

UNITED STATES PATENT OFFICE

2,179,065

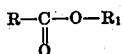
MANUFACTURE OF SULPHURIZED MONO-ESTERS OF FATTY ACIDS

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No Drawing. Application October 29, 1936,
Serial No. 108,305

16 Claims. (Cl. 260—327)

This invention relates to the manufacture of sulphurized mono-esters of fatty acids, and it comprises methods of making such sulphurized esters from unsaturated fatty aliphatic mono-esters having the following formula:



wherein R and R₁ represent straight chain aliphatic groups, one of said groups being saturated and the other being unsaturated, to produce substantially neutral organic sulphides readily soluble in mineral oils.

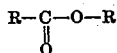
The sulphurization of fatty oils is well known, the usual practice being to mix relatively large amounts of sulphur with the fatty oil and heat the mixture until a sulphurized fatty oil is obtained. Such sulphurized fatty oils have been used for many purposes in the industrial arts. For instance, sulphurized fatty oils obtained by adding sulphur to a fatty oil such as lard oil, etc., and heating the mixture for several hours have been frequently used in making the so-called cutting oils. Such cutting oils are primarily mixtures of mineral oil with sulphurized fatty oils. These oils and other mixtures of mineral oil and sulphurized fatty oil are well known in various arts.

Likewise, it is well known that the addition of sulphurized oil to mineral oils, imparts extreme pressure characteristics to them. There being a demand for lubricants which in the form of thin films are capable of withstanding high pressures, such as occur in the gear and transmission combination of modern automobiles and other machines, it has been proposed to use mixtures of mineral oil and sulphurized fatty oil for lubricating such machines. However, it has been found that the usual mixtures are not sufficiently stable in storage or in use or both and that they are more corrosive than is permissible.

The ordinary fatty oils or esters heretofore employed for said purposes are glycerides, they being tri-esters of glycerine in which the glycerine is esterified with three mols of fatty acid. I have found that it is somewhat difficult to control the sulphurization of such tri-esters and that many of the sulphurized products obtained from them are not suitable for blending with lubricating compositions for several reasons. For one thing, they frequently lack sufficient solubility for blending with many of the usual lubricating bases. Again, when sufficiently soluble to permit blending with mineral oil under some conditions, they are insufficiently miscible over a range of conditions to permit the production of good stable compounded lubricants. Further, many of the mixtures of sulphurized tri-esters of fatty acids and mineral oils are often corrosive to various metals or alloys such as used for gears and bearings, particularly certain alloys such as binary and ternary alloys of silver, cadmium, nickel, copper and lead. In many cases this corrosive-

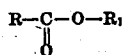
where R and R₁ represent straight chain aliphatic groups, one of said groups being saturated and the other being unsaturated, by chemically combining such mono-ester with sulphur to saturate the unsaturated groups thereof and to produce substantially neutral organic sulphur compounds, the sulphurization being advantageously effected by gradually adding sulphur to preheated mono-esters and maintaining the mixture between 300° and 380° F. until substantially all the sulphur has combined, and it also comprises the substantially neutral sulphurized mono-esters so obtained, said sulphurized esters being soluble in and miscible with petroleum oils and like hydrocarbons and being useful as improvement agents for petroleum products and capable of imparting extreme pressure characteristics to mineral lubricating oils and other lubricants and of improving the other properties of such petroleum products; all as more fully hereinafter set forth and as claimed.

In my application Serial No. 60,357, filed Jan. 22, 1936, I have described and claimed improved lubricants containing sulphurized fatty mono-esters derived from unsaturated aliphatic mono-esters having the following formula:



wherein R represents an aliphatic group, at least one of said aliphatic groups being unsaturated, and methods of making such lubricants; that application being a continuation-in-part of my application Ser. No. 715,551, filed March 14, 1934, now Patent No. 2,056,247. The present application is a continuation-in-part of my said prior applications.

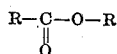
The present invention and application is directed to certain of the sulphurized mono-esters disclosed in my prior application Serial No. 60,357 and to methods of making such sulphurized mono-esters wherein sulphur is reacted and chemically combined with unsaturated aliphatic mono-esters having the following formula



ness, while not apparent in the freshly prepared compounded lubricant, develops during storage or in use.

I have found that the unsaturated mono-esters of fatty acids with aliphatic monohydric alcohols are characteristically different from the fatty oils or tri-esters of glycerine and that they yield sulphurized esters which are also quite different from the sulphurized fatty oils. The unsaturated mono-esters of fatty acids with aliphatic monohydric alcohols can be readily sulphurized to obtain substantially neutral organic sulphur compounds. These sulphurized mono-esters have many properties which render them advantageous as an ingredient in compounded lubricants. As stated in my companion application Serial No. 60,357, superior compounded lubricants are obtained with such sulphurized mono-esters. The said advantageous properties of these sulphurized mono-esters also render them useful for other purposes.

The unsaturated mono-esters of aliphatic monohydric alcohols with aliphatic monovalent acids are oily compounds of aliphatic character and are unsaturated in the aliphatic chain, that is, contain double bonds capable of being saturated with sulphur to form substantially neutral organic bodies. In a sense, they are liquid waxes but are characteristically different from the ordinary paraffin waxes in that they contain an ester group. Such unsaturated mono-esters containing a single ester group, may be represented by the following generic formula



wherein R represents an aliphatic group or chain of relatively high molecular weight, at least one of said aliphatic groups being unsaturated.

In practicing my invention, pure mono-esters or mixtures thereof may be employed. The esters or mixtures which are liquid at room temperature and which have a boiling point substantially above 370° F. are advantageous. To produce high grade sulphurized products, for the present purposes, I find it advantageous to use, as the starting material, unsaturated aliphatic esters containing a single ester group and having the following properties:

Specific gravity, 60°/60° F.	0.878-0.884
Viscosity, S. U. V., 100° F.	95-110
Flash, O. C., °F.	minimum 490
Pour, °F.	maximum +40
Color, N. P. A., not darker than	1.5
Neutralization number	maximum 0.5
Oleic acid eq., percent	maximum 0.25
Saponification number	125-135
Iodine number	80-90

Good grade sperm oils having such properties are readily available and as described in my companion copending application Ser. No. 108,306 such sperm oils are generally useful in the commercial manufacture of my new sulphurized mono-esters. In that application I claim such sulphurized sperm oils and methods of making the same.

As set forth in that application, it is known that sperm oil is a mixture of mono-esters of the general type given ante; the characteristic esters thereof being mono-esters of unsaturated fatty acids of the oleic series and monohydric alcohols of the ethylene series.

That is, in the general practice of my invention one or more of the mono-esters present in sperm oil may be used to produce sulphurized mono-

esters which are substantially neutral organic sulphides.

Likewise, I have found that other unsaturated mono-esters, such as mono-esters of unsaturated aliphatic monovalent acids with saturated aliphatic monohydric alcohols and of saturated aliphatic mono-basic acids with unsaturated aliphatic monohydric alcohols, can be employed to also produce substantially neutral organic sulphur compounds. For instance, the mono-esters of simple alcohols such as methyl, ethyl, etc., may be used when the aliphatic chain of the unsaturated acid is sufficiently long to give the ester the desired physical properties. That is, with esters of the higher fatty acids of the oleic series, the aliphatic group of the alcohol may be a relatively short chain; the total length of the whole ester chain being important in securing the results here obtained. However, with the higher alcohols, the esters are more balanced in relation to the ester group and this is advantageous for many purposes.

Likewise, it is advantageous to employ esters in which there is unsaturation in the aliphatic group of the alcohol component; the aliphatic group of the acid component being saturated. Illustrative examples of such esters are given post.

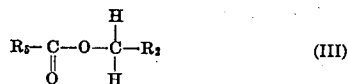
The various major types of mono-esters, useful for making my substantially neutral organic sulphur compounds, may be represented by the following formulae:



wherein both R₂ and R₃ are olefinic aliphatic chains; the R₂ and R₃ being advantageously chains having the formula —C_nH_{2n-1}. When n is at least 3 and each chain has a terminal —CH₃ group, good sulphurized products are readily obtained; the sulphurized esters being quite miscible with mineral oils.

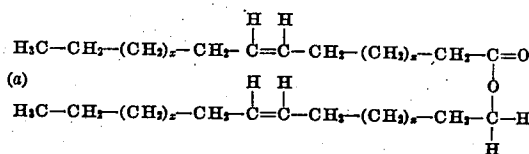


wherein R₃ is an olefinic aliphatic chain and R₄ is a saturated aliphatic group. The statements made ante, as to the advantageous types of olefinic aliphatic groups, are also applicable to this class of mono-ester.

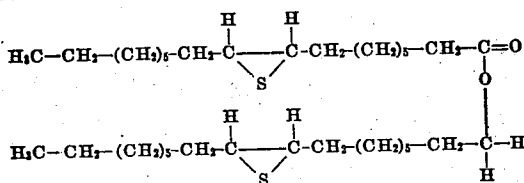


wherein R₅ is a saturated aliphatic group and R₂ is an olefinic aliphatic chain. Advantageously, the R₂ may be a chain containing a terminal —CH₃ group and having the formula —C_nH_{2n-1}, with n being at least 3.

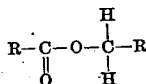
I have found that in lieu of natural mixtures of esters, such as sperm oil, etc., the esters of Class I are likewise advantageous. They are representative of the characteristic esters of sperm oil. That is, the ester is unsaturated (contains double bonds) in both the acid and alcohol components thereof. Generally, the esters of oleic acid and other monocarboxylic acids of the oleic series with unsaturated monohydric wax alcohols may be employed. For instance, the mono-esters having the following formula:



wherein x is from 1 to 7, have various properties both in the original and sulphurized state, that are desirable in these methods. The oleates are satisfactory and are ordinarily employed. The neutral stable sulphide of the oleate of oleyl alcohol may be represented by the following formula:



The oleate of oleyl alcohol is typical of the balanced esters wherein the acid is esterified with the corresponding alcohol; such esters having the formula

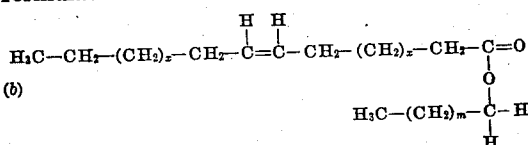


wherein the groups represented by R are like olefinic aliphatic groups. However, the alcohol component of the ester does not necessarily have to correspond with the acid component thereof. The oleates of any of the olefinic alcohols present in sperm oil may be used.

The following specific esters are typical and illustrative of the general Class I:

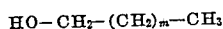
Allyl oleate
Decylene oleate
Dodecylene oleate
Pentadecylene oleate

The esters of Class II are similar to those of Class I except that the alcohol component is a saturated aliphatic compound. Here again, the oleates are satisfactory and are ordinarily used. Generally, for most purposes, satisfactory results are obtained with the esters having the following formula:



wherein m and x are at least 1; particularly those in which x is 1 to 7 and m is 1 to 20.

However, any of the unsaturated mono-esters of the monohydric alcohols having the formula



wherein m is 4 to 16 are advantageous for many purposes. Theoleate of dodecanol is illustrative of such esters.

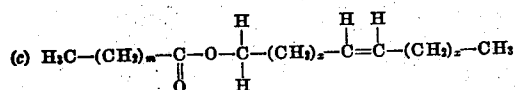
Again, the methyl, ethyl, propyl or butyl esters of olefinic monocarboxylic acids such as oleic acid may be used.

The following specific esters are typical and illustrative of the general Class II:

Methyl oleate
Iso-propyl oleate
Hexyl oleate
Lauryl oleate
Cetyl oleate

On the other hand, the mono-esters of Class III are similar to those of Class I, except that they contain a saturated fatty acid component. The esters of the olefinic monohydric alcohols of sperm oil with appropriate fatty acids may be

employed. In using this class of mono-esters, those containing the same alcohol component as shown in Class I, are employed. The mono-esters of this class which have the following formula:



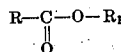
wherein m and x are at least 1, are advantageous. They are high-molecular weight mono-esters of saturated fatty acids with alcohols of the ethylene series. The fatty acid component thereof may be any of those having an aliphatic chain within the range indicated which will produce the desired physical properties and boiling ranges.

The following specific esters are typical and illustrative of Class III:

Allyl palmitate
Decylene laurate
Dodecylene caprylate
Oleyl butyrate

Any of the above mono-esters may be readily sulphurized to obtain neutral organic sulphur compounds useful for the present purposes. Generally, esters of Classes II and III require less sulphur to form the neutral compounds than do the esters of Class I; they only having unsaturation (double bond) on one side of the ester group.

In the broad practice of the present invention any unsaturated mono-ester within the scope of the following formula, may be used with advantage to produce the new sulphurized mono-esters here claimed:



wherein R and R₁ represent straight chain aliphatic groups, one said group being saturated and the other being unsaturated. This formula is generic to the mono-esters of the Classes II and III set forth ante.

In preparing the sulphurized mono-esters here claimed, the said unsaturated fatty mono-esters may be sulphurized with sulphur by reacting and chemically combining the sulphur with such mono-esters, using any method which yields substantially neutral organic sulphur compounds, recoverable as such, in a form that is sufficiently free of corrosive and insoluble bodies. Advantageously the mono-ester may be reacted with suitable amounts of sulphur at a temperature between 300 and 380° F., the reaction being continued until the sulphur is combined in the form of neutral organic sulphur compounds. Usually from 5 to 20 parts of sulphur to 100 parts of ester are employed. Generally I employ substantially the amount of sulphur that is necessary to saturate the double bond of the ester used. The degree of the unsaturation of the ester can be readily determined by means of its iodine value or number.

In one method of controlling the sulphurization, the mono-ester is first preheated to about the lower reaction temperature (300° F.) and then the required amount of sulphur is gradually added to the preheated ester, the rate of addition being adjusted so that the temperature of the reaction mixture is gradually and quietly increased to just below the upper limit (380° F.). After all the sulphur has been added, the temperature tends to drop slightly and then the reaction mixture is maintained at about 340° F. until the reaction is complete. The course of the reaction

may be easily followed by withdrawing test samples and determining the change in viscosity. After the proper viscosity has been obtained the end point can easily be determined by diluting the sulphurized oil with a standard amount of mineral oil and determining its corrosive action upon a copper strip. When the copper strip remains unattacked or shows only a slight stain, the reaction is complete. Then the sulphurized ester is cooled to room temperature. It can be stored in metal drums and other suitable containers.

The copper strip test here employed was devised by me in 1917 for determining the relative corrosiveness of lubricating oils. The procedure is as follows:

A mechanically polished copper strip half inch by 3 inches is immersed in 25 cc. of lubricant contained in a test tube which is placed in a boiling water bath, and held at the temperature of boiling water for 3 hours. At the end of this time the strip is removed and adhering oil washed off with a light naphtha and examined for evidence of corrosion. A negative test is one in which the strip shows only a slight stain or discoloration. The positive test is one where the strip shows considerable discoloration or tendency to scale, indicating presence of corrosive constituents in the lubricant.

In preparing the diluted sample for a test, I ordinarily use a standard mineral oil having the following properties:

Gravity, °A. P. I.	27.1
Specific gravity, 60°/60° F.	0.8922
Viscosity, S. U. V., 100° F.	1059
Viscosity, S. U. V., 130° F.	420
Viscosity, S. U. V., 210° F.	89
Viscosity index	92
Flash, O. C., °F.	470
Fire, O. C., °F.	545
Pour, °F.	+5
Color, N. P. A. dilution	4.25
Carbon residue, per cent.	0.44
Neutralization number	0.01

The sample of sulphurized ester is diluted with the above mineral oil in the ratio of 10:90 to obtain the sample used in determining the corrosion by the copper strip method. The copper strip is removed from the heated oil sample after 3 hours, and then wiped dry and inspected in the usual manner. Sometimes, a test mixture the same as the desired compounded lubricant is used in the above test.

With the above mentioned controlled methods of sulphurization there is but little loss of sulphur; the percentage of combined sulphur in the sulphurized ester is approximately that in the reaction mixture. During the sulphurization very little hydrogen sulphide is formed. With careful operation, finely divided sulphur may be gradually added to the preheated ester by sifting, etc., with little or no mechanical loss of sulphur.

The viscosity of the ester increases as the sulphur is added and upon combination of most of the sulphur the viscosity tends to remain substantially constant as the heating is continued. While the reaction temperature should be sufficiently high to obtain the best combination of the sulphur, exceeding high temperatures should be avoided to prevent undesirable side reactions.

In such methods, all the sulphur is usually added within about 2 hours and ordinarily from 16 to 24 hours further heating at a temperature between 300 and 380° F. is required to combine the

added sulphur. The sulphurized esters so obtained have a combination of properties rendering them particularly useful as an ingredient in compounded lubricants. Similar sulphurized esters may also be obtained by other methods wherein sulphurization is appropriately controlled.

The most advantageous sulphurized esters, for many purposes, are characterized by the following properties:

Gravity, °A. P. I.	12.6-15.6
Viscosity, S. U. V., 210° F.	100-300
Pour, °F. (not greater than)	+45
Sulphur, per cent.	6.0-16.0
Neutralization number	1.0-6.0

However, as set forth post, sulphurized esters having somewhat different properties may be used in special cases to produce particular types of lubricating compositions.

The sulphurized fatty mono-esters produced according to the present invention are really soluble in the ordinary grades of lubricating oils. They are fully miscible and compatible with the high gravity oils such as paraffinic base oils (Pennsylvania, etc.) and solvent refined oils, etc., over a wide range of conditions such as temperature, proportions, etc. They may be employed in making improved lubricants as described in my copending applications Serial Nos. 60,355 and 60,357, which are directed to improved lubricants containing sulphurized fatty mono-esters and sulphurized sperm oils. In those applications there are given numerous illustrative embodiments of such commercial blended lubricants. Also my sulphurized fatty mono-esters obtained by the present invention may be used in making improved pipe thread lubricants as disclosed in my copending application Serial No. 60,356, (now Patent No. 2,065,248) filed January 22, 1936, that application being directed to such improved pipe thread lubricants.

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

Example 1.—This example illustrates the sulphurization of an ester of Class I; a balanced ester being employed.

The oleate of oleyl alcohol is sulphurized at temperatures between 325 and 360° F. with about 12 per cent of sulphur by weight on the said oleate, by reacting 500 parts of said oleate with 60 parts of sulphur. There is obtained a sulphurized mono-ester containing 10.7 per cent of sulphur and having a viscosity S. U. V. at 210° F. of approximately 200-350.

The oleate of dodecylene alcohol may be likewise sulphurized. This oleate requires 14.38 per cent sulphur to convert it into a substantially neutral sulphide containing 12.5 per cent combined sulphur. In practice a good product is obtained by sulphurizing 100 parts of this oleate with 14 parts sulphur. Again the decylene acid ester of decylene alcohol may be employed. It requires 17.0 per cent of sulphur on the ester to convert it into a substantially neutral sulfide containing 14.9 per cent of combined sulphur.

Example 2.—This example illustrates the sulphurization of an ester of Class II; a simple alkyl ester of an unsaturated fatty acid being employed.

Ethyl oleate is sulphurized at temperatures between 300 and 360° F. with about 12 per cent of sulphur by weight on the said ethyl ester. There

is obtained a sulphurized mono-ester having the following properties:

Gravity, °A. P. I.	15.4
Specific gravity, 60°/60° F.	0.9632
5 Viscosity, S. U. V.:	
100° F.	128
210° F.	44
Pour, °F.	+20
Sulphur (B), per cent.	10.08
10 Neutralization number	5.5

In the above table, the symbol (B) signifies that the percentage of sulphur was determined by A. S. T. M. method D 129-34.

- 15 In lieu of the ethyl oleate, the propyl oleate may be employed. This oleate requires about 11 per cent of sulphur to form the substantially neutral sulphide.

Likewise, the ester of higher saturated alcohols may be used. The oleate of dodecyl alcohol requires 8.8 per cent sulphur, by weight on the ester, to form a neutral sulphide containing 6.8 per cent sulphur. In practice, 100 parts of this ester is sulphurized with 9 parts of sulphur. A commercial form of dodecyl alcohol is "Lorol", a trade product obtained by hydrogenating the fatty acids of coconut oil. The sulphurized mono-ester obtained from this oleate has the following properties:

30 Gravity, °A. P. I.	15.0
Specific gravity, 60°/60° F.	0.9659
Viscosity, S. U. V., 210° F.	94
Pour, °F.	+25
Sulphur (B), per cent.	6.5
35 Neutralization number	2.0

Example 3.—This example illustrates the sulphurization of an ester of Class III; an unsaturated alcohol ester of a saturated fatty acid being employed.

40 The decylene palmitate is sulphurized at temperatures between 300 and 360° F. with about 10 per cent of sulphur by weight on said ester by reacting 90 parts of the said ester with 10 parts of sulphur in the manner described ante. There is obtained a sulphurized mono-ester having the following properties:

Gravity, °A. P. I.	14.8
Specific gravity, 60°/60° F.	0.9672
50 Viscosity, S. U. V., 210° F.	95
Pour, °F.	+25
Sulphur (B), per cent.	8.3
Neutralization number	1.9

55 Any of the sulphurized mono-esters obtained in Examples 1, 2 and 3 may be employed in making excellent extreme pressure lubricants, by incorporating them in various grades and types of mineral lubricating oils.

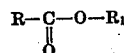
60 While in the foregoing examples I have described direct sulphurization of the mono-esters, I at times find it advantageous to sulphurize them in the presence of a diluent oil, as for instance a petroleum hydrocarbon oil, which may well be the same as the oil used for the base for manufacturing the compound lubricant. That is, some of the mineral oil may be mixed with the mono-ester prior to the addition of the sulphur. The use of relatively high boiling diluents with the lower boiling mono-esters is advantageous, as in this way molten sulphur can be readily brought into contact with the ester. Also by employing diluent oil, the reaction mixture may be maintained in a freely mobile state, even with the 75 esters of the greatest molecular weight.

When a mixture of sulphurized esters is to be employed, I sometimes blend together two or more sulphurized products, instead of sulphurizing a mixture of esters. In this way a more direct control and adjustment of the properties of the sulphurized material, for addition to special lubricants, may be obtained. Also, as stated, ante, a mixture of mono-esters may be employed as the starting material for sulphurization and thus a mixture of sulphurized esters directly obtained.

In this specification and the claims, the term "sulphurizing" means sulphurizing with sulphur itself, that is, reacting and chemically combining sulphur with the aliphatic mono-esters set forth ante. Likewise in this specification and claims the "sulphurized" esters are those containing the sulphur in chemical combination with the mono-ester. These sulphurized mono-esters are free of chlorine and are substantially neutral organic sulphides. That is, the processes and products of this invention are characteristically different from the sulpho-chlorinated fatty oils and esters obtainable by reacting sulphur chloride with fatty oils, etc.

What I claim is:

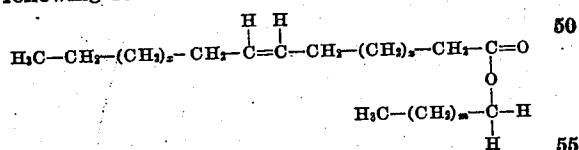
1. As an improvement in the manufacture of sulphurized esters, the improved process which comprises sulphurizing an unsaturated fatty aliphatic mono-ester having the following formula



wherein R and R₁ represent straight chain aliphatic groups, one of said aliphatic groups being saturated and the other being unsaturated, by chemically combining said ester with sulphur to saturate said unsaturated group and to produce substantially neutral organic sulphur compounds.

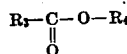
2. In the process of claim 1, the steps which comprise preheating the said unsaturated fatty mono-ester to a temperature between 300 and 380° F., gradually adding finely divided sulphur to the hot ester and maintaining the reaction mixture at said temperature until a substantially neutral sulphurized product is obtained.

3. The process of claim 1 wherein said unsaturated fatty mono-ester is an ester having the following formula:



wherein x is a number from 1 to 7 and m is a number from 0 to 20.

4. As an improvement in the manufacture of sulphurized esters, the improved process which comprises sulphurizing an unsaturated aliphatic mono-ester having the following formula



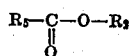
wherein R₂ is a mono-olefinic, straight chain aliphatic group and R₄ is a saturated straight chain aliphatic group, by chemically combining said ester with sulphur to produce substantially neutral organic sulphur compounds.

5. The process of claim 4 wherein said unsaturated mono-ester is dodecyl oleate.

6. The process of claim 4 wherein said unsaturated mono-ester is ethyl oleate.

7. As an improvement in the manufacture of sulphurized esters, the improved process which

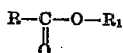
comprises sulphurizing an unsaturated aliphatic mono-ester having the following formula:



5 wherein R_2 is a saturated aliphatic group and R_1 is an olefinic aliphatic group.

8. The process of claim 7 wherein said unsaturated mono-ester is decylene palmitate.

10 9. As a new product, a sulphurized fatty mono-ester comprising the reaction product of sulphur and a mono-ester having the following formula



15 wherein R and R_1 represent straight chain aliphatic groups, one of said aliphatic groups being saturated and the other being unsaturated, said sulphurized ester being miscible with mineral lubricating oils and being a substantially neutral organic sulphur compound.

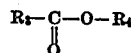
20 10. A new composition of matter comprising the reaction product of elemental sulphur and a mono-ester of an unsaturated monovalent aliphatic acid and a monovalent saturated aliphatic alcohol.

25 11. As a new product, the sulphurized fatty mono-esters of claim 9 having the following properties:

30 Gravity, °A. P. I.	12.6-15.6
Viscosity, S. U. V., 210° F.	100-300
Pour, °F. (not greater than)	+45
Sulphur, per cent.	6.0-16.0
35 Neutralization number	1.0-6.0

said sulphurized esters being miscible with mineral oils and capable of improving the lubricating qualities of said mineral oils.

12. As a new product, a sulphurized fatty mono-ester comprising the reaction product of sulphur and a mono-ester having the following formula

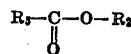


10 wherein R_3 is a mono-olefinic, straight chain aliphatic group and R_4 is a saturated straight chain aliphatic group, said sulphurized ester being miscible with mineral lubricating oils and being a substantially neutral organic sulphur compound.

15 13. As a new product, sulphurized dodecyl oleate.

14. As a new product, sulphurized ethyl oleate.

20 15. As a new product, a sulphurized fatty mono-ester comprising the reaction product of sulphur and a mono-ester having the following formula:



25 wherein R_5 is a saturated aliphatic group and R_2 is an olefinic aliphatic group, said sulphurized ester being miscible with mineral lubricating oils and being a substantially neutral organic sulphur compound.

30 16. As a new product, sulphurized decylene palmitate.

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