Sulfurization and P_2S_5 treatment of a fatty oil

EXAMINER

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PREPARATION OF HIGH-VISCOSITY EXTREME PRESSURE BASE BY AIR-BLOWING

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This invention relates to lubricant additives and to method of preparing same.

In Whittier Patent No. 2,211,306 there is disclosed and claimed a method for making a lubricating stock by sulfurizing and phosphorizing fatty bodies. In accordance with the method there outlined, it is customary to react the materials in open kettles with constant agitation. We have found, however, that when using fatty oils or esters of high-boiling fatty acids which contain a relatively high content of free fatty acid, it is not possible to prepare a sulfurized and phosphorized stock of high viscosity in the manner hereinbefore disclosed.

Sulfurized and phosphorized fatty oils and esters are particularly useful as E. P. additives in connection with Gulf Coast or naphthene base oils, since the additive is completely soluble in oils of this type, whereas it tends to separate from Pennsylvania base oils. However, Gulf Coast oils have notoriously low viscosity indexes and as a result exhibit low viscosity at elevated temperatures. Lubricating oil made by blending Gulf Coast mineral lubricating oil with sulfurized and phosphorized fatty oil, made in accordance with Whittier Patent No. 2,211,306, although eminently satisfactory for ordinary use in motor vehicles, will not in general meet the 85 minimum V. I. federal government specification for a universal gear lube (specification 2-105 B).

We have discovered that lubricant additives of high viscosity, which can be blended with Gulf Coast oils to meet government V. I. specifications, can be made from fatty oils and from esters of high-boiling fatty acids and polyhydric alcohols, in general, containing a relatively high, free acid content by conducting the sulfurization operations in the presence of finely dispersed air brought into intimate contact with the materials undergoing reaction. Viscosity of the product can be further increased by also conducting the phosphorization step in the presence of finely dispersed air brought into intimate contact with the materials undergoing reaction.

Our invention is directed to sulfurization and phosphorization of those fatty oils and esters of high-boiling, fatty acids and polyhydric alcohols in general which contain relatively high amounts of free fatty acids, as for example, oils containing 5% or more of free fatty acids. The invention is applicable to natural animal, vegetable and fish oils and to synthetic esters of high-boiling fatty acids and polyhydric alcohols, which are contaminated with free fatty acids. Oils or esters useful in preparing additives in accordance with our invention are those having a fatty acid radical containing a single double bond and from 10 to 24 carbon atoms in the radical in combination with a polyhydric alcohol such as glycol or glycerin. Mixed esters in which saturated as well as unsaturated fatty acids are present in free or combined form, as for example, a mixture of olein and stearin, are suitable provided the content of highly unsaturated esters, i. e. esters containing more than one double bond, is sufficiently low so that the esters and free fatty acids do not exhibit drying properties. Examples of oils which are suitable are lard, tallow and olive oils. Examples of esters that are suitable are glycol oleate and glycerol oleate.

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In preparing lubricant additives in accordance with our invention, the fatty oil or ester contaminated with free fatty acid is cooked with elementary sulfur in an amount of approximately 5-9% by weight of the oil or ester at temperatures of approximately 300 to 350° F. for a period of time sufficient to obtain a good copper strip corrosion test as disclosed in the aforesaid Whittier Patent No. 2,211,306. Reaction is carried out with constant stirring or agitation and in general it has been found that a reaction period of about seven and one-half hours at 330 to 340° F. will give a satisfactory copper strip corrosion test. The copper strip corrosion test indicates whether or not the sulfur has all been chemically combined with the fatty oil or ester. In preparing our product, it is important that substantially no sulfur remain dissolved in the reaction mixture in the uncombined state. It will be understood that the period of reaction may be more or less than seven and one-half hours depending upon the attainment of a good copper strip corrosion test.

In carrying out the process, we prefer to mix with the fatty oil or ester a small amount of mineral oil of the type with which the finished additive is to be blended, in order to reduce the viscosity of the oil or ester and facilitate handling thereof. For this purpose, we have found that approximately 5 to 10 parts by weight of mineral oil per 100 parts of fatty oil or ester is sufficient for this purpose. The fatty oil or ester mixed with the small amount of mineral oil is heated slowly to a temperature above the melting point of sulfur, but below 300° F. and finely-divided flowers of sulfur are slowly added to the heated oil while being agitated. After the sulfur is all added, the temperature of the mixture is then raised to the desired reaction temperature, preferably 330–340° F., and maintained at this temperature with constant agitation and with intimate contact of air. A suitable method of introducing finely-dispersed air into the mixture undergoing reaction is to attach a porous stone, such as corundum, or fritted glass, to the end of a pipe through which air is forced so that the air leaving the end of the pipe is forced through the interstices in the stone or fritted glass, thereby breaking the air into minute particles in which form it bubbles upwardly through the mixture undergoing reaction. The bubbling of air through the reaction mixture may be continued during the entire cooking period or for only a portion thereof, depending upon the viscosity of the product desired and the rate at which air is forced through the mixture undergoing reaction. By trial, the proper rate for feeding air to a mixture can be determined so that air can be introduced continuously during the entire reaction period and the desired viscosity obtained.

When the viscosity of the sulfurized oil and the copper strip corrosion test are satisfactory, the reaction is discontinued and the mixture allowed to cool to a temperature of approximately 200° F. or lower. Phosphorus in the form of phosphorus sesquisulfide is then added in an amount equivalent to approximately 0.1 to 0.6% by weight of phosphorus based on the sulfurized fatty oil or ester. The mixture is then heated to a reaction temperature of approximately 200–230° F. with constant agitation until the product when blended with mineral oil to make a finished lubricant gives a satisfactory Timken test. In general, the phosphorization period is approximately five hours. The length of the phosphorization cooking period can be determined by making periodic Timken tests and determnng when the Timken test no longer improves. When the Timken test has reached its maximum value, there is no point in cooking for a longer period of time.

Air blowing of the mixture during the phosphorization period may or may not be practiced, depending upon the viscosity of the product prior to phosphorization. During phosphorization some increase in viscosity takes place, but if the viscosity is not in the vicinity of the finally desired viscosity, air-blowing or intimate contact with air, in the same manner as conducted during the sulfurization step, may be continued during phosphorization until the desired viscosity is obtained.

The following is an example of the method in preparing a product in accordance with our invention:

To 87.6 parts by weight of lard oil (50% prime lard oil and 50% No. 1 lard oil) was added 5 parts by weight of Gulf Coast lubricating oil of 200 to 210 Saybolt Universal viscosity at 100° F. and the entire mixture was violently agitated. The mixture was then slowly heated to a temperature of 285° F. while being agitated, and then 7.4 parts by weight of finely divided flowers of sulfur were slowly added. The addition of the flowers of sulfur took place over a period of one-half hour and the temperature of the mixture was maintained at approximately 285° F. to 295° F.

After the addition of the flowers of sulfur, the temperature of the mixture was raised to 330° F. Then a porous stone fixed at the end of a tube was immersed deeply into the mixture and measured amounts of air were introduced through the tube and porous stone with a resulting fine and intimate dispersion of air into the base during cooking. The agitation and air-blowing was continued for a period of at least 7½ hours while the temperature was maintained at from 330° F. to 340° F. Corrosion tests of the mixture were made from time to time by immersing a polished copper strip therein for one minute. At the end of sulfurization the strip no longer showed a black coating and the cooking and air-blowing of the mixture was discontinued. The sulfurization period gave a "peacock" corrosion strip which was satisfactory. At this point the mixture was cooled to room temperature.

The sulfurized base was then phosphorized by heating the mixture to approximately 185° F. to 195° F. and adding 0.4% finely divided phosphorus sesqui-sulfide. The mixture was agitated and cooked for 5 hours at 220° F. to 230° F. Air-blowing of the mixture was continued during the phosphorization period until the desired viscosity was reached.

A number of samples of sulfurized and phosphorized lard oil additives were prepared in accordance with the process just outlined, with the exception that in some cases no air-blowing was practiced and in other cases the amount of air fed to the reaction mixture differed with different samples. The lard oil used in preparing all samples was a mixture of 1 part of No. 1 lard oil containing about 15% by weight of free fatty acid and 1 part of prime lard oil containing about 1% by weight of free fatty acid. The data with respect to the preparation of the various samples and the viscosity of the final product are given in the following Table I:

Table I

Base No.	Cu. Ft. of Air Introduced by Blowing During Sulfurization	Period of Sulfurization	Vis./210° F. after Sulfurization	Cu. Ft. of Air Introduced by Blowing During Phosphorization	Period of Phosphorization	Vis./210° F. after Phosphorization
		Hours			*Hours*	
1	No Air Blowing	7½	262	No Air Blowing	5	321
2	do	11½	317	do	5	387
3	½ cu. ft. per hour	7½	323	do	5	431
4	1 cu. ft. per hour	7½	367	do	5	462
5	24 cu. ft. per hour	7½	389	29 cu. ft. per hour	5	688
6	17 cu. ft. per hour	12½	433	No Air Blowing	5½	708
7	16 cu. ft. per hour	7½	435	do	5½	732
8	Quantity Unknown	12	730	Quantity Unknown	5	1,194

The effect of increasing the amount of air blown through the mixture during cooking in increasing the viscosity is apparent from the comparison of Bases Nos. 1, 3, 4 and 7. The effect of rapid agitation or stirring as compared to slow stirring is shown by a comparison of Bases Nos. 6 and 7. In the preparation of Base No. 6 slow agitation was used and as a result, in 12½ hours the viscosity was slightly less than that obtained in 7½ hours in connection with Base No. 7 with a slightly lower rate of air blowing. This more rapid agitation expedites rates of viscosity increase.

In the preparation of Base No. 8, the object was to obtain a certain viscosity and no measurement of the quantity of air blown through the mixture was made. It was not possible to obtain a viscosity as high as 700 seconds Saybolt at 210° F. without air-blowing. Note Base No. 2 in which sulfurization was carried out in 11½ hours and phosphorization in 5 hours. The finished material had a viscosity of only 387 seconds Saybolt at 210° F.

Products made in accordance with our invention not only have a higher viscosity than those prepared in the absence of intimate contact with air, but increase the viscosity index of the finished lubricant in which they are blended. Moreover, the finished lubricant containing sulfurized and phosphorized base, prepared in accordance with our invention, produces a finished lubricating oil having a lower pour point than those oils produced from sulfurized and phosphorized bases prepared without air-blowing. The load carrying ability of the finished lubricants made from our additives exhibit excellent Timken tests and give successful results when tested in an automobile. These lubricants also meet the approval of the Army Ordnance Department.

In order to demonstrate the superior viscosity index and pour point characteristics of bases made in accordance with our invention, a series of blends was made containing 18% of sulfurized and phosphorized lard oil base prepared in accordance with the example previously given, except that in some cases no air-blowing was used and in other cases different amounts of air-blowing were used. The lubricating oil with which the base was blended was a mixture of Gulf Coast pale oil having a Saybolt Universal viscosity at 100° F. of approximately 200 seconds and a Gulf Coast bright stock having a viscosity of approximately 160 seconds Saybolt at 210° F. The viscosity of the base, viscosity of the finished lubricating oil blend, viscosity index and the pour point of the finished lubricating oil are given in Table II:

Table II

Vis./210° F. of Base Used in Lube Blend	Amount of Air Blowing of the Base	Vis./210 of Lube Blend	Vis./100 of Lube Blend	V. I. of Lube Blend	Pour Point of Lube Blend
					°F.
387	No air blowing	86.2	1,168	75	+10
400	do	88.0	1,220	74	+10
431	½ cu. ft. per hour	----	----	----	+10
537	23 cu. ft. per hour	87.6	1,105	84	----
688	24 cu. ft. per hour	86.1	1,026	88	+5
[1] {708 / 732	17 cu. ft. per hour / 16 cu. ft. per hour	83.8	957	90	0

[1] Two samples combined.

From Table II it is apparent that the last two lubricants listed had a viscosity index in excess of 85 and had a pour point somewhat lower than the lubricating oils made from sulfurized and phosphorized base made without air-blowing.

Bases made in accordance with our invention are particularly useful when blended with Gulf Coast oils for the preparation of extreme pressure lubricants for use in automotive transmissions and differentials. Generally, it is preferred not to use bases made in accordance with our invention in Pennsylvania grade oils, since the base has a tendency to separate from the oil. Gulf Coast oils have notoriously low viscosity index characteristics. However, additives made in accordance with our invention raise the viscosity index of the finished lubricant so that the finished lubricant will meet government requirements.

It will be seen, therefore, that by carrying out the sulfurization and the phosphorization of fatty oils and esters of high-boiling fatty acids, and polyhydric alcohols contaminated with substantial quantities of free fatty acids, while intimately contacting the mixture with finely dispersed air, an additive can be prepared having sufficiently high viscosity to impart to mineral lubricating oils a superior viscosity index and pour point.

It is claimed:

1. The method of preparing a high viscosity extreme pressure additive comprising, reacting sulfur with a non-drying fatty oil containing a substantial amount of free fatty acid, at temperatures of approximately 300–350° F. while maintaining said non-drying fatty oil in intimate contact with finely dispersed air, said finely dispersed air being injected rapidly into the reaction mixture by passing air through a solid porous body immersed in the mixture of said oil and sulfur until a good copper corrosion strip test is obtained and then phosphorizing the sulfurized product with phosphorous sesquisulfide at a temperature of approximately 220–230° F., and continuing the reaction until a sulfurized and phosphorized product having a viscosity of at least about 700 seconds Saybolt at 210° F. is produced.

2. Method in accordance with claim 1 in which finely dispersed air is intimately contacted with the mixture undergoing reaction during the phosphorization step.

3. The method of preparing a lubricant additive comprising, reacting a non-drying ester of a fatty acid containing from 10 to 24 carbon atoms in the molecule and a polyhydric alcohol, contaminated with at least 5 per cent of free fatty acid, with about 3 to 9 per cent by weight of sulfur at a temperature of approximately 300–350° F. while intimately contacting the body of the reaction mixture with dispersed air and accomplishing the aeration by forcing air through a solid porous body immersed in the mixture of said ester and sulfur, continuing the reaction until the product gives a good copper strip corrosion test and then phosphorizing the resulting product, and continuing the reaction until a sulfurized and phosphorized product having a viscosity of at least about 700 seconds Saybolt at 210° F. is produced.

4. Method in accordance with claim 1 in which the resulting product is phosphorized with a small amount of phosphorus sesquisulfide at temperatures of approximately 220–230° F. while in-

timately contacting the mixture with finely dispersed air.

5. Method in accordance with claim 1 in which the resulting product is phosphorized by reacting it at about 220–230° F. with phosphorus sesquisulfide equivalent to approximately 0.1 to 0.6% of phosphorus, based on said product while intimately contacting the reaction mixture with finely dispersed air.

6. Method in accordance with claim 1 in which the fatty oil is No. 1 lard oil.

7. Method in accordance with claim 1 in which the fatty oil is a mixture of prime and No. 1 lard oil.

8. The method of preparing a high viscosity extreme pressure additive comprising cooking a mixture of the following constituents in the following proportions by weight:

No. 1 lard oil	43.8
Prime lard oil	43.8
Gulf Coast lubricating oil	5
Sulfur	7.4

at a temperature of approximately 330–340° F., while intimately contacting the mixture with finely dispersed air, said air being passed into the mixture in dispersed form by forcing it through a solid porous body immersed in the mixture, until the reaction product exhibits a good copper strip corrosion test, then reacting the resulting product with phosphorus sesquisulfide in the proportions of 100 parts by weight of the former to about 0.4 part by weight of the latter, at a temperature of about 220 to 230° F., while intimately contacting the mixture with dispersed air and continuing the reaction until a product is obtained which imparts an optimum Timken test to a finished lubricant containing said product, said product being a sulfurized and

phosphorized material having a viscosity of at least 700 seconds Saybolt at 210° F. and being capable of imparting a viscosity index greater than about 85 to a finished lubricant containing said product blended with a low viscosity index Gulf Coast Pale oil in the amount of about 18 per cent.

9. The method of preparing a high viscosity extreme pressure lubricant additive comprising, reacting sulfur with a non-drying oil composed in substantial part of an ester of a polyhydric alcohol and a high boiling fatty acid containing from 10 to 24 carbon atoms per molecule and one double bond in the acid molecule, said oil containing a substantial amount of a free fatty acid, at temperatures in the range from about 300 to 350° F., while aerating said oil with a stream of finely dispersed air created by passing air through a porous body immersed in said mixture and continuing the reaction and aeration until the oil shows a good copper corrosion test, and then phosphorizing the sulfurized material with phosphorus sesquisulfide at a temperature of about 220° to 230° F., and continuing the reaction until a viscosity of about 700 seconds Saybolt at 210° F., is developed in the product.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,211,306	Whittier	Aug. 13, 1940