No. 217,680

8 Claims. (Cl. 252—33.3)

1

This invention relates to improvements in lubricant compositions, and more particularly relates to compositions having improved demulsibility characteristics and to the method of preparing the same.

In many applications of lubricant compositions such as gear lubricants, extreme pressure lubricants, etc., which contain one or more additives, such as soaps, particularly lead soaps, organic halogenated compounds, sulfur-containing compounds, etc. to impart desired properties to such lubricants, the products become contaminated with water resulting in the formation of emulsions. If the lubricant composition does not readily demulsify or separate from the water, the use of such products as lubricants materially decrease and must often be discarded.

It is an object of the present invention to provide a lubricant composition having improved demulsibility characteristics. Another object of the invention is to provide a compounded lubricant composition which will readily separate from water when contaminated or emulsified with water. A still further object of the invention is to provide a lubricant composition which is resistant to the formation of emulsions when used in the presence of water or when contaminated with water. Another object of the invention is to provide a method of imparting demulsibility characteristics to lubricant compositions. Other objects and advantages of the present invention will become apparent from the following description thereof.

The present invention is particularly directed to leaded gear lubricant compositions containing sulfur and which contain, in addition to the viscous hydrocarbon lubricating oil, additives which tend to promote the formation of emulsions in the presence of water. Such additives are, for example, asphalts, lead soaps of high molecular weight carboxylic acids, such as saturated and unsaturated mono-basic carboxylic acids of 10 or more carbon atoms or naphthenic acids and sulfur-containing organic compounds, such as sulfurized sperm oil, sulfurized lard oil and sulfurized olefin polymers. The lubricant composition can contain, in addition, halogen-containing compounds, such as halogenated organic compounds, particularly the chlorinated compounds, sulfur-containing and/or phosphorus-containing organic compounds, organic sulfides, acids of phosphorus, etc. Such additives are usually employed in amounts of from about 0.25% to about 15% or more.

Illustrative of the type of lubricants to which the present invention is directed are lubricants

2

used in the lubrication of gears and heavy machinery in which because of high temperature and pressure encountered, so-called extreme pressure gear lubricants are employed. Such lubricants usually comprise viscous hydrocarbon oils, asphalts or residuum and at least two extreme pressure agents one of which is a lead soap, such as for example, a lead fatty acid soap or lead naphthenate in association with a sulfurized compound, such as sulfurized sperm oil. An example in which such lubricants are employed is the equipment used in the rolling of metals. Frequently, in the rolling of metals, water or water emulsions, known as "rolling solutions" are sprayed on the rolled sheets to loosen and wash away scale and as coolants for the rolls and in the case of rolling solutions to act as rust preventives. The water or rolling solution frequently contaminates the extreme pressure gear lubricant and emulsions are formed.

Usually such emulsions have to be stored, in a quiescent state, for sixteen to twenty-four hours or more to permit the stratification and separation of lubricant and water. In accordance with the present invention the addition in combination of from about 0.25% to about 3.0% of an alkaline earth soap of a preferentially oil-soluble sulfonic acid and from about 0.2% to about 2.0% sulfated castor oil to such lubricant compositions enables such emulsions to break and separate in a relatively short time; the time required for such emulsions to break and separate depending of course on the type of service and the degree of oil and water mixing.

While both the alkaline earth sulfonate and the sulfated castor oil have fairly good demulsibility properties by themselves demulsification in the presence of the sulfonate alone is too slow while the sulfated castor oil in the absence of the sulfonate leaches out of the oil too rapidly. The quantity of the sulfonate and the sulfated castor oil used in accordance with this invention is critical in that the sulfonate in excess of about 3.0% is not beneficial and an excess of 2.0% of the sulfated castor oil inverts the emulsion beyond the desirable point and tends to form stable oil-in-water emulsions. Hence, the invention herein described lies in the delicate balance afforded by the combination of two different types of products, namely the oleophylic sulfonate and the hydrophylic sulfated castor oil, which when used in the amounts specified causes the separation of water that may be mixed in the lubricant during operation.

Typical lubricants to which the present invention is directed comprise the following constitu-

ents in approximately the following weight percentages:

	Permissible Range	Preferred Range
	Percent	*Percent*
Oil-soluble Lead Soap	3 to 20	5 to 10
Organic sulfur-containing E. P. Agent	3 to 20	3 to 10
Oleic Acid	0 to 10	2 to 5
Asphalt	1.0 to 25	2 to 6
Solvent Extract of a Petroleum Lubricating Oil	0 to 25	2 to 6
Oil-soluble Alkaline Earth Sulfonate	0.25 to 3.0	1.0 to 2.0
Sulfated Castor Oil	0.25 to 2.0	0.4 to 0.8
Hydrocarbon Lubricating Oil	50 to 92.5	65 to 80

Examples of suitable oil-soluble lead soaps are lead soaps of naphthenic acids and lead soaps of high molecular weight fatty acids, such as lead soaps of lauric acid, oleic acid, palmitic acid and lead soaps of various fish oils, although I prefer to use the lead naphthenate. The lead naphthenate can be readily prepared by reacting lead oxide with napthenic acids or by other well-known methods.

The organic sulfur-containing E. P. agent can be suitably a sulfurized fat or fatty acid such as for example, sulfurized lard oil, sulfurized esters, such as sulfurized sperm oil, sulfurized olefins and olefin polymers with non-corrosive sulfur, sulfurized vegetable oils, etc. One of the preferred compounds is sulfurized sperm oil.

The alkaline earth soaps of preferentially oil-soluble sulfonic acids used in the present invention are preferably the soaps of the sulfonic acids obtained in the treatment of hydrocarbon oils, such as petroleum lubricating oils, with strong sulfuric acid, i. e., concentrated sulfuric acids of at least about 95% strength or fuming sulfuric acid. The alkaline earth soaps of other preferentially oil-soluble sulfonic acids, such as those obtained by the sulfonation of olefin polymers having at least about 22 carbon atoms in the molecule or those obtained by the sulfonation of alkylated aromatics having at least about 19 carbon atoms can also be used.

Preferentially oil-soluble petroleum sulfonic acids are those obtained in the treatment of petroleum oils to obtain highly refined products of the type of technical insulating oils, turbine oils, medicinal white oils, technical white oils, etc., in which the petroleum oils are treated successively with a number of portions of concentrated sulfuric acid, i. e., above about 95% strength, or fuming sulfuric acid. A variety of sulfur-containing compounds are formed by chemical reaction of the sulfuric acid upon the oil, including sulfonic acids, organic esters of sulfuric acid, and partial esters of sulfuric acid. Most of these compounds are relatively insoluble in the oil under treating conditions and separate from the oil together with unreacted sulfuric acid as a sludge which is separated from the oil after each treatment. The sulfuric acid is usually added in "dumps" of about one-half pound per gallon of oil, the total quantity of acid added depending upon the oil being treated and the final product. Usually, from about three pounds to about nine pounds of sulfuric acid per gallon of oil are used. Some of the sulfonic acids resulting from the treatment of the oil with the sulfuric acid are preferentially oil-soluble and remain in the oil layer after removal of the acid sludge. The sulfonic acids in the acid-treated oil can be extracted therefrom with an aqueous alcohol, for example, ethyl or isopropyl alcohol, of about 50–80% strength and the extracted sulfonic acids neutralized with a basic alkaline earth compound, such as for example, lime. Because of the characteristic mahogany color of the sulfonates they are known as mahogany soaps in the petroleum art. While the majority of the proportions of the preferentially oil-soluble sulfonates are obtained from the acid-treated oil there can be recovered from the acid sludge by suitable solvents, preferentially oil-soluble sulfonates or sulfonic acids. The term "preferentially oil-soluble sulfonates" therefore includes the oil-soluble sulfonates recovered from the acid-treated oil and the acid sludge.

While any of the preferentially oil-soluble alkaline earth sulfonates, such as calcium, barium or strontium sulfonates can be used, I prefer to employ those obtained from the preferentially oil-soluble sulfonic acids having combining molecular weights in the range of from about 350 to about 525, and preferably those in the range of from about 420 to about 500. The sulfonic acid soaps obtained in the manner described contain from about 30% to about 60% sulfonate, from about 30% to about 60% oil, up to about 2.0% water and less than 0.5% inorganic salts.

The viscous hydrocarbon oil used in such lubricant compositions can be any hydrocarbon oil having a Saybolt Universal viscosity within the range of from about 80 seconds at 100° F. to about 500 seconds at 210° F. The oil can be a petroleum distillate or residuum oil or mixtures thereof or can be a synthetic hydrocarbon oil falling within the above-described viscosity range. There is also used with the hydrocarbon oil asphaltic materials, such as heavy residuums or blown or oxidized residuums. The choice of the oil used will be determined by the nature of the service to which the lubricant is designed.

The asphalt used in lubricant compositions of the type herein described can be either a catalytic-cracked asphalt, an asphalt obtained as a residue in the distillation of petroleum or a blown asphalt as obtained by the air-blowing of petroleum residuum. Suitable asphalts are those having an A. S. T. M. penetration of between about 5 to about 40 under a load of 5 grams at 5 seconds at 77° F. and an A. S. T. M. ring and ball softening point of between about 140° F. to about 220° F. Blown asphalts having a penetration of between about 10 to about 20 under the above conditions and a softening point of between about 160° F. to about 220° F. are preferred.

The lubricating oil solvent extract which may be a component of lubricant compositions of the type herein described is the extract obtained in the well known processes for the solvent extraction of petroleum oils. Selective solvents, such as dichlorethyl ether ("Chlorex") phenol, cresol, furfural, nitrobenzene, chlorphenol, sulfur dioxide and solvent mixtures containing one or more of these solvents are used to extract components which impart undesirable properties to lubricating oils, for example, aromatics and/or polynuclear naphthenic compounds, leaving in the oil compounds of mononuclear and/or relatively paraffinic nature. Solvent extracts of lubricating oil stocks in general can be suitably employed; I have found Chlorex extract of an SAE 20 lubricating oil stock to be particularly suitable.

The lubricant composition can contain other additives, such as for example, antioxidants, antifoam agents, metal deactivators, pourpoint depressors, corrosion inhibitors, etc.

The following examples, illustrative of lubricant compositions of the present invention, are

given by way of illustration and are not intended to be indicative of the scope of the invention:

	Example								
	1	2	3	4	5	6	7	8	9
Lead Naphthenate	*Percent* 10	*Percent* 10	*Percent* 10	*Percent* 5	*Percent* 10	*Percent* 10	*Percent*	*Percent* 10	*Percent* 10
Lead Fish Oil Soap							5		
Sulfurized Sperm Oil	5	5	5	15	5	5	5	5	5
Fatty Acid:									
Oleic Acid	2	4	4		4	4	4		4
Palmitic Acid								4	
Asphalt	3	1	10	3	3	3	3	3	3
Chlorex Extract	3	1	10	3	3	3	3	3	3
Calcium Mahogany Soap	1	1	1	1	2	1.5	1	1	1
Sulfated Castor Oil	0.5	0.5	0.5	0.5	1	0.5	0.5	0.5	1
Hydrocarbon Lubricating Oil	75.5	77.5	59.5	72.5	72.0	73.0	78.5	73.5	73.0

The effectiveness of the combination of an alkaline earth soap of a preferentially oil-soluble sulfonic acid and a sulfated castor oil, in improving the demulsibility characteristics of lubricant compositions is demonstrated by the data in Table I. These data were obtained in a demulsibility screen sequence test which is conducted in the following manner: 300 grams of the lubricant composition and 30 cc. of water are poured into a tall 500 cc. glass beaker and the mixture stirred with a glass stirrer at a speed of about 2200 R. P. M. for ten minutes at room temperature (about 70° F.). The beakers are then placed in an oven, kept at a temperature of 200° F. for a period of 16 to 18 hours at which times the beakers are removed and inspected. There are usually two layers formed in the beakers, the upper layer comprising essentially oil and the lower layer comprising essentially either water or an emulsion of oil and water. Whenever water separates, the test is repeated by drawing off and measuring the separated water, and adding 30 cc. more of water to the beaker and repeating the hereinbefore described procedure. The test is repeated through a number of sequences until the amount of water recovered becomes increasingly smaller or complete emulsification takes place. With an efficient demulsifier the procedure may be repeated well over ten times and the test be concluded thereafter. The control lubricant composition used in obtaining the data was composed of 5% sulfurized sperm oil, 10% lead naphthenate, 4% oleic acid, 3% asphalt, 3% Chlorex extract of S. A. E. 20 lube oil stock and 75% lubricating oil having a Saybolt Universal viscosity at 100° F. of about 1100 seconds. To this basic formulation were added various amounts of the preferentially oil-soluble sulfonic acid soaps (mahogany soap) and sulfated castor oil and combinations thereof.

TABLE I

Demulsibility screen sequence test

Demulsifier	cc. H_2O Separated After Each Sequence				
	Sequence 1	Sequence 2	Sequence 3	Sequence 4	Sequence 5
1. Control	0	(2)	(2)	(2)	(2)
2. 1% Ca Mahogany Soap	23	22	30	24	25
3. 0.25% Sulfated Castor Oil	0	0	0		
4. 0.5% Sulfated Castor Oil	23	0	0		
5. 1.0% Sulfated Castor Oil	23	(3)	(3)	(3)	(3)
6. 1.0% Na Mahogany Soap	22	26	27	4	
7. 1.0% Na Mahogany Soap; 0.5% Sulfated Castor Oil	21	(3)	(3)	(3)	(3)
8. 1.0% Ca Mahogany Soap; 0.5% Sulfated Castor Oil	21	25	23	19	(4) 29
9. Same as 8 [1]	23	34	25	26	21
10. 0.5% Ca Mahogany Soap; 0.25% Na Mahogany Soap	22	18	8		

[1] Also contains 2 p. p. m. silicone polymer (Dow 200) as anti-foam agent.
[2] No separation. [3] Forms heavy emulsion. [4] Still separating water after 20 sequences.

While the calcium mahogany soap (Example 2) alone appears to be effective by the demulsibility screen test, its deficiency as a demulsifying agent compared to the combination of calcium mahogany soal and sulfated castor oil is demonstrated by the data in Table II, which were obtained by the so-called "Herschel emulsion test," which is carried out in the following manner:

Forty cubic centimeters of distilled water and forty cubic centimeters of the oil being tested are placed in a 100 cc. graduate, which is then placed in a water bath until the contents thereof reach a temperature of 130° F. The mixture of oil and water is then thoroughly mixed by agitation for five minutes with a paddle rotated at 1500 R. P. M. At the end of the stirring time the graduate with contents are placed in a water bath, maintained at a temperature of 130° F., and inspected at the end of twenty-four hours. The water separated in twenty-four hours is recorded, drawn off and replaced with distilled water to a total (oil and water) of eighty cubic centimeters and the procedure repeated three times. The procedure is a modification of the Herschel demulsibility test (which uses 53 cc. water and 27 cc. oil) described in "The Examination of Petroleum," by Hamor and Padgett, page 562.

TABLE II

Demulsification by Herschel test method

Demulsifier	cc. H_2O Separated in Twenty-four Hours		
	Sequence 1	Sequence 2	Sequence 3
1. None (control)	4	(1)	(1)
2. (1)+1% Calcium Mahogany Soap	15	15	18
3. (1)+0.5% Sulfated Castor Oil	37	40	10
4. (1)+1% Calcium Mahogany Soap; 0.5% Sulfated Castor Oil	35	40	33

[1] No effect.

These data show the superior demulsifying property of the combination of the herein-described invention. The demulsifying effect of the sulfated castor oil is lost in a relatively short time by being leached out from the oil.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

While the present invention has been described by reference to preferred embodiments thereof the same have been given by way of illustration only and are not intended to limit the invention which includes within its scope such modifications and variations as come within the scope of the appended claims.

I claim:

1. A lubricant composition resistant to the formation of stable emulsions with water comprising essentially a major proportion of a hydrocarbon lubricating oil and the following constituents in the following approximate weight percentages:

	Per cent
Oil-soluble lead soap	3 to 20
Organic sulfur-containing E. P. agent	3 to 20
High molecular weight fatty acid of at least 12 carbon atoms	0 to 10
Asphalt	1 to 25
Solvent extract of hydrocarbon oil	0 to 25
Oil-soluble alkaline earth sulfonate	0.25 to 3
Sulfated castor oil	0.25 to 2

said organic sulfur-containing E. P. agent being selected from the group consisting of a sulfurized fat, a sulfurized fatty acid, a sulfurized ester, a sulfurized vegetable oil and a sulfurized olefin, and said solvent extract of hydrocarbon oil containing compounds selected from the group consisting of aromatic compounds, polynuclear naphthenic compounds, and mixtures thereof.

2. A lubricant composition as defined in claim 1 in which the organic sulfur-containing E. P. agent is sulfurized sperm oil.

3. A lubricant composition as defined in claim 1 in which the organic sulfur-containing E. P. agent is sulfurized lard oil.

4. A lubricant composition as defined in claim 1 in which the oil-soluble alkaline earth sulfonate is a calcium sulfonate.

5. A lubricant composition as defined in claim 1 in which the oil-soluble alkaline earth sulfonate is a barium sulfonate.

6. A lubricant composition as defined in claim 1 in which the oil-soluble alkaline earth sulfonate is a strontium sulfonate.

7. A lubricant composition resistant to the formation of stable emulsions with water comprising essentially a major proportion of a hydrocarbon oil, from about 5% to about 10% lead naphthenate, from about 3% to about 10% sulfurized sperm oil, from about 2% to about 5% oleic acid, from about 2% to about 6% asphalt, from about 2% to about 6% dichlorethyl ether extract of a petroleum lubricating oil, from about 1.0% to about 2.0% of a calcium soap of a preferentially oil-soluble petroleum sulfonic acid, and from about 0.4% to about 0.8% sulfated castor oil.

8. A lubricant composition resistant to the formation of stable emulsions with water comprising essentially a major proportion of a hydrocarbon lubricating oil, about 10% lead naphthenate, about 5% sulfurized sperm oil, about 4% oleic acid, about 3% asphalt, about 3% of dichlorethyl ether extract of a petroleum lubricating oil, about 1% calcium soap of a preferentially oil-soluble sulfonic acid, and about 0.5% sulfated castor oil.

HELEN SELLEI BERETVAS.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,165,436	Zimmer	July 11, 1939
2,214,634	Dombrow	Sept. 10, 1940
2,231,168	Lazar	Feb. 11, 1941
2,285,940	Norring	June 9, 1942
2,355,255	Zimmer	Aug. 8, 1944