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EXTREME PRESSURE LUBRICANTS

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This invention relates to extreme pressure lubricants and more particularly to improved petroleum base cutting oils and gear lubricants containing stably dissolved sulfur.

Lubricating oils containing dissolved sulfur are well known and have been found useful in applications where extreme pressures are encountered, such as in the metal cutting arts and in gear assemblies. In the application of these compositions the dissolved sulfur presumably reacts at the hot spots encountered during the sliding process forming a metal sulfide film upon the fresh metal surfaces formed. This sulfide film is of lower shear strength than the original metal surfaces and consequently lowers the frictional forces involved as well as wear.

However, lubricating oils are not good solvents for sulfur and the amount which may be dissolved varies depending upon the particular lubricating oil used. For instance, only from about 0.3 to 0.7 percent sulfur can be dissolved in a mineral oil, the amount increasing with increasing aromaticity of the oil. Moreover, dissolved sulfur may be to a substantial degree precipitated from a mineral oil by a drop in temperature. This may seriously damage an extreme pressure lubricant, for once separated the sulfur does not readily redissolve, even upon warming to ambient temperature.

In order to increase the sulfur content over and above that of dissolved sulfur, many expedients have been tried. One method of increasing the sulfur content is to add the sulfur to a suitable base stock at a temperature sufficiently high to cause the sulfur to chemically unite with the base oil. This adversely affects the color and viscosity of the final product and the process is complicated in that hydrogen sulfide is evolved and an inert atmosphere is generally required to prevent excessive oxidation of the base stock.

There are many other expedients available to impart extreme pressure properties to lubricating oil stocks. One such expedient is that of adding a relatively pure sulfur containing compound to the base stock. Such compounds are quite expensive, however, and the sulfur is combined rather than in the free state and rather large amounts of the compounds are thus necessary to impart the desired E.P. properties.

It is an object of this invention to provide a method of preparing an improved extreme pressure lubricant comprising a mineral oil solution of high sulfur content which is stable at both high and low temperatures. It is a further object of this invention to provide a method of preparing an improved extreme pressure composition comprising a stable solution of sulfur in which the dissolved sulfur content is greater than the normal saturation solubility of sulfur in a lubricating oil and which composition has a viscosity and color substantially the same as the base lubricating oil. Still another object is to provide an improved extreme pressure lubricant having a high free sulfur content. Other objects will be apparent to those skilled in the art as the description of the invention proceeds.

We have found that when an oil soluble, organic, sulfur-containing material is added to a lubricating oil, there occurs a change in the ability of the oil to hold in solution added amounts of sulfur, such as flowers of sulfur. A greater amount of sulfur is held in solution by the lubricating oil solution containing a sulfur containing organic derivative than can be held in solution by the mineral oil alone, at corresponding temperatures, and this increased amount of dissolved sulfur is not precipitated even at temperatures as low as 32° F. Thus the foregoing objects can be accomplished by dissolving in a suitable lubricating oil base stock elemental sulfur and an oil soluble, organic, sulfur-containing material. The elemental sulfur is dissolved at a temperature lower than the temperature at which the sulfur will react, preferably lower than about 300° F., in the lubricating oil and the sulfur-containing material is dissolved at a temperature at which it is stable, preferably at a temperature lower than about 200° F. Thus, both the sulfur and sulfur-containing material may be added simultaneously or independently.

The term "oil soluble, organic, sulfur-containing material" as used herein and in the appended claims includes pure sulfur containing organic chemicals as well as complex sulfur-containing mixtures either naturally occurring or obtained by sulfurizing at elevated temperatures a reactive organic material such as an olefin, a mineral oil, or the like.

Examples of sulfur-containing materials which we have found effective are as follows:

Aliphatic sulfides, disulfides and polysulfides
Alicyclic sulfides, disulfides and polysulfides
Aromatic sulfides, disulfides and polysulfides
Mixed combinations of any of the foregoing
Mercaptans
Thiophenols and substituted thiophenols
Complex, naturally occurring sulfur-containing products, such as a reduced crude containing combined sulfur
Sulfurized fatty materials
Sulfurized olefins such as octene, hexadecene, vinyl toluene, or α-methyl styrene
Sulfurized petroleum stocks, such as SAE 10 mineral oil, extract from phenol extraction of mineral oil, a reduced crude or the like.

The foregoing examples are merely illustrative of the many sulfur-containing materials applicable to the invention and are not to be considered limitative since many other materials will be apparent to those skilled in the art. Moreover, while all of the foregoing are applicable to the invention they are not necessarily equally effective under all conditions, but vary in their effectiveness with different lubricating oils, conditions of use and the like.

The amount of sulfur-containing material incorporated in the extreme pressure lubricant in accordance with our invention may be varied substantially, although an optimum amount of additive is required for stabilization of a maximum amount of sulfur. This is illustrated in Table I for a pale paraffin oil of 80 S.U.S. viscosity at

Table I

Percent of Sulfur-Containing Material	Percent Stabilized Elemental Sulfur		
	Octyl Polysulfide	Sulfurized Extract	Sulfurized Reduced Crude
2	0.97	1.81	1.64
4	1.04	2.07	1.60
6	1.02	2.30	1.86
10	1.12	1.77	1.82
15	1.37	1.43	1.56

100° F., wherein percent stabilized elemental sulfur is shown as a function of concentration of three oil soluble, organic, sulfur-containing materials, i.e., octyl polysulfide, sulfurized phenol extract of lube oil and sulfurized reduced crude. The percent stabilized elemental sulfur was determined by analyzing the lubricant for free sulfur after cooling the stabilized mixture to 32° F.

The elemental sulfur content with octyl polysulfide gradually increases with increasing concentration of the additive, while for the other two additives there is a maximum at about 6% concentration. In general the amounts of additive may vary from 1 to 15% to obtain as high an amount of stably dissolved sulfur as in usually required for an extreme pressure lubricant composition. Particularly good results are obtained with concentrations of about 6 percent of additive.

We have found that our invention is applicable for increasing the amount of sulfur which can be dissolved in an extreme pressure lubricant regardless of the base oil which is used. Thus, for a cutting oil, the viscosity of the base oil may range from 50 to about 300 S.U.S. at 100° F., while for gear oils the viscosity may range from 500 to 1500 S.U.S. at 100° F. The base oil does not appreciably affect the efficacy of the additive. Thus if we use 10% of a sulfurized reduced crude as the additive, we find that the variation in elemental sulfur content is only as follows:

Table II

Base Oil	Elemental Sulfur, Percent
Pale paraffin oil 80 S.U.S. at 100° F.	1.97
Wax free coastal oil 80 S.U.S. at 100° F.	1.70
Midcontinent 20 SAE	1.53
Solvent extracted Midcontinent 20 SAE	1.12

We have observed that for each base oil, the optimum quantity of additive required to stabilize the maximum quantity of sulfur is not always the same but must be determined in accordance with methods well known to those skilled in the art.

The term "lubricating oil" as used herein and in the appended claims include not only petroleum lubricating oils as illustrated hereinbefore, but also includes lubricating oils of animal, vegetable or synthetic origin. Thus, for example, lubricating oils such as those obtained by the polymerization of olefins, as well as synthetic lubricating oils of the alkylene oxide types, and the polycarboxylic acid ester type, such as the oil-soluble esters of adipic acid, sebacic acid, azelaic acid, etc., may be employed as base stocks for our improved extreme pressure lubricant.

In preparing an extreme pressure lubricant in accordance with our invention, we prefer to mix sulfur, either as flowers or as a liquid, into the oil heated to a temperature in the range of from about 200 to 300° F. A temperature of about 270–300° F. effects a more rapid solution of the sulfur. Higher temperatures result in oxidation and darkening of the product, and hydrogen sulfide evolution. The solution of sulfur in oil is then preferably cooled to about 200° F. and the sulfur-containing, stabilizing agent is added.

As an example of our invention, we have compounded a cutting oil from 1 part of liquid sulfur in 96.5 parts of pale paraffin oil (80 S.U.S. viscosity at 100° F.) at 250° F. Upon cooling to 170° F., 2.5 parts by weight of octyl polysulfide (40% sulfur) was added to make a stable oil containing 1% elemental sulfur. On cooling this composition to 32° F., the mineral oil retained all the sulfur in a stably dissolved state. When, however, 1 percent of liquid sulfur was dissolved in the same base oil at 250° F., but without any additive, a portion of this dissolved sulfur was precipitated when the solution was cooled to 32° F. This cold solution contained but 0.6 percent by weight of sulfur. The octyl polysulfide therefore had increased the sulfur content 0.4 percent by weight over the amount of sulfur stably dissolved at 32° F. in the mineral oil alone.

The relative efficacy of various sulfur-containing additives may best be illustrated by referring to Table III in which 10 percent by weight of the indicated oil soluble, organic, sulfur-containing materials are used in a mineral oil to stabilize the indicated amount of elemental sulfur.

Table III

Sulfur-Containing Additive	Elemental Sulfur, Percent
None	0.60
2-mercapto menthene	0.83
Methyl-4-thiahexadecanoate-1	0.70
N-dodecyl mercaptan	0.95
Dibenzyl disulfide	1.35
α-toluenethiol	1.95
Isoamyl disulfide	0.83
Isoamyl sulfide	0.77
Octyl polysulfide	1.12
Reduced crude (2.7% naturally occurring S)	1.95
Sulfurized oleic acid	1.00
Sulfurized lard oil	1.32
Sulfurized hexadecene	0.94
Sulfurized α-methyl styrene	1.19
Sulfurized vinyl toluene	1.46
Sulfurized pale paraffin oil	1.97
Sulfurized phenol extract of lube oil	1.77
Sulfurized reduced crude	1.82

To illustrate the effectiveness as extreme pressure lubricants of the compositions prepared in accordance with our invention, the following lubricants were used in a lathe performance test wherein tool wear rate was measured using a radioactive tracer technique.

Lubricant A:
Pale paraffin oil having a viscosity of 80 S.U.S. at 100° F.

Lubricant B:
Lubricant A having dissolved therein 0.6% elemental sulfur (maximum stable amount)

Lubricant C:
Lubricant A heated to 250° F., elemental sulfur dissolved therein, cooled to 170° F. and octyl polysulfide added to give the following composition:
Pale paraffin oil, 96.5 parts
Free sulfur, 1.0 part
Octyl polysulfide, 2.5 parts

The tool wear rate test was run on 1015 S.A.E. steel tubing using a high-speed steel tool with a radioactive level of 7 millicuries at a feed of 0.011 inch per revolution and a cut depth of 0.250 inch at a cutting speed at 120 feet per minute. The results of the tests are outlined in Table IV.

Table IV

Lubricant No.	Description	Composition, percent	Wear Rate, Counts/Sec./gr. of chips
A	Pale paraffin oil, 80 S.U.S.	100	0.450
B	Pale paraffin oil, 80 S.U.S.	99.4	0.160
	Sulfur	0.6	
C	Pale paraffin oil, 80 S.U.S.	96.5	0.084
	Sulfur	1.0	
	Octyl polysulfide	2.5	

Thus, the lathe performance test demonstrates that an extreme pressure lubricant prepared in accordance with our process is twice as effective as a lubricating oil containing an equilibrium amount of dissolved elemental sulfur and five times as effective as a lubricating oil without sulfur. Moreover, we have observed that if only octyl polysulfide is present in the lubricating oil, in the absence of elemental sulfur, almost twice as much is needed to obtain the same wear rate as with Lubricant C. Furthermore, the surface finish on the work piece using Lubricant C is more than three times as smooth as when using only octyl polysulfide in oil.

Having described our invention with reference to preferred specific embodiments, it is to be understood that these embodiments are merely by way of illustration. Modifications and variations will be apparent from our description to those skilled in the art.

We claim:

1. A method of increasing the amount of soluble sulfur in a petroleum lubricating oil having a viscosity of from about 50 SUS to about 1500 SUS at 100° F. to improve the extreme pressure properties thereof, which method comprises dissolving in said oil an amount of elemental sulfur greater than the normal saturation solubility amount in said oil by heating the said oil to a temperature within the range of from about 200° F. to about 300° F. and lower than the temperature at which said sulfur will react with said oil, said amount of said sulfur being essentially soluble within said temperature range, cooling the oil and sulfur mixture to a temperature lower than about 200° F., and dissolving in the cooled oil and sulfur mixture an oil soluble organic sulfur-containing material selected from the class consisting of aliphatic sulfides, disulfides and polysulfides, alicyclic sulfides, disulfides and polysulfides, aromatic sulfides, disulfides and polysulfides, mercaptans, thiophenols and substituted thiophenols, reduced crude containing combined sulfur, sulfurized fatty materials, sulfurized olefins, and sulfurized petroleum stocks, at a temperature at which said sulfur-containing material is stable and in sufficient amount to maintain the added sulfur in solution.

2. The method of claim 1, wherein from about 1% to about 15% of said oil soluble, organic, sulfur-containing material is dissolved in said lubricating oil.

3. The method of preparing an extreme pressure lubricant comprising the steps of heating a petroleum lubricating oil having a viscosity of from about 50 SUS to about 1500 SUS at 100° F. to about 300° F., dissolving a greater than normal saturation solubility amount of elemental sulfur in said lubricating oil, cooling the lubricating oil-sulfur mixture to a temperature lower than about 200° F. and adding to said mixture from about 1% to about 15% of an oil soluble, organic, sulfur-containing material selected from the class consisting of aliphatic sulfides, disulfides and polysulfides, alicyclic sulfides, disulfides and polysulfides, aromatic sulfides, disulfides and polysulfides, mercaptans, thiophenols and substituted thiophenols, reduced crude containing combined sulfur, sulfurized fatty materials, sulfurized olefins, and sulfurized petroleum stocks.

4. The method of claim 3 wherein said lubricating oil is a petroleum derived pale paraffin oil.

5. The method of claim 3 wherein about 1% by weight of said elemental sulfur is dissolved in said lubricating oil.

6. The method of claim 3 wherein said oil soluble, organic, sulfur-containing material is octyl polysulfide and about 2½% thereof is dissolved in said lubricating oil-sulfur mixture.

7. The method of preparing an extreme pressure lubricant comprising the steps of heating a pale paraffin oil of about 80 SUS to a temperature of about 250° F., dissolving in said lubricating oil about 1% of elemental sulfur, cooling said oil-sulfur mixture to about 170° F. and dissolving therein about 2½% of octyl polysulfide.

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