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[54] **SULFURIZED FATTY OILS**

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[58] **Field of Search** 252/48.6, 125

[56] **References Cited**

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[57] **ABSTRACT**

Sulfurization with elemental sulfur of a fatty mixture consisting essentially of about 80–95 weight percent prime burning lard oil and about 5–20 weight percent alkyl oleate yields a sulfur-containing oil-soluble product suitable for use as a substitute for sulfurized sperm oil additives for imparting extreme pressure properties to high aniline point mineral oil lubricants.

5 Claims, No Drawings

SULFURIZED FATTY OILS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an improved sulfur-containing lubricant additive suitable for use in preparing lubricating oil compositions having improved extreme pressure properties for metalworking purposes. More particularly it relates to sulfurized fatty materials that can be used as a substitute for sulfurized sperm oil extreme pressure additives in high aniline point mineral oil lubricants.

2. Prior Art

Mineral lubricating oils containing sulfurized addition agents have been extensively used as metalworking lubricants and especially as cutting oils. In recent years, it has been found that the mineral oil component of such lubricants contain constituents that may be toxic or carcinogenic in nature and therefore undesirable due to the potential harm that might occur when brought in contact with the human body. It has been found that the polycyclic aromatic constituents naturally present in most mineral lubricating oils are the undesirable constituents. Accordingly, it is necessary to remove these constituents from the oil in order to have a mineral lubricating oil suitable for the preparation of metalworking oils that are not harmful to the human body. The polycyclic aromatics are highly polar and can be removed by suitable solvent extraction methods well known to the art. Naturally occurring paraffinic or naphthenic petroleum oils or solvent extracted oils contain less than about 10 percent carbon in aromatic bonding, as determined by the n-d-M Method used for determining the hydrocarbon type analysis of lubricating oils, have been found to be relatively free of toxicity and carcinogenicity characteristics. A description of the n-d-M Method may be found on p. 226 of "Physical Chemistry of Lubricating Oils" by A. Bondi, Reinhold Publishing Corp., N.Y., 1951. Such oils containing minor amounts of the polar aromatic constituents are relatively poor solvents for organic sulfur compounds. Such oils, which are highly refined oils having an aniline point of at least 190°F, are now used as the principal component of commercial metalworking lubricants.

Conventional sulfurized liquid triglycerides, such as the naturally occurring fatty oils of animal, vegetable, or mineral origin, are well-known additives for use in the preparation of mineral oil-based metalworking lubricants. Due to the change of the mineral oil used as the base for making compounded metalworking lubricants and the lack of solvency characteristics thereof, it is not possible to form satisfactory oil blends of more than 2–3 percent of sulfurized fatty oils in mineral oil. In other words, the prior art sulfurized fatty oils are substantially insoluble in the aforesaid mineral oils containing minor amounts of polar aromatic constituents. The use of the sulfurized fatty oils are desirable for imparting additional lubricity to the mineral oil metalworking fluids.

Another well-known class of sulfurized fatty materials are the sulfurized unsaturated mono-esters of fatty acids as exemplified by methyl oleate.

A widely used sulfurized fatty material is sulfurized sperm oil, for in addition to good solubility, it provides good lubricity, anti-wear properties, and resistance against thermal and oxidative resistance when used as an additive in high aniline point mineral oils. Importation of sperm oil is now prohibited by the Federal government. Thus, a replacement product is required.

Sulfurized lard oil is not a suitable replacement because of its poor solubility in high aniline point mineral oils and also poor thermal and oxidation stability. Methyl oleate has good solubility in high aniline point mineral oils but it has very poor thermal and oxidation stability.

SUMMARY OF THE INVENTION

It has been discovered that a mixture consisting essentially of about 80 to about 95, preferably 85 to 93, weight percent prime burning lard oil and about 5 to about 20, preferably 7 to 15, weight percent alkyl oleate can be sulfurized with elemental sulfur to form a sulfurized product containing from about 8 to about 12, preferably about 9–11, weight percent sulfur in the bound form and less than about 0.3 weight percent free sulfur, having the attributes of sulfurized sperm oil. The sulfurized product of this invention is a suitable replacement for sulfurized sperm oil for use as extreme pressure additives in high aniline point mineral oils.

The term "prime burning lard oil" as used herein and in the claims refers to and means the prime burning lard oil of commerce. It is highly refined lard oil that has been caustic treated to remove free fatty acids, slimes and proteins normally present in commercial lard oil. It typically contains less than 1 percent free fatty acid, as oleic, has a saponification number of about 197 and an iodine number of about 69.

The term "alkyl oleate" as used herein and in the claims refers to and means a mixture of alkyl esters of saturated and unsaturated fatty acids having 14 to 18 carbons, said mixture containing at least 50 weight percent unsaturated fatty acids with not more than 10 weight percent of unsaturated fatty acids containing conjugated double bonds in the unsaturated fatty acid fraction, said alkyl group containing 1 to 3 carbon atoms. A particularly suitable alkyl oleate is the methyl oleate; methyl oleate is obtained by the alcoholysis treatment of lard oil with methanol which is a well-known ester interchange reaction. The purified methyl ester mixture typically contains less than 1.5 percent free fatty acids, about 37 percent saturated fatty acids, and about 58 percent unsaturated fatty acids which includes about 7 percent linoleic acid. In addition, technical grade methyl oleate product typically contains about 7 percent of C_{14-16} saturated fatty acids and about 93 percent of C_{16-18} unsaturated fatty acids which include about 6 percent of linoleic acid, is also suitable for use in this invention.

Sulfurization of the prime burning lard oil and methyl oleate mixture with elemental sulfur is conducted in accordance with conventional sulfurization procedures. Generally this comprises simply heating the mixture with requisite amount of elemental sulfur at a temperature of about 300°–400°F for about 1–8 hours.

The aniline point (ASTM D-611) measures the solubility temperature of aniline and the lubricating oil. The aniline point is, therefore, a measure of solvency characteristics of the lubricant. The higher the aniline point, the poorer the solvency of the lubricating oil.

DESCRIPTION OF PREFERRED EMBODIMENTS

A series of sulfurized fatty materials, identified as samples A-H and described below, were prepared.

Each of the materials contained 10 weight percent sulfur. The methyl oleate used in Samples A, C, E, F, and H was the product derived by alcoholysis of lard oil and in Sample D it was the technical grade product, as described above. For purposes of brevity, the prime burning lard oil will hereinafter be referred to as "PBLO."

Sample A: sulfurized mixture of 10% methyl oleate and 90% PBLO.

Sample B: sulfurized PBLO.

Sample C: a physical mixture of 10% sulfurized methyl oleate and 90% sulfurized PBLO.

Sample D: sulfurized mixture of 10% methyl oleate and 90% PBLO.

Sample E: sulfurized mixture of 20% methyl oleate and 80% PBLO.

Sample F: sulfurized mixture of 50% methyl oleate and 50% PBLO.

Sample G: sulfurized sperm oil.

Sample H: sulfurized methyl oleate.

Each of the above samples of sulfurized fatty materials was tested for oxidation stability and solubility in a high aniline point mineral lubricating oil by dissolving 5 weight percent of the sample in a solvent extracted SAE 10 mineral lubricating oil having an aniline point of 200°–210°F. The oxidation test used was the Accelerated Breakdown Test No. H-150 of the American Society of Lubrication Engineers Standard for Machine Tool Fluid. In this test, 40 grams of test oil and steel and copper coupons are placed in an open beaker which is then held without agitation for 70 hours at 215°F in an oven. The dilute color (ASTM D-1500) of the test oils is determined before and after the oxidation test. Color of the copper coupons at the end of the test is determined by ASTM D-130. Steel coupons visually examined for deposits. The solubility was determined by placing 100 ml of the mixture in an ASTM 8-inch centrifuge tube and stored at 35°F for 48 hours at which time the tube is visually examined for separation. The results of the aforesaid tests are set forth in the following table:

OXIDATION TEST

SAMPLE NO.	COLOR BEFORE	COLOR AFTER	SLUDGE	COPPER	STEEL	SOLUBILITY
A	2.0	3.5	None	3B-4A	No Deposit	Bright & Clear
B	2.5	4	None	3B	No Deposit	Separation
C	2.5	6	None	4A-4B	No Deposit	Separation
D	2.5	4	None	3B-4A	No Deposit	Bright & Clear
E	3	6.5	Trace	3B-4A	No Deposit	Bright & Clear
F	6.5	8+	Heavy	4B	Stain + varnish	Bright & Clear
G	2.5	4	None	3B-4A	No Deposit	Bright & Clear
H	3.5	4	Heavy	4-C	Stain	Bright & Clear

These data show that samples A, D and E, of this invention are comparable to Sample G, sulfurized sperm oil in solubility and thermal and oxidation stability. Sample C, a physical mixture only of the separately sulfurized methyl oleate and PBLO shows such mixture does not have the requisite solubility contra Sample A. It is therefore apparent that co-sulfurization of a methyl oleate and PBLO mixture is required in order to obtain a sulfurized fatty material that is a suitable replacement for sulfurized sperm oil. Further, samples B and H show that either sulfurized methyl oleate or sulfurized PBLO alone is unsatisfactory.

The extreme pressure properties as measured by the Falex Test of the test oils, containing 5 weight percent of Samples A-C, G and H, were essentially the same. The stick-slip numbers as measured by ASTM D-2877-70 for these test oils were essentially equivalent.

The compositions of this invention are suitable replacements for sulfurized sperm for use as additives in lubricating oils for metal working purposes. If desired, an improvement in low temperature solubility can be obtained through the incorporation of about 0.1–2 percent of an oil-soluble mono-alkyl phenols, such as nonylphenol in lubricating oil blends containing the sulfurized additives of this invention. In high performance industrial oils, for use as gear oils, guide and way oils, mist oils, rock drill oils and multipurpose oils, the properties of lubricating oil blends containing the sulfurized oil compositions of this invention can be further enhanced by the incorporation of small amounts of the well-known zinc dialkyl dithiophosphates lubricant additives without any noticeable antagonism in such blends.

It is to be understood that additive concentrates comprising the sulfurized product can be formulated with the additives referred to above as well as other additives, such as silicone defoamer agents and tackiness agents conventionally used in the lubricating amount. Comparative cutting oils using sulfurized sperm oil and the sulfurized products of this invention showed equivalent performance.

We claim:

1. A sulfurized fatty oil composition consisting essentially of a blend of (a) about 80 weight percent to about 95 weight percent prime burning lard oil and (b) about 5 weight percent to about 20 weight percent alkyl oleate sulfurized to contain about 8 weight percent to about 12 weight percent bound sulfur and not more than 0.3 weight percent free sulfur, said alkyl oleate being a mixture of alkyl esters of saturated and unsaturated fatty acids having 14 to 18 carbons containing at least 50 weight percent unsaturated fatty acids with not more than 10 weight percent of unsaturated fatty acids containing conjugated double bonds in the unsaturated fatty acid fraction and said alkyl group having 1 to 3 carbon atoms.

2. The composition of claim **1** wherein (b) is methyl oleate.

3. The composition of claim **2** wherein the amount of bound sulfur is about 9 weight percent to about 11 weight percent.

4. The composition of claim **2** wherein (a) is about 85 weight percent to about 93 weight percent, and (b) is about 7 weight percent to about 15 weight percent.

5. The composition of claim **2** wherein (a) is about 80 weight percent, (b) is about 20 weight percent, and the amount of bound sulfur is about 10 weight percent.

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