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MANUFACTURE OF NEUTRAL ORGANIC SULPHUR COMPOUNDS

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This invention relates to the manufacture of neutral organic sulphur compounds and compositions containing the same.

In particular, it relates to the manufacture of synthetic sulphurized mono-esters of fatty acids and compositions containing the same, especially compounded lubricants comprising a major amount of lubricating oil and a minor amount of such sulphurized mono-esters, the compounded lubricants having many advantageous properties and being useful for various purposes, particularly in lubricating metal surfaces under ordinary and higher pressures; all as more fully hereinafter set forth and as claimed.

More specifically, this invention is directed to new and improved methods of making sulphurized mono-esters from glycerides of unsaturated fatty acids, such as lard oil and other fatty oils, with recovery of glycerine as a valuable by-product.

In my improved methods, fatty oils or glycerides containing unsaturated fatty acids are reacted with sulphur to form sulphur addition products and the sulphurized oils or glycerides are converted into sulphurized mono-esters by reaction with a monohydric alcohol, advantageously in the presence of a catalyst such as concentrated sulphuric acid; the glycerides being completely decomposed and the glycerine being liberated by alcoholysis of the sulphurized fatty glycerides.

The sulphurized mono-esters so obtained are separated from the glycerine. They may be further refined, usually with activated clay, to remove any deleterious by-products, if present. Further, the sulphurized mono-esters may be blended with mineral lubricating oils to obtain various compounded lubricants; the sulphurized mono-esters being sometimes mixed with mineral oil prior to such refining. That is, the present invention achieves various improvements in making sulphurized mono-esters and utilizing them in lubricants and other compositions, the recovery of valuable glycerine being one of the advantageous features of this invention.

The manufacture of sulphurized mono-esters of fatty acid and of lubricating oil compositions containing such sulphurized esters are well known. For instance, in my Patents 2,179,060 and 2,179,061, I have described and claimed improved lubricants comprising a mineral oil lubricating base and a minor amount of sulphurized fatty mono-esters. As there shown, such lubricants have many advantageous properties and uses.

In my Patent 2,179,060 I have specifically claimed lubricants containing sulphurized sperm oil and like mono-esters. As there pointed out, sperm oil, though often termed a fatty oil, is quite different from the ordinary fatty oils which are esters of glycerine; sperm oil being composed principally of fatty esters of monohydric alcohols. Further, the mono-esters of sperm oil contain unsaturated aliphatic groups and are capable of reacting with sulphur to form simple addition compounds which are substantially neutral and advantageous improvement agents in lubricating compositions.

The superiority of sulphurized mono-esters, as a class, in making improved lubricants is further shown in my Patent 2,179,061, wherein I broadly claimed improved lubricants containing these sulphurized mono-esters.

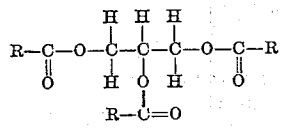
In my companion Patents 2,179,065 and 2,179,066 I have described and claimed such sulphurized fatty mono-esters and methods of making the same. In general, as there shown, sulphurized mono-esters of fatty acids can be easily prepared by sulphurizing unsaturated fatty or aliphatic mono-esters having the formula

$$R—\overset{\overset{O}{\|}}{C}—O—R'$$

wherein R and R′ represent straight chain aliphatic groups, at least one of said groups being unsaturated. In the methods there described, the said mono-esters are reacted with sulphur to produce sulphur addition products, which are substantially neutral organic sulphur compounds. As shown in my patents, the sulphurization may be advantageously effected by gradually adding the sulphur to preheated sperm oil (or like mono-esters) and maintaining the mixture between 300–380° F. until substantially all of the sulphur has combined. In such methods, naturally occurring mono-esters such as sperm oil, etc., are ordinarily employed, this being specifically claimed in my Patent 2,179,066. However, as disclosed in my above patents, synthetic unsaturated aliphatic mono-esters such as obtained by esterifying suitable fatty acids with appropriate alcohols may likewise be sulphurized to produce sulphurized mono-esters.

I have now found that such sulphurized mono-esters of fatty acids can be prepared with advantage from glycerides of unsaturated fatty acids, such as fatty oils or mixtures of such fatty oils, by new and improved methods, yielding glycerine as a valuable by-product, as well as excellent sulphurized mono-esters useful in improving mineral lubricating oils and lubricants.

As is well known, most fatty oils and fats are complex mixtures of fatty glycerides; their main constituents being tri-glycerides. Generically, these tri-glycerides may be represented by the following formula:



wherein R represents the aliphatic group of a fatty acid which may be saturated or unsaturated. On the other hand, the main distinction between fats (solid glycerides) and fatty oils (liquid glycerides) is that the former are mostly glycerides of saturated acids, whereas the latter are mostly glycerides of unsaturated fatty acids. For instance, stearin, which is the main constituent of many fats, is the triglyceride of stearic acid. On the other hand, olein, which is the main constituent in many fatty oils, is the triglyceride of oleic acid; a fatty acid containing one double bond in the aliphatic chain thereof. For instance, lard oil contains substantial amounts of olein. This particular glyceride is also present in many other fatty oils, particularly the vegetable oils. However, vegetable oils also contain glycerides of other fatty acids, including fatty acids containing 2 or 3 double bonds in the aliphatic chain, such as linoleic, linolenic, and similar acids. In fact, many oils contain substantial amounts of mixed fatty glycerides wherein the hydroxyl groups of the glycerine are esterified with different fatty acids, the three hydroxyl groups being sometimes esterified with three different acids respectively. Likewise, many fats also contain mixed glycerides, varying amounts of unsaturated fatty acids being sometimes present in addition to saturated acids. Such mixed glycerides, upon hydrolysis, yield two or three different fatty acids. That is, ordinarily, fats and fatty oils are not simple triglycerides of fatty acids. Instead, they usually contain varying amounts of mixed glycerides, in addition to one or more triglycerides of single fatty acids of the type predominantly characteristic thereof, this being particularly true with most commercial animal or vegetable oils. In other words, commercial fats and oils are complex mixtures of several glycerides, and a wide variety of fatty acids can be obtained therefrom.

Thus, by the present invention, a wide range and variety of sulphurized mono-esters may be obtained by processing commercial fatty oils and mixtures thereof according to my improved processes.

In my improved methods of making sulphurized mono-esters, I first sulphurize the fatty oils or glycerides with sulphur, so as to obtain sulphur addition products, and then convert these sulphurized glycerides into the desired sulphurized mono-esters by reaction with monohydric alcohols, usually in the presence of a catalyst such as sulphuric acid. The sulphurized mono-esters so obtained are separated from the glycerine and may be further refined, if desired. Likewise, the separated glycerine is recovered and may also be refined as desired. In this way, I obtain valuable glycerine as a by-product, as well as desirable sulphurized mono-esters; both products being high-grade materials.

In preparing the sulphurized fatty glycerides, a wide variety of fatty oils or other glycerides of unsaturated fatty acids may be employed. In general, any fatty glyceride containing at least one mol of unsaturated fatty acid is useful in the present processes; tri-glycerides containing 2 or 3 mols of unsaturated fatty acid being advantageous.

In particular, I find that fatty oils having iodine numbers ranging from 70 to 130 can be readily sulphurized and converted into sulphurized mono-esters which are particularly advantageous improvement agents for lubricating oils. For example, lard oil having an iodine number of approximately 72 yields particularly advantageous products when processed by my new methods. While lard oil contains substantial amounts of olein as the main constituent thereof, it also contains varying amounts of glycerides of other fatty acids, some saturated and some unsaturated, and the final product obtained from it is a mixture of mono-esters of such acids; the sulphur being added to the double bond of the unsaturated acids. However, the products obtained from lard oil contain relatively large amounts of mono-esters of sulphurized oleic acid. In fact, olein is typical of the glycerides of unsaturated fatty acids which are particularly useful and advantageous in the present processes. However, I may also employ with advantage other glycerides and mixtures of glycerides having iodine numbers ranging from 70 to 130; many of the commercial fatty oils having iodine numbers within this range. Other glyceride mixtures having iodine numbers within this range can be readily prepared by blending together various fatty oils. For instance, lard oil may be blended with other fatty oils, such as cottonseed oil, menhaden oil, soya oil, corn oil, tung oil, linseed oil, and other oils having relatively high iodine numbers. That is, by selecting the fatty oils employed, or blending together various fatty oils, or both, final products having particularly advantageous properties can be readily obtained.

In sulphurizing such fatty oils or glycerides, the reaction is so controlled as to produce sulphur addition compounds and to prevent the formation of any substantial amount of hydrogen sulphide. These sulphur addition compounds or sulphurized glycerides are formed by saturating all or part of the double bonds of the fatty acid radicals with sulphur. Accordingly, the amount of sulphur employed in this reaction does not exceed that required for complete saturation of all of such double bonds. Usually, I employ somewhat smaller amounts of sulphur than are necessary to satisfy completely the unsaturation of the glycerides. In this way, I can control both the unsaturation and the content of sulphur in the sulphurized glycerides and in the final sulphurized mono-esters.

In preparing the sulphurized glycerides, the fatty oils are reacted with the desired amount of sulphur at elevated temperatures preferably between 320° and 380° F.; the mixture being maintained at such temperatures until all of the sulphur has combined. This may be advantageously done by preheating the fatty oil to 300–

320° F. and then gradually adding the sulphur to the hot oil in small doses, the sulphur being added at such a rate as to maintain a steady increase in temperature to between 320° and 380° F. by the exothermic heat of reaction. After all of the sulphur has been added and combined, the sulphurized glyceride is cooled usually to approximately room temperature. The sulphurized fatty oils so obtained are liquid materials and can be readily converted into sulphurized mono-esters.

In converting the sulphurized glycerides into the corresponding mono-esters, the sulphurized fatty oils are saponified and esterified with monohydric alcohols, the sulphurized glycerides being reacted with an excess of the alcohol, usually in the presence of an acid catalyst. An advantageous catalyst is concentrated sulphuric acid, such as 90–105 per cent sulphuric acid. In one advantageous procedure, the alcohol is admixed with the sulphuric acid and the acidulated alcohol is added to the sulphurized glyceride with stirring. While continuing the stirring, the mixture is heated to temperatures between 150° and 220° F., until the reaction is complete. Usually, the mixture is heated under reflux, any vaporized alcohol being condensed and returned by the reflux. After the sulphurized glyceride has been completely converted into mono-ester, the stirring is discontinued and the mixture stratified into two layers, an upper ester layer and a lower acid-glycerine layer. The two layers are separated and may be refined as described post.

In forming the sulphurized mono-esters, various alcohols may be reacted with the sulphurized glycerides and a wide range of sulphurized mono-esters obtained. Advantageous products are obtained with primary aliphatic alcohols, particularly the lower alcohols, such as methanol, ethanol, propanol, butanol, and pentanol. Particularly good products are obtained with butanol. In general, other alcohols may also be used. For instance, branch chain alcohols such as iso-propanol iso-butanol, etc., may be employed. Likewise, secondary aliphatic monohydric alcohols may be used, as well as primary alcohols.

In general, any monohydric alcohol may be reacted with the sulphurized glyceride to form useful sulphurized mono-esters and liberate the glycerine. After this reaction is complete, the reaction mixture is permitted to stratify into an upper mono-ester layer and a glycerine layer. When sulphuric acid or other acid is employed as a catalyst in the reaction, the glycerine layer is somewhat acid, and the separated glycerine is usually further refined to obviate this acidity before recovering the glycerine.

After the sulphurized mono-esters have been separated from the glycerine layer, they are usually further refined by clay contacting. In doing so, an appropriate amount of activated clay is added to the sulphurized mono-esters and the mixture agitated until the clay absorbs the matter to be removed. The clay treated mixture is then filter pressed to remove the clay and other insolubles. To facilitate such removal, filter aids may be added to the mixture prior to filtering. For this purpose, commercial filter aids such as Supercel, etc., are advantageous. Furthermore, in refining the sulphurized mono-esters, it is sometimes advantageous to treat them with lime to remove residual acidity prior to clay contacting. In such cases, the lime in excess of that necessary to obviate the mineral acidity, may be added and the mixture stirred until substantially neutral. The calcium sulphate and excess lime may be settled out and filtered off prior to clay treatment. However, complete removal prior to clay treating is not essential, and, in many cases, the liming and clay treatment may be combined in one operation. In such combination refining, a small amount of lime may be used and the activated clay added to the mixture after it is substantially neutral; then all of the insoluble matter is removed in one operation by filter pressing.

In recovering and refining the glycerine, the separated acid-glycerine layer may be processed in several ways. As stated ante, this acid layer is usually neutralized with lime when sulphuric acid catalyst is used. In refining such by-product glycerine, the glycerine layer is admixed with an excess of hydrated lime, in the form of a slurry, and the mixture agitated until substantially neutral. The so-treated glycerine is then filter-pressed to remove the calcium sulphate and excess lime. The recovered glycerine is a high grade material. It may be further refined, if desired. For instance, the filtrate may be vacuum distilled to recover substantially anhydrous glycerine. All of the various glycerine by-products obtained in these processes are useful, per se, for many purposes.

From the foregoing description, it will be evident that in the practice of my invention, many and various embodiments thereof may be employed. In general, the several steps in my improved processes are interrelated and correlated to obtain high grade sulphurized mono-esters from fatty oils, with recovery of useful by-product glycerine. In the most advantageous embodiments thereof, my improved processes include reacting sulphur with fatty oils containing glycerides of unsaturated fatty acids to obtain sulphur addition products thereof, reacting the sulphurized glycerides with monohydric alcohol in the presence of sulphuric acid to convert them into sulphurized mono-esters, separating such mono-esters from the glycerine, and refining the separated sulphurized mono-esters, usually with lime and clay. Likewise in recovering and refining the glycerine, the acid glycerine layer is treated with lime or otherwise refined to obtain pure glycerine. These and other embodiments of my invention are further illustrated in more detail by the specific examples given post.

The following examples are illustrative embodiments of the methods and products broadly set forth ante, and are not limitative of my invention.

Example 1.—Into a suitable vessel equipped with means for agitating and for heating and cooling the reaction mixture, there were charged 88 pounds of a mixture of fatty glycerides having an iodine number of 89 and prepared by blending together 55 parts of prime lard oil and 45 parts of crude cottonseed oil, by weight. The mixed oils were heated to approximately 330° F. and 12 pounds of sulphur were gradually added to the hot oil in small doses over a period of approximately one-half hour; the temperature being held between 340° and 350° F. during the introduction of the sulphur. After all of the sulphur was added, the reaction mixture was maintained at said temperatures until the reaction was complete. The sulphurized oil so obtained was cooled to approximately room temperature. The yield of sulphurized oil was substantially 100 pounds.

The sulphurized glycerides so obtained were

charged into a suitable vessel fitted with an agitator and a reflux condenser. While agitating the charge, a mixture of 22 pounds of normal butanol and 5 pounds of 96 per cent sulphuric acid were added and this reaction mixture heated at 200–220° F. for four hours. After the reaction was complete, the gitation was stopped and the mixture stratified into two layers, an upper ester layer and a lower acid-glycerine layer, whereupon the acid-glycerine layer was drawn off. The sulphurized mono-esters so obtained had a slight acidity, due to residual mineral acid dissolved therein, and were treated with sufficient lime to neutralize the mineral acidity. In doing so, the sulphurized mono-esters were admixed with 2 pounds of hydrated lime and the mixture agitated until a substantially neutral product was obtained. The excess lime and other insolubles were settled out and removed.

The substantially neutral sulphurized mono-esters were then further refined by contacting with activated clay. In doing so, 9 pounds of activated clay were added to the sulphurized mono-esters and the mixture agitated and maintained at 275° F. for about 2½ hours. The so-treated mixture was then filter pressed to separate the clay from the treated oil, a small amount of filter aid being used to facilitate the separation. The filtrate so obtained was a mixture of butyl esters of sulphurized fatty acids and was a high grade improvement agent for lubricating oils and like lubricants. The detailed properties of the initial glyceride mixture, the sulphurized glycerides and the final refined sulphurized mono-esters were as follows:

	Original glyceride mixture	Sulphurized glycerides	Refined sulphurized mono-esters
Gravity, °API	22.3	8.9	17.0
Viscosity, SUV, seconds:			
100° F	190.9		152.1
210° F		1,011	47.7
Flash, OC, °F			415
Fire, OC, °F			455
Pour, °F	+35		+35
Color, NPA	5		
Sulphur, B, per cent		11.4	10.0

The separated glycerine-acid layer weighed approximately 15 pounds and was further refined to recover glycerine. In doing so, the glycerine layer was admixed with 4 pounds of hydrated lime and agitated until the sulphuric acid was neutralized. The mixture was then settled and filtered to separate the substantially pure glycerine from the calcium sulphate and excess lime. The recovered glycerine may be further refined, such as by vacuum distillation or other known methods, if desired.

Example 2.—Another superior improvement agent comprising a mixture of butyl esters of sulphurized fatty acids was obtained by processing 88 pounds of a mixture of fatty glycerides having an iodine number of 89 and comprising 80 per cent prime lard oil and 20 per cent of menhaden oil by weight, according to the procedure given in Example 1 ante; this mixture of lard and menhaden oils being sulphurized with 12 pounds of sulphur, the sulphurized glycerides reacted with acidulated normal butanol, and the sulphurized mono-esters separated from the glycerine and refined by clay contacting as described in Example 1.

The properties of the initial glyceride mixture, the sulphurized glycerides and the refined sulphurized monoesters were as follows:

	Original glyceride mixture	Sulphurized glycerides	Refined sulphurized mono-esters
Gravity, °API	22.7	8.7	16.4
Viscosity, SUV, seconds:			
100° F	195.3		183.4
210° F		1,514	50.5
Flash, OC, °F			405
Fire, OC, °F			450
Pour: °F	+40		+40
Color, NPA	3.25		
Sulphur, B, per cent		11.6	10.3

Here again, the separated glycerine-acid layer was refined to recover high grade glycerine, as described in Example 1.

In the foregoing examples, blends of two fatty oils were employed in preparing mixtures of glycerides having iodine values advantageous for the present purposes. Likewise, I may blend several oils to obtain other mixtures which are advantageous starting materials for my present processes. This is indicative of the versatility of the present invention and is further illustrated post.

Further, mineral oils may be also incorporated in the sulphurized oils during the processing. For instance, mineral lubricating oils may be admixed with the sulphurized mono-esters prior to refining them with clay. Such embodiments of my invention are illustrated in the following example.

Example 3.—A mixture of fatty glycerides having an iodine number of 91.6 and prepared by blending together 58.6 per cent of lard oil, 20.7 per cent of cottonseed oil, and 20.7 per cent of soybean oil, by weight, was processed by the following procedure:

Into a suitable vessel there were charged 88 pounds of the above glyceride mixture and after heating to 340° F. with stirring, 12 pounds of sulphur were gradually added. The heating was continued until all of the sulphur was combined. The sulphurized oil so obtained was cooled to approximately room temperature and then admixed with acidulated alcohol prepared by blending 25 pounds of normal butanol and 5 pounds of 96 per cent sulphuric acid. After the addition of the acidulated alcohol, the mixture was then heated to 200–220° F. for four hours. After the saponification and esterification were complete, the mixture was stratified into an ester layer and glycerine layer and the glycerine layer withdrawn. The ester layer was then diluted with an equal weight of mineral lubricating oil, namely a Pennsylvania oil having a viscosity of 70 seconds (SUV) at 100° F. This oil mixture was then clay contacted at 275° F. for two hours and filter pressed through a ½ inch layer of Supercel. The filtrate was a clear solution of butyl esters of sulphurized fatty acids dissolved in the mineral lubricating oil. It is an excellent lubricant, per se. Also, it may be further diluted with lubricating oil to prepare other lubricants.

The separated acid-glycerine layer was also recovered and refined as described in Example 1.

In the above example, in lieu of the particular mixture of fatty oils employed ante, other blends of fatty oils may be employed. In this way, a wide range of sulphurized mono-esters can be readily obtained. This is further illustrated in Table 1, wherein the properties of the sulphurized products obtainable from blends of several fatty oils by the procedure of Example 3 are given, together with the composition of the glyceride mixtures from which they were obtained.

Table I

	Mixture No. 1	Mixture No. 2	Mixture No. 3	Mixture No. 4
Make-up, per cent by weight:				
Prime lard oil	58.6	68.0	27.0	59.6
Crude cottonseed oil	20.7	------	36.5	------
Crude soya bean oil	20.7	------	------	------
Winter pressed fish oil	------	16.0	------	------
Refined peanut oil	------	16.0	------	------
No. 3 castor oil	------	------	36.5	------
Beef tallow	------	------	------	20.2
Raw linseed oil	------	------	------	20.2
Glyceride mixture:				
Inspection—				
Gravity, ° API	22.6	22.0	20.1	23.0
Viscosity, SUV, 210° F.	63.3	56.4	61.0	53.7
Pour, ° F.	+35	+40	+30	+45
Color, NPA	4.75	2.25	5.5	2.25
Neutralization No.	1.56	5.00	3.48	2.10
Iodine No., Mod. Hanus	91.6	86.7	89.2	86.8
Sulphurized oil:				
Inspection:				
Gravity, ° API	8.8	8.8	7.7	10.1
Viscosity, SUV, 100° F.	1,090	1,782	1,265	803
Sulphur, B, per cent	11.3	11.9	11.6	12.2
Neutralization No.	0.92	3.52	2.20	1.76
Finished clay-treated sulphurized esters:				
Inspection:				
Gravity, ° API	25.5	25.7	24.9	25.8
Viscosity, SUV:				
100° F.	99.4	96.3	110.5	92.4
210° F.	40.3	40.3	40.5	40.3
Flash, OC, ° F.	355	360	355	355
Fire, OC, ° F.	395	400	395	400
Pour, ° F.	+25	+30	+25	+35
Color, NPA	4.75	5.0	6.0	5.5
Sulphur, B, per cent	4.84	4.72	4.89	4.62

Other blends of various fatty oils may be employed as a starting material in the present processes. However, the present invention is not limited to the use of blended oils. In fact, advantageous products can be obtained from various natural fatty oils or glycerides having iodine values between 70 and 130. For instance, lard oil is an advantageous starting material. It can be readily sulphurized and converted into sulphurized mono-esters, as illustrated in the following example.

Example 4.—In this embodiment of my invention, 332 pounds of prime lard oil were heated to 320° F. and 45 pounds of sulphur were gradually added to the hot oil in small doses over a period of two and one-half hours. After all of the sulphur was added, the mixture was further heated at 320–350° F. for ten hours, and then cooled to room temperature. A yield of 374 pounds of sulphurized lard oil was obtained.

The properties of the original lard oil and the sulphurized glycerides obtained therefrom were as follows:

	Original lard oil	Sulphurized glycerides
Gravity, °API	22.9	9.5
Viscosity, SUV, seconds, 100° F.	198	1,123
Pour, °F.	+35	+50
Color, NPA	1.25	------
Iodine number, Hanus	72	------
Sulphur, B, per cent	------	10.9
Neutralization number	------	0.8
Saponification number	194.5	------

The sulphurized lard oil having the above properties is advantageous in that it can be readily converted into sulphurized mono-esters by reaction with various alcohols.

In making butyl esters from the above sulphurized glycerides, 300 pounds of the sulphurized lard oil were admixed with 85 pounds of acidulated butyl alcohol prepared by admixing 15 pounds of 96 per cent sulphuric acid with 70 pounds of butanol. This reaction mixture was agitated and gradually heated to 220° F. in approximately one and one-half hours, and then maintained at this temperature for four hours while continuing the agitation. After the reaction was complete, the stirring was discontinued and the mixture stratified into an ester layer and a glycerine-acid layer. The glycerine layer was withdrawn and 339 pounds of the sulphurized mono-esters so obtained were admixed with 15 pounds of lime and 40 pounds of activated clay and the mixture maintained at 275° F. with agiation for three hours. After this clay contacting, the refined sulphurized mono-esters were filter pressed to remove the clay and other insoluble matters. The filtrate was an excellent improvement agent for mineral oils and lubricants.

The separated glycerine-acid layer weighed approximately 45 pounds and was further treated to recover the glycerine. In refining the glycerine layer, the procedure described in Example 1 was employed; the glycerine-acid mixture being limed and the so-treated glycerine being filtered to remove the insolubles such as calcium sulphate and excess lime and vacuum distilled.

In the above examples, other monohydric alcohols may be used in lieu of the normal butanol, the proportions being suitably adjusted according to the particular alcohol employed. For instance, isopropanol, or methanol may be used to esterify the sulphurized lard oil and produce excellent sulphurized mono-esters. In the following Table II are given typical properties of the sulphurized mono-esters obtained by reacting the sulphurized lard-oil with butanol, isopropanol, and methanol, respectively, according to the procedure of Example 3.

Table II

Alcohol used for esterification	n-Butanol	Isopropanol	Methanol
Clay-treated sulphurized ester:			
Gravity, °API	16.7	17.0	14.6
Viscosity, SUV, seconds:			
100° F.	217	201	159
210° F.	60.3	51.1	46.8
Flash, OC, °F.	410	375	360
Fire, OC, °F.	445	420	405
Sulphur, B, per cent	9.79	9.76	9.80

The sulphurized mono-ester compositions given in the above table are merely illustrative of certain embodiments of this invention, and other alcohol esters of sulphurized fatty acids can be prepared in like manner. Also, mineral oils such as the usual grades of lubricating oil, may be incorporated with the sulphurized mono-esters during the processing. Such oils may be advantageously admixed with the sulphurized mono-esters prior to clay refining, as in this way concentrates or lubricants can be directly obtained. For instance, in the embodiments illustrated in Examples 1, 2 and 4, varying amounts of mineral lubricating oil, advantageously a Pennsylvania base neutral oil having a viscosity of 70 (SUV) at 100° F., may be readily incorporated prior to the clay treatment, and the mineral oil solution of the sulphurized mono-esters then refined with clay to produce concentrated solutions, which are good lubricants and are useful in producing other lubricants containing small amounts of these improvement agents. I have prepared a large number of such mineral oil compositions in accordance with this invention, and the make-

up and properties of a few of them are given in the following Table III.

Table III

Mineral oil, per cent by weight	Sulphurized mono-ester: Per cent by weight	Prepared from— Fatty oil mixture	Alcohol	Gravity, °API	Viscosity, SUV 100° F.	Viscosity, SUV 210° F.	Flash OC, °F.	Fire OC, °F.	Sulphur, per cent
50	50	Lard oil and cottonseed oil	n-Butanol	25.4	127	42.7	365	440	4.8
50	50	do	Methanol	23.7	299	55.1			4.3
50	50	Lard oil and menhaden oil	n-Butanol	25.0	134	44.0	365	445	4.9
50	50	Soya bean oil	do	23.1		61.1	440	495	5.67
50	50	do	Ethanol	20.3		81.9	445	500	6.89
50	50	Cottonseed oil	n-Butanol	24.3	295	56.4	440	495	4.30
50	50	do	Ethanol	23.7		65.6			4.52
50	50	Lard oil	n-Butanol	23.1	378	61.3	425	475	4.83
30	70	do	do	23.4	162.3	47.2	390	450	5.68
50	50	do	Isopropanol	26.8	160.7	46.2	400	445	4.30
50	50	do	n-Propanol	25.3	227	51.8	420	470	4.38
50	50	do	Ethanol	22.6	541	61.9	420	475	4.79
30	70	do	do	21.8	177.7	48.4	380	430	6.5
50	50	do	Methanol	25.9	155.0	40.0	390	440	4.80
50	50	Lard oil and soya bean oil	n-Butanol	24.8		56.2			4.75

Example 5.—In a one-barrel stirring still equipped with a reflux condenser, 300 pounds of sulphurized lard oil was treated with a mixture of 70 pounds of normal butanol and 15 pounds of 96 per cent sulphuric acid catalyst. The acidulated alcohol was admixed with the sulphurized lard oil and the temperature raised to 220° F. over a period of 1½ hours. The mixture was then maintained at 220° F. for 4 hours. At the conclusion of the treatment, the glycerine layer, amounting to 45 pounds, was drawn off and 339 pounds of sour oil were obtained.

The sour oil was treated with the theoretical quantity of hydrated lime necessary to neutralize the mineral acidity, and the temperature was raised to 270° F. over a period of one hour. Filtrol was added and the mixture contacted at 275° F. for three hours. The mixture was then filtered through a Sweetland filter press.

Properties of the clay-treated, sulphurized esters so obtained were as follows:

Gravity, °API	20.4
Viscosity, SUV:	
100° F	86.8
210° F	40.7
Flash, OC, °F	350
Fire, OC, °F	400
Pour, °F	+35
Color, NPA	6.5
Sulphur, B, per cent	8.90

The separated glycerine mixture was neutralized by pouring into a lime slurry containing 10 per cent excess lime, and filtered. The filtrate had the following properties:

Sp. gr., 60°/60° F	1.147
Color	Straw yellow

Example 6.—Prime lard oil was sulphurized by adding to 437 pounds of the oil, in a one-barrel stirring still, 52.5 pounds or 12 per cent by weight of sulphur. The lard oil was heated to 330° F. and the sulphur was added to the oil at this temperature over a period of 2.5 hours. Agitation of the mixture was continued for 16 hours at 330–350° F. Properties of the lard oil and the sulphurized oil were as follows:

	Prime lard oil	Sulphurized lard oil
Gravity, °API	23.1	9.5
S. gr., 60°/60° F	0.9153	1.0035
Viscosity, SUV, seconds:		
100° F	193	457
210° F	+35	+55
Pour, °F	1.5	
Color, NPA	1.35	5.8
Neutralization number		10.9
Sulphur, B, per cent	71.5	
Iodine No., Hanus	192.5	
Saponification number		

The sulphurized lard oil was placed in a one-barrel stirring still connected with a reflux condenser and treated at 150° F. with 92.5 pounds (19 per cent by weight on the sulphurized lard oil) of formula 30 denatured alcohol (91 per cent of 190° proof ethanol and 9 per cent anhydrous methanol) in the presence of 24.3 pounds of 103 per cent sulphuric acid (5 per cent by weight of the sulphurized lard oil). After adding the acidulated alcohol, heating of the mixture was continued for 11 hours at 180–220° F. The sour oil was separated from the glycerine-sulphuric acid-alcohol mixture by centrifuging, neutralized with a theoretical quantity of hydrated lime, and treated with two pounds of Filtrol per gallon of sulphurized ester at 275° F. for 2 hours. The clay-treated product had the following properties:

Gravity, °API	16.0
Viscosity, SUV:	
100° F	120.1
210° F	43.2
Flash, OC, °F	365
Fire, OC, °F	410
Pour, °F	+45
Color, NPA	8.0
Sulphur, B, per cent	10.1

All of the sulphurized mono-ester compositions, prepared by the example given ante, are excellent improvement agents for mineral lubricating oils and like lubricants. By adding minor proportions of these mixtures of sulphurized fatty acid mono-esters to mineral oil lubricants, say 0.1 to 20% by weight on the mineral oil, a wide variety

of excellent improved lubricants can be prepared. I have prepared a large number of such improved lubricants containing these sulphurized mono-esters and found by test that they have many advantageous properties. The properties of a few of such improved lubricants are given in the following Table IV.

Table IV

Properties	Base composition	Composition No. 1	Composition No. 2	Composition No. 3
Gravity, °API	31.1	31.0	31.3	31.0
Viscosity, SUV:				
100° F	370	364	358	369
210° F	58.9	58.2	57.8	58.0
Flash, OC, °F	430	425	440	430
Fire, OC, °F	495	490	490	490
Pour, °F	0	0	−5	+5
Color, NPA	2.25	2.5	2.25	2.75
Sulphur, B, per cent		0.13	0.05	0.12
Copper strip test, 212° F., 3 hr.	(1)	(1)	(1)	(1)
Falex wear test:				
1,000 lb. gauge load, 15 min.—				
Wear, No. of teeth	(2)	5	3	4
Gauge load at seizure, lb		1,900	1,800	1,800
Sligh oxidation No	1	3	4	3
Corrosion test, mod. Underwood:				
Cadmium-silver bearing	(2)	(1)	(1)	(1)
Copper-lead bearing	(2)	(1)	(1)	(1)
Oxidized oil—				
Viscosity, SUV, 210° F	75.0	58.9	58.6	58.0
Viscosity increase	28.6	1.2	1.4	0
Carbon residue, per cent	1.02	0.18	0.18	0.16
Sludge, per cent	2.50	0.01	0.01	Nil

[1] Passes. [2] Fails.

In the above table, the base composition contains only a high grade Pennsylvania lubricating oil, it being included for purposes of comparison.

Composition No. 1 comprises the base oil plus 0.25 per cent by weight of the ethyl esters prepared from sulphurized lard oil.

Composition No. 2 comprises the base oil plus 0.25 per cent by weight of the butyl esters prepared from a sulphurized mixture of lard, menhaden, and peanut oils.

Composition No. 3 comprises the base oil plus 0.25 per cent by weight of the ethyl esters prepared from sulphurized mixture of lard and cottonseed oils.

The above compositions are excellent motor oils. Other improved lubricants can also be readily prepared, such as lubricants for automobile gears. In fact, excellent automobile gear lubricants can be made by incorporating from 5 to 10 per cent by weight of these sulphurized mono-esters in a suitable base oil. The properties of two such gear lubricants, together with those of the base oil employed, are given in the following Table V.

Table V

	Base oil No. 1	Gear lubricant No. 1	Base oil No. 2	Gear lubricant No. 2
Gravity, °API	27.6	26.8	27.2	26.4
Viscosity, SUV:				
100° F	1,385	1,182	2,190	1,910
210° F	112.0	102.8	163.0	141.3
Flash, OC, °F	510	455	525	475
Fire, OC, °F	600	530	620	540
Pour, °F	+5	+10	+5	+10
Color, NPA	3.75	4.75	4.25	5.0
Sulphur, B, per cent	0.14	0.95	0.16	0.85
Sulphur added, combined, per cent		0.81		0.81
Carbon residue, per cent	0.33	0.35	0.40	0.41
Copper strip test, 212° F., 3 hr.	(1)	(2)	(1)	(2)
Centrifuge test:				
Separation, per cent				
1500 RPM, room temp., 2 hr.	Trace	Trace	Trace	Trace
Almen test, lever load, pound	8	16+	6	16+
Timken test, lever load, pound	12	42+	14	42+

[1] Passes. [2] Sl. tarnish.

In the above table, gear lubricants Nos. 1 and 2 were prepared by adding to the base oils 1 and 2, respectively, approximately 8 per cent by weight of the ethyl mono-esters prepared from sulphurized lard oil.

In general, sulphurized mono-esters containing from 5 to 15 per cent by weight of combined sulphur are excellent improvement agents for mineral lubricating oils and lubricants and such advantageous improvement agents can be readily prepared by the present invention from glycerides of unsaturated fatty acids, such as commercial fatty oils or mixtures thereof, with recovery of useful by-product glycerine.

Accordingly, in the broad practice of the present invention, in addition to the specific embodiments that are given ante, other and different embodiments within its generic scope may be employed.

What I claim is:

1. In the manufacture of sulphurized mono-esters, the improvement which comprises reacting a sulphurized glyceride with a monohydric aliphatic alcohol acidified with sulphuric acid to completely liberate the glycerine from said glyceride and to convert the same into sulphurized fatty mono-esters of said alcohol, and separately recovering the sulphurized mono-esters and glycerine so obtained.

2. In the manufacture of sulphurized mono-esters, the improved process which comprises heating sulphurized glycerides with a monohydric aliphatic alcohol in the presence of sulphuric acid until said sulphurized glycerides are converted into sulphurized fatty mono-esters of said alcohol and the glycerine is completely liberated therefrom, and separately recovering the sulphurized mono-esters and glycerine so obtained, the said sulphurized mono-esters and the glycerine being subsequently refined to neutralize and remove any residual sulphuric acidity.

3. The process of claim 2, wherein the glycerine is neutralized with an excess lime and the neutral glycerine is filtered to remove the excess lime, calcium sulphate and other insoluble matter.

4. The process of claim 2, wherein the sulphurized mono-esters are refined with activated clay.

5. In the manufacture of sulphurized mono-esters, useful as improvement agents for mineral lubricating oils and lubricants, the improved process which comprises reacting sulphur with a fatty oil containing glycerides of unsaturated fatty acids to form sulphur addition products thereof and then converting said sulphurized glycerides into sulphurized mono-esters by reacting the so sulphurized fatty oil with monohydric aliphatic alcohol acidified with sulphuric acid to saponify the sulphurized glycerides and convert the same into sulphurized fatty mono-esters of said alcohol, separating the glycerine so liberated from said glycerides, and recovering and refining the sulphurized monohydric esters so produced to obtain substantially neutral sulphurized mono-esters useful as improvement agents for mineral lubricating oils and lubricants.

6. The process of claim 5, wherein said fatty oil is a non-drying oil.

7. The process of claim 5, wherein said fatty oil is lard oil.

8. The process of claim 5, wherein said fatty oil comprises a mixture of non-drying and semi-drying oils.

9. The process of claim 5, wherein said fatty oil

comprises a mixture of non-drying and drying oils.

10. The process of claim 5, wherein said fatty oil comprises a mixture of lard oil and fatty oils having an iodine number greater than 130, the mixed oils having an iodine number between 70 and 130.

11. The process of claim 5, wherein the fatty oil has an iodine number between 70 and 130.

12. In the manufacture of sulphurized mono-esters from fatty oils and mixtures of fatty oils having an iodine number between 70 and 130 and containing glycerides of unsaturated fatty acids, the improved process which comprises heating such fatty oils with sulphur to form sulphur addition products, reacting the sulphurized fatty oils with a monohydric aliphatic alcohol in the presence of sulphuric acid to form sulphurized fatty acid mono-esters of said alcohol and to liberate glycerine, separating the acid glycerine from the sulphurized mono-esters, refining the separated sulphurized mono-esters by contacting with activated clay and separating the refined sulphurized mono-esters from the clay.

13. The process of claim 12, wherein the separated glycerine is neutralized with an excess of lime and the neutral glycerine is separated from the excess lime, calcium sulphate and other insoluble matter.

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