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LUBRICANTS

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This invention relates to the field of lubricants and to methods of preparing same; more particularly it relates to novel sulfurized oils and novel methods of effecting the sulfurization of oils.

When oils such as mineral oils or fatty oils are used as lubricants for reducing the friction of, or preventing seizure of, moving metal parts, many of the conditions of use are so severe that the straight mineral oils will not satisfactorily withstand the high pressures and frequent high temperatures which develop, and therefore permit excessive wear or scoring or seizure of the metal parts. To reduce or prevent these dangers, the oil, such as a light mineral lubricating oil, has sometimes been sulfurized by cooking sulfur into it at an elevated temperature, generally in the range of about 325° to 375° F.; however, this procedure has a disadvantage that an oil having a color as light as 10 or 10½ Robinson will darken substantially to a color of 1 or 2 Robinson during the sulfurization treatment. This darkening is probably due to an oxidation or polymerization of unsaturated or other constituents in the oil by the sulfur. One reason why this darkening is harmful is that when the oil is used as a cutting oil by a machinist, the latter is unable to watch carefully the cutting action of the tool due to the dark color of the cutting oil. Another reason why the darkening is objectionable is that it is an indication that high molecular weight constituents have been formed which will more readily cause gumming and sticking of the lubricant in use, especially when subjected to high temperatures such as often encountered in the high speed machining of metal with cutting tools.

The primary object of the present invention is to accomplish a suitable sulfurization of the oil without the undesirable darkening. This and other objects and advantages of the invention will appear more fully from the following description.

It has now been found that if a small amount of sulfurization promoter, such as sulfuric acid, is added to the mineral oil before the treatment with sulfur, the sulfurization can be carried out at a substantially lower temperature than heretofore, i. e., at temperatures substantially below 250° F. and preferably below 220° F., and that during the sulfurization the oil will not darken appreciably.

The invention may be carried out in a number of different ways but one of the simplest is to start with a relatively crude mineral lubricating oil base stock, treat it with sulfuric acid, using for instance about 10 lbs. of 98% acid per barrel of oil at a temperature of about 80° to 100° F., adding a small percentage of water, allowing the mixture to settle so that a substantially tar-free acidulated oil may be decanted off from the resultant tarry precipitate, and then finely divided sulfur, either in the form of flowers of sulfur or a finely crushed sulfur flour, mostly finer than 100 mesh and preferably mostly finer than 200 mesh, is mixed with the acidulated oil and agitated at a temperature of about 90° F. for a period of about 2 hours, after which any free acid is neutralized with caustic soda and heated to a suitable sulfurizing temperature such as about 140° F. to 200° F. preferably about 180° F. and the resultant neutralized sulfurized oil is water washed and is ready for use either as such or after addition of other optional addition agents, such as for instance a small amount of fatty material, such as oleic acid with or without further heating to insure thorough incorporation of such fatty material. If desired, the acidulated oil and sulfur mixture may be heated to sulfurizing temperature, e. g. 140° to 180° or 220° F., preferably 160° to 180° F., before neutralizing with caustic soda. The neutralized oil may be cooled to 140° F. or so, if desired, before or during neutralization. Also, if the mixture is heated before neutralization, the heating time may be reduced to an hour or so or even as little as ½ hour.

In such a process the oil to be used, especially if intended for cutting oil purposes, should be a mineral oil having a viscosity of about 100 to 600 seconds Saybolt at 100° F. and is preferably obtained from a naphthenic base crude, because this type of oil absorbs more sulfur, although, if desired, a paraffinic base oil may be used, and even mixtures of mineral oils with small amounts of fatty oils may be used. The amount of sulfur to be added depends upon the type of oil being sulfurized, being about in the range of 0.5% to 2% or 3% and even higher amounts such as up to 5% in the case of some oils.

The sulfuric acid to be used should have a concentration approximately between the limits of 50% and 100% strength and of course the amount to be used will vary inversely according to the concentration and inversely according to the temperature used, but normally the amount should correspond to about .01% to 5.0% by weight of acid having a concentration of about 95% to 98%, and preferably the amount of such acid should be between .05% and 3.0%.

Although it is more convenient to apply the invention as just described, it is also possible to add a small amount of sulfuric acid to an oil which has already been previously acid treated, neutralized, and washed. As a further alternative, the oil to be used might be any other suitable light colored lubricating oil base stock, which had been refined by any other suitable method such as by clay treating, solvent extraction, propane-deasphaltizing treatment with active halides, such as aluminum chloride, etc. In any case it is desirable to use a mineral oil base stock

having a Robinson color not substantially lower than 8 and preferably not lower than 10.

Although sulfuric acid is the only sulfurization promoter specifically mentioned thus far, other compounds containing a polybasic acid radical may be used. Thus phosphoric acid and a water-soluble sodium sulfonate, as well as an oil-soluble sodium sulfonate, may be used.

Although the theory as to the mechanism of the operation of the invention is not well understood, it is believed that the sulfonic acids produced by the treatment of the mineral oil with sulfuric acid may be responsible either directly as such or in the form of the corresponding sodium sulfonate salts for the catalyzing effect in permitting the sulfurization of the oil to take place at a lower temperature than is possible in the absence of such compounds resulting from the treatment of oil with sulfuric acid.

The products of this invention have the outstanding characteristic that they are lighter in color than prior art sulfurized products having a similar content of active sulfur. The term "active sulfur" is intended to mean the amount of sulfur removable by powdered copper at 300° F. for one hour. This test is described in a paper presented before the American Society of Metals, dated October 20–24, 1941 (Philadelphia), entitled "Study of cutting oils with and without added sulfur," by O. W. Boston and J. C. Zimmer. The sulfurized products of this invention will generally have a Robinson color of not lower than 2 units (oftentimes only 1 unit) below that of the oil before sulfurization. The products of this invention also have an additional advantage of better storage stability than prior art sulfurized products, because according to the present invention sulfurization at temperatures below 250° F. and especially below 220° F. preclude the formation of high molecular weight polymerized and/or oxidized products which tend to precipitate out of solution during storage, especially during alternate changes of temperature. This invention is especially applicable to sulfurized mineral oils containing at least 0.8% of active sulfur and preferably 0.9% or 1.0% or more. Neutralizing before heating produces lightest colored product.

For the sake of illustration but without intending to limit the invention unnecessarily to the specific materials, conditions or procedure used, the following experimental data are given.

Example 1

A lubricating oil distillate derived from a West Texas crude was acid treated with sulfuric acid (using about 10 lbs. of 98% acid per barrel of oil) by agitating with air. A small amount of water was used to coagulate the acid tar. The acidulated oil was allowed to settle for 4 hours, and then drawn off from the tar and transferred to a wash agitator. Powdered sulfur (using about 1.2% by weight on the oil) was added to the oil and agitated for one hour at a temperature of 80° to 100° F. It was then neutralized with sodium hydroxide and heated to 180° F. while agitating. About ⅓ part by volume of water was added to wash out any free sodium hydroxide, sodium sulfates and water-soluble sodium sulfonates. Agitation was stopped and the oil allowed to settle, the aqueous layer being drawn off. The washing was repeated at 180° F. and after drawing off the wash water, the oil was heated to 195° to 205° F. while agitating. 0.5% of Elaine oil (commercial oleic acid) was added, and agitation continued at 195° to 205° F. for two hours.

The oil, before and after treatment, had the following inspection:

	Before treatment	After treatment
Saybolt viscosity at 100° F ..... seconds	162	160
Color (Robinson)	2½	9¼
Gravity (A. P. I.) ..... degrees	23.9	
Flash ..... °F	345	
Sulfur (bomb) ..... per cent	1.86	2.53
Active sulfur ..... do	0.00	1.05
Odor		(1)
Sulfur stability [2]		(3)

[1] Satisfactory.
[2] A sample of the sulfurized oil is stored at a temperature of 0° F. for 7–14 days, to note if any sulfur settles out. A pass indicates no more than a trace of sulfur separated in this period.
[3] Passes.

This test shows that the sulfurization of a lubricating oil distillate can be very satisfactorily carried out at the relatively low temperature of 185° F. in the presence of the acid compounds dispersed throughout the oil as a result of the acid treating. It is also notable that although the oil contains as high as 1.05% active sulfur, it has both a satisfactory odor and passes the sulfur stability test.

Example 2

As another example of the operation of the invention, four tests (A, B, C, and D) were made in order to study the effect of only a catalytically small amount (0.1%) of sulfuric acid. In test A substantially the same procedure was used as in the above Example 1, but 0.1% by weight of sulfuric acid was used. The neutralization (after addition of the sulfur) was effected by a 10% by weight addition of 5% caustic soda solution, the agitation at 180° F. by air being continued for one hour. Test B was similar to A, except that no sulfuric acid was used. In test C, sulfuric acid (same amount 0.1%) was used (as in test A) but no caustic soda. In test D no acid was used but a small amount of sodium hydrosulfide was added so that together with a small amount of sodium hydroxide and the sulfur, some sodium disulfide (Na_2S_2) would be formed. The mineral oil used in these tests was a naphthenic base oil obtained from a West Texas crude, and had the following inspection:

Gravity (A. P. I.) ..... degrees	24.2
Flash ..... °F	355
Fire ..... °F	410
Saybolt viscosity at 100° F	160
Pour point ..... °F	+5
Color (Robinson)	10½
Sulfur (natural) ..... per cent	1.53

The percent of total sulfur and active sulfur present in the finished oil in each of these tests are shown in the following table:

Test No.	Treating agent	Percent total sulfur	Percent active sulfur
A	Acid+alkali	2.70	1.07
B	Alkali only	2.52	0.85
C	Acid only	2.61	0.92
D	Sodium disulfide	1.71	0.08

Without either acid or alkali, the amount of active sulfur probably would be less than 0.7%. Thus from the above tests it is clear that since the percent of active sulfur is substantially and unexpectedly higher in A than in B and higher in

C than in D, and higher in C than without either acid or alkali, the addition of sulfuric acid to the oil prior to sulfurization must be responsible for the improved sulfurization at the relatively low temperature used, namely, 180° F.

Example 3

A West Texas lubricating oil distillate was treated with 5 lbs. of 98% acid per barrel and then transferred to a wash agitator. 50% by volume of straw oil (having a viscosity of about 110 seconds Saybolt at 100° F. or about 40 seconds Saybolt at 210° F.) was blended with the acidulated oil. 1.3% sulfur was added and agitated for one hour at 85° F., after which the oil was neutralized with sodium hydroxide and the temperature raised to 180° F. and agitated for five hours. The oil was then washed with water, settled overnight, the water wash drawn off, and the washing repeated, settled three hours, and water drawn off. 0.5% Elaine oil (commercial oleic acid) was added and agitated for two hours at 195° to 205° F.

Example 4

Example 3 was repeated, except that in place of 50% of straw oil, 52% of a lubricating oil base stock having a viscosity of about 70 seconds Saybolt at 210° F. and derived from a naphthenic base crude was used.

Tests of the finished cutting oils made as above described in Examples 3 and 4 are shown in the following table:

	Example 3	Example 4
Gravity ---- degrees	26.5	22.1
Flash ---- °F.	355	380
Viscosity at 100° F ----	101	357
Pour ---- °F.	30	30
Color (N. P. A.) ----	4¼	4½
Sulfur (total) ---- per cent	2.060	2.144
Sulfur (active) ---- do	1.088	1.294
Sulfur stability test ----	(1)	(1)

[1] Passes.

Example 5

A West Texas lubricating oil distillate was treated with 5 lbs. of 98% acid per barrel, using a small percentage of water to coagulate acid tar, settled for three hours and transferred to the wash agitator. 50% by volume of a low viscosity naphthenic base oil (having a viscosity of about 75–85 seconds Saybolt at 100° F.) was added to the acidulated oil, and after addition of 1.2% of sulfur, the oil was agitated for two hours at 85° F. It was then neutralized with sodium hydroxide and the temperature raised to 160° to 180° F. and the agitation continued for eight hours. It was washed twice with water and the water was drawn off. 0.5% of Elaine oil was added and agitated for two hours at 195° to 205° F. The resultant finished cutting oil showed the following inspection:

Gravity ---- degrees	24.1
Flash ---- °F.	340
Viscosity at 100° F ----	109
Pour ---- °F.	5
Color (N. P. A.) ----	4
Sulfur stabilitiy test ----	[1] Passes
Sulfur (total) ---- percent	2.015
Sulfur (active) ---- do	1.141

[1] Very slight precipitate.

Example 6

0.25% of oil-soluble sodium sulfonate (obtained from the treatment of petroleum lubricating oil with fuming sulfuric acid) was added to a West Texas lubricating oil distillate which had previously been treated with 5 lbs. of 98% sulfuric acid per barrel and had been neutralized and water washed. 1.2% of sulfur was added and agitated at 160° to 180° F. for fourteen hours. After water-washing, settling and drawing off the wash-water (three washings were required to remove the sulfonates), 0.5% of Elaine oil was added, and agitation continued for two hours at 195° to 205° F. The finished cutting oil had the following inspection:

Gravity ---- degrees	23.3
Flash ---- °F.	350
Viscosity at 100° F ----	149
Pour ---- °F.	30
Color (N. P. A.) ----	3
Sulfur stability test ----	[1] Passes
Sulfur (total) ---- percent	2.630
Sulfur (active) ---- do	1.247

[1] Very slight precipitate.

Example 7

0.25% of phosphoric acid was added (in the form of a solution in 100 cc. of water) to one gallon of a lubricating oil distillate which had been acid treated, neutralized, and water washed. After addition of 1.2% of sulfur, the temperature was raised to 180–190° F., and the oil was agitated with compressed air for five hours. The oil was then washed with water, settled, and the water drawn off. (It was necessary to wash this batch four times to remove phosphates.) 0.5% of Elaine oil was added and agitated for two hours at 195° to 205° F. The finished oil showed the following inspection:

Gravity ---- degrees	23.4
Flash ---- °F.	350
Viscosity at 100° F ----	148
Pour ---- °F.	30
Color (N. P. A.) ----	3¼
Sulfur (total) ---- percent	2.750
Sulfur (active) ---- do	1.108

This cutting oil carried seven weights in the Almen Shock Load Test with a heavily scratched pin.

Example 8

A West Texas petroleum lubricating oil distillate was treated with 8 lbs. of 98% sulfuric acid per barrel at about 80° to 100° F., adding a small percentage of water to coagulate tar, and the sludge was withdrawn. 1.2% of sulfur was added to the residual acid oil and agitated one hour at about 85° F. The oil was then neutralized with sodium hydroxide (using an aqueous solution of about 3–20% concentration) and the oil was then heated to a temperature of about 160° to 180° F. with agitation for two hours. After drawing off the caustic solution, the oil was water washed several times. A sample of the resultant cutting oil had the following inspection:

Gravity ---- degrees	24.1
Flash ---- °F.	345
Viscosity at 100° F ----	150
Pour ---- °F.	45
Color (R.) ----	9¼
Color (N. P. A.) ----	3½
Sulfur (total) ---- percent	2.395
Sulfur (active) ---- do	1.011

This product showed satisfactory sulfur stability both alone as well as with an addition of 0.5% oleic acid (which, if used, should be blended in by agitation for about two hours at 195° to 205° F.).

Example 9

0.1% of water-soluble sulfonate (obtained from an acid sludge resulting from treating petroleum lubricating oil with fuming sulfuric acid) was dissolved in water and thoroughly agitated with a West Texas petroleum lubricating oil which had already been acid treated, neutralized and water washed. The resulting mixture was heated to 230° F. to remove water, then cooled to 195° F., and 1.2% of sulfur were added and agitated for two hours at 195° to 205° F. 0.5% of Elaine oil was added and agitated for an additional two hours at 195° to 205° F.

Example 10

Example 9 was repeated, except that instead of the water-soluble sulfonate, 0.25% of oil-soluble sulfonate was used, and since no water was used with this sulfonate, it was not necessary to heat the oil to drive off water. The lubricating oil used for Examples 9 and 10 had the following inspection:

Gravity	degrees	24.4
Flash	°F	345
Viscosity at 100° F		150
Pour	°F	35
Neutralization No.		.187
Color (Robinson)		10¼+

The cutting oils of Examples 9 and 10, after sulfur treatment, showed the following inspection in regard to sulfur:

		Example 9	Example 10
Total sulfur	percent	2.560	2.572
Active sulfur	do	1.049	1.073
Sulfur stability		(1)	(1)

1 Passes.

It is not intended that this invention be limited to any of the particular examples which have been given merely for the sake of illustration nor unnecessarily by any theory suggested as to the mechanism of the operation of the invention, but only by the appended claims in which it is intended to claim all novelty inherent in the invention as well as any other modifications coming within the scope and spirit of the invention.

I claim:

1. The process of sulfurizing a mineral lubricating oil base stock which comprises adding thereto a small amount of sulfuric acid, adding powdered sulfur to the resultant mixture and heating the mixture to a temperature not higher than 250° F.

2. The process according to claim 1 in which the oil to be sulfurized is a refined mineral oil having a Robinson color at least as high as 8.

3. The process of preparing sulfurized mineral oils which comprises acid treating a mineral lubricating oil base stock, removing tarry constituents, adding sulfur to the acidulated oil, neutralizing, and heating the resultant mixture to a temperature between the approximate limits of 180° to 200° F., and washing with water to remove any free acid.

4. The process of preparing sulfurized mineral oils which comprises treating a mineral oil having a viscosity between the approximate limits of 100 to 600 seconds Saybolt at 100° F. with sulfuric acid having a concentration between about 50% and 100%, using a sufficient amount of acid to remove tar-forming constituents from the oil and to produce an oil having a Robinson color at least as high as 8, removing tar formed by such acid treatment, mixing about 1.2% of sulfur with the acidulated oil, neutralizing with caustic soda, heating the resultant mixture to a temperature of about 180° to 220° F., washing the neutralized oil with water, settling and removing the aqueous constituents to leave a refined sulfurized mineral oil containing at least 0.8% of active sulfur and having a Robinson color at least as high as 8.

5. The process of preparing sulfurized mineral oils which comprises treating a mineral oil having a viscosity between the approximate limits of 100 to 600 seconds Saybolt at 100° F. with sulfuric acid having a concentration between about 50% and 100%, using a sufficient amount of acid to remove tar-forming constituents from the oil and to produce an oil having a Robinson color at least as high as 8, removing tar formed by such acid treatment, mixing about 1.2% of sulfur with the acidulated oil, heating the resultant mixture to a sulfurizing temperature not above 200° F., neutralizing with caustic soda, washing the neutralized oil with water, settling and removing the aqueous constituents to leave a refined sulfurized mineral oil containing at least 0.8% of active sulfur and having a Robinson color at least as high as 8.

6. A sulfurized mineral lubricating oil containing at least 0.8% of active sulfur, and obtained by sulfurization at a temperature below 250° F. in the presence of a small amount of a sulfurization promoter selected from the group consisting of sulfuric acid, phosphoric acid and sulfonic compounds obtainable by sulfonating lubricating oil stocks.

7. The process which comprises sulfurizing a mineral lubricating oil base stock in the presence of a small amount of a sulfurization promoter selected from the group consisting of sulfuric acid, phosphoric acid and sulfonic compounds obtainable by sulfonating lubricating oil stocks, at a temperature not higher than 250° F. to form a product having cutting oil characteristics.

8. The process according to claim 7 in which the sulfurization promoter is a sodium sulfonate obtained by sulfonating a lubricating oil stock.

9. A sulfurized mineral lubricating oil containing sulfur in the ratio of up to 5% of total sulfur to at least 0.8% of active sulfur and obtained by sulfurization at a temperature not higher than 250° F. in the presence of a small amount of a sulfurization promoter selected from the group consisting of sulfuric acid, phosphoric acid and sulfonic compounds obtainable by sulfonating lubricating oil stocks.

10. A cutting oil comprising a sulfurized mineral lubricating oil containing sulfur in the ratio proportionate to the ratio of up to 5% of total sulfur to at least 0.8% of active sulfur, having a Robinson color at least as high as 8, and having good storage stability, said sulfurized mineral lubricating oil having been obtained by sulfurization at a temperature not higher than 250° F. in the presence of a small amount of a sulfurization promoter selected from the group consisting of sulfuric acid, phosphoric acid and sulfonic compounds obtainable by sulfonating lubricating oil stocks.

11. A cutting oil comprising a sulfurized mineral lubricating oil containing 2–3% of total sul-

fur and at least 0.8% of active sulfur, having a Robinson color at least as high as 8 and having good storage stability, said sulfurized mineral lubricating oil having been obtained by sulfurization at a temperature not higher than 250° F. in the presence of a small amount of a sulfurization promoter selected from the group consisting of sulfuric acid, phosphoric acid and sulfonic compounds obtainable by sulfonating lubricating oil stocks.

12. The process of sulfurizing mineral lubricating oil stocks which comprises adding to said stocks a small amount of a sulfurization promoter selected from the group consisting of sulfuric acid, phosphoric acid and sulfonic compounds obtainable by sulfonating lubricating oil stocks, adding finely divided sulfur to the mixture and heating the mixture at a temperature not higher than 250° F.

13. A cutting oil comprising a sulfurized mineral lubricating oil obtained by sulfurization of a mineral lubricating oil stock at a temperature not higher than 250° F. in the presence of a small amount of a sulfurization promoter selected from the group consisting of sulfuric acid, phosphoric acid and sulfonic compounds obtainable by sulfonating lubricating oil stocks.

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