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METHODS OF MAKING SULPHURIZED SPERM OILS AND THE LIKE

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This invention relates to improved methods of making sulphurized mono-esters of fatty acids and it comprises methods wherein sperm oils and like unsaturated mono-esters are quickly sulphurized under controlled conditions and the sulphurized esters so obtained are refined to remove various deleterious by-products as may be present therein, the sulphurized esters being sometimes admixed with another oil, such as mineral oils, etc., prior to or during or subsequent to such refining; and it also comprises the improved oil compositions so obtained; all as more fully hereinafter set forth and as claimed.

The manufacture of sulphurized sperm oils and like mono-esters and of lubricating oil compositions containing such sulphurized esters are described and claimed in co-pending applications, Serial No. 60,355 and Serial No. 60,357, filed January 22, 1936, by Herschel G. Smith, one of the present applicants. In the methods there described, the sperm oil is controlledly sulphurized to produce simple addition products and to prevent or retard various side reactions by which deleterious by-products are formed, the sulphurization being effected between 300° and 385° F., with the main part of the reaction occurring between 335° and 360° F. Within the latter temperature range no appreciable amounts of such by-products are formed. To readily accomplish this, the sperm oil is preheated to about 320° F., and to this preheated oil sulphur is slowly added at such a rate that the temperature of the mixture is gradually and quietly raised to within the said temperature range by the heat of the exothermic reaction. By controlling the temperature and rate of reaction, over-vulcanization and undesirable side reactions are substantially avoided. The sulphurized mono-esters so obtained, being substantially free of undesirable by-products, etc., and containing the sulphur combined in the form of neutral organic sulphur compounds, are excellent improvement agents for mineral lubricating oils and other petroleum products.

As pointed out in the said applications, the undesirable by-products are formed when the reaction with sulphur becomes too vigorous and the temperature exceeds 385° F.

We have now discovered that the deleterious by-products formed at temperatures between 360° and 400° F. may be effectively removed from the sulphurized sperm oil by suitable means. They can be removed by treating the sulphurized mono-esters with adsorbent clay, with or without preliminary acid treatment, according to the methods set forth in our co-pending application Serial No. 103,051, filed September 28, 1936. As there stated, acid-washed clays, etc., are capable of fixedly adsorbing such deleterious impurities from oil compositions containing sulphurized sperm oils; and, as further stated, the preliminary treatment with acid, such as concentrated sulphuric acid, facilitates refining such compositions. Any of the procedures and materials described in that application may be employed in the present invention for refining the sulphurized sperm oils here produced by quick sulphurization.

Thus we have found that the exacting control of sulphurization described ante is not the only means by which the deleterious effect of by-products in the sulphurized sperm oil may be avoided. The sulphurized sperm oils produced by the present methods are also excellent improvement agents for mineral oils and like purposes. Further, by procedures given post, we obtain sulphurized sperm oils and compositions thereof even superior in color, viscosity, and other properties to the materials directly obtained by the previous processes for controlled sulphurization of sperm oil.

In addition to yielding superior oil compositions, there are many other advantages in the multi-step process of the present invention wherein the sperm oil is sulphurized and then refined, as set forth post. Certain of these advantages are inherent in the process procedure itself.

Certain advantageous improvements are now possible in the rapid sulphurizing procedure, the first step of the present method. As the formation of some by-products is now permissible, their being subsequently removed, the time required for combining substantially all of the sulphur and producing the sulphurized sperm oil is shorter. That is, by the present methods the sperm oil is quickly sulphurized in an advantageous manner.

This is accomplished by pre-heating the oil and adding the sulphur as fast as it will dissolve in the hot oil; the mixture being positively cooled to dissipate the heat of the reaction and control the temperature. In this way the time required for adding the sulphur and fixedly combining it with the oil in the form of simple sulphur-addition products may be materially shortened.

By these operations, performed at somewhat higher temperatures than in the prior methods described ante, the sulphur dissolves more quickly and the reaction is faster. At the temperatures between 360° and 450° F. here employed and with the oil pre-heated to about 340° F., the time re-

quired for producing the sulphurized sperm oil is reduced to a minimum. In the present methods, the heat of the reaction quickly raises the temperature of the sperm oil to the desired reaction temperature, which is held below 400° F. by suitable cooling means. External or internal circulation of a suitable cooling medium may be employed. Either jacketed reaction vessels or those equipped with internal cooling coils may be used in making the sulphurized sperm oil.

Although the temperatures are relatively high, the time required to complete the reaction is sufficiently short to prevent substantial decomposition of the desirable sulphur-addition products, even though the reaction is relatively vigorous.

While the range of temperatures permissible in the present sulphurization methods is more flexible, the temperature is again controlled to prevent any appreciable over-vulcanization. That is, the conversion of the sperm oil into sulphurized products which at room temperatures are semi-solid or solid gelled materials is avoided. Such gelled products are relatively insoluble or immiscible with mineral oils and are not satisfactory for the present purposes. The production of such solid sulphurized oil products represents loss of valuable starting materials, even when the amounts formed are insufficient to render the reaction mixture difficultly miscible with petroleum oil.

Over-vulcanization and decomposition of the valuable sulphurized mono-esters are avoided by holding the reaction temperature below 400° F., as described ante. Thus the reaction is effectively controlled although it is vigorous and rapid.

After the sulphur has combined, the reaction mixture is rapidly cooled below 360° F. In this way any undesirable side reactions are checked. This may be accomplished by various cooling means. Advantageously, cooling may be effected by quenching the hot mixture with cool mineral oil. For instance, an equal amount by weight of mineral oil can be mixed with the hot sulphurized sperm oil. The solution of sulphurized mono-esters in mineral oil so obtained is readily adapted to the subsequent refining treatments and yields a valuable intermediate product for making a wide range of lubricants. Also, the hot sulphurized sperm oil can be cooled by means of a suitable cooling medium rapidly circulated in the jacketed reaction vessel or through coils immersed in the reaction mixture. This is also advantageous, as a similar external or internal cooling means may be employed to control the reaction temperature. For instance, the same means for dissipating the heat of reaction is also utilized to cool the sulphurized sperm oil at the end of the reaction.

As pointed out in application Serial No. 60,355, mentioned ante, sperm oil while frequently termed a fatty oil is quite different from the fatty oils which are tri-esters of glycerine. Sperm oil is composed principally of fatty esters of monohydric alcohols of relatively high molecular weight, and, being a mono-ester, sperm oil is a liquid wax of the ester type. Being an ester, it is also different from the paraffin hydrocarbons commercially known as waxes. Sperm oil is obtained from the head cavities and blubber of the cachelot or sperm whale (*Physeter macrocephalus*). The crude oil contains varying amounts of spermaceti and like solid waxes of the ester type. In refining the oil these waxes are removed by refrigeration and pressing to obtain commercial sperm oils. The commercial oils are known as winter sperm oil, spring sperm oil, etc., and are substantially free from solid waxes. The commercial sperm oil is a thin, yellow liquid and, when of good quality, is nearly free from odor.

As set forth in application Serial No. 60,357, also mentioned ante, mono-esters of the sperm oil type may be synthetically prepared. By the methods described therein, synthetic sperm oils of controlled color, viscosity, and other desirable properties may be readily prepared. By those methods a wide range of unsaturated mono-esters of fatty acids and mono-hydric alcohols can be obtained, all of which are capable of being sulphurized to produce valuable sulphurized products useful as improvement agents for mineral oils. In the practice of the present invention any mono-esters of those characteristic types may be employed. However, sperm oil ordinarily is here employed. Usually a good grade of commerical sperm oil is used, as they are readily available in quantity and yield good sulphurized materials.

Advantageously we may employ as the starting material commercial sperm oils having the following properties:

Specific gravity, 60°/60° F.	0.878–0.900
Viscosity, S. U. V. at 100° F., seconds	90–120
Flash, O. C., °F.	450–500
Pour, °F.	+35–+65
Color, N. P. A.	1.0–3.0
Neutralization number	0–3.0
Oleic acid equiv., percent	0–1.5
Saponification number	120–150
Iodine number	80–100

The sulphur employed should be of good quality and free from any abrasive material such as sand, fossil fragments, etc., and sublimed sulphur such as flowers of sulphur is advantageous. However, and finely ground sulphur, such as sulphur flour may be used.

The amount of sulphur used to sulphurize the above-mentioned mono-esters may be varied according to the particular mono-esters being processed and the specific characteristics desired in the final product. Generally, with the mono-esters as a class capable of sulphurization, the ratio of sulphur to oil may be between 5:95 and 20:80, and good sulphurized esters are obtained, having desirable amounts of sulphur combined therewith in the form of substantially neutral sulphur compounds. Here, the amount of sulphur added to the pre-heated sperm oil is substantially less than that necessaray to completely saturate all of the sperm oil used. In the present sulphurization methods, it is advantageous to add between 5 to 12 parts of sulphur per 100 parts of the usual commercial sperm oil by weight on the oil. Such amounts of sulphur can be rapidly added to and combined with the sperm oil and the sulphurized sperm oils obtained by the subsequent refining are of special quality. The refined sulphurized esters are thinly mobile and have a light color and other properties rendering them particularly advantageous as improvement agents for high grade lubricants, such as highly refined motor oils, etc.

By means of the improved sulphurizing procedures of the present invention, small amounts of sulphur, as indicated ante, give high grade materials, and by the subsequent procedures here employed. Using the relatively small amounts of sulphur in such procedures, the rapid sulphuriza-

tion is further facilitated. Ordinarily, the sulphurization may be completed within about three hours. As the sulphur almost immediately combines with the sperm oil after it goes into solution therein, the sulphurization is completed shortly after the last portion of sulphur has been added. Sometimes the reaction may be completed within as short a time as 45 minutes after the sulphur is all added to the reaction mixture, the time depending upon the size of the batch, the temperature and other factors. After the sulphur is all added to the hot reaction mixture, the mixture is quickly cooled as described ante.

In the usual practice of this invention, the sperm oil is pre-heated to about 340° F., and from 5 to 12 per cent of finely divided sulphur is added as fast as it will dissolve. As soon as the first of the sulphur has dissolved, the cooling of the reaction mixture is started to prevent such sudden rise in temperature by the heat of the reaction as will cause the reaction to become unmanageable. As the reaction proceeds the cooling medium is adjusted to maintain the desired temperatures, which are ordinarily held in the neighborhood of 375° F. While vigorous cooling is employed until all the sulphur has been added, after most of the sulphur has been combined less cooling is required to dissipate the heat of the reaction. With proper cooling, the above amounts of sulphur may be added within 30 minutes, and the reaction is substantially complete within 1.5 hours after all the sulphur has been added. At that stage the sulphurized oil, if cooled to room temperature, is thinly mobile, being much less viscous than the prior sulphurized sperm oil.

To cool the sulphurized oil quickly after the reaction is completed, it is pumped into a sufficient amount of mineral lubricating oil to lower its temperature below 300° F., the mixture being agitated during this operation. Sometimes the mineral oil is poured into the sulphurized oil while still in the reaction vessel. Either of these procedures is an advantageous means to quench the hot mixture of sulphurized oil and reaction products. The warm solutions so obtained are intermediate products in the manufacture of lubricants and they can be advantageously refined. Although the sulphurized sperm oil at the end of the sulphurization is relatively hot, say at about 375° F., the addition of mineral oil readily produces mineral oil solutions thereof which are substantially below 300° F. The amount and temperature of the mineral oil so added is generally adjusted to produce oil mixtures having a temperature similar to that employed in the next operation of these processes. By adding an equal weight of mineral oil at ordinary temperature (room temperature) to the hot sulphurized sperm oil, the oil compositions produced are at approximately 200° F.

The oil composition now being at a temperature of about 200° F. is ready for the acid treatment, that temperature being within the range at which the acid treatment is particularly effective, namely between 150° and 225° F. To the warm oil composition there is added sufficient concentrated sulphuric acid, containing 80 to 100 per cent H_2SO_4, to effect the desired acid refining of the oil composition. Ordinarily, 5 to 25 pounds of such acid to a barrel (400 pounds) of oil composition is sufficient. After adding the acid, the mixture is thoroughly agitated while maintained at the above temperatures, here at about 220° F. After the acid treatment is substantially complete, the agitation is discontinued and the acid sludge permitted to settle out of the sour oil. With the temperature above 150° F., the stratification is sharp and no appreciable amount of refined oil remains mechanically trapped in the acid sludge under ordinary conditions. The acid sludge is withdrawn and the sour oil so separated is ready for the clay treatment. In the above operation control of temperature is important because at temperatures below 125° F. the acid sludge does not properly separate and little or no stratification of the sour oil is obtained. In fact, the temperatures may be advantageously in the upper part of the range specified for acid treatment. By using temperatures between 200° and 225° F., the acid sludge is converted into a hard, solid material which will readily separate from the sour oil composition. In such procedure the hardened acid sludge is separated by filtration rather than by settling; any residue of hardened sludge remaining in the sour oil being removed by filter pressing after the bulk of the acid sludge has settled out and been removed.

Irrespective of the exact manner in which the acid sludge is formed and removed, the sour oil composition may be readily refined by treatment with clay.

In the clay-refining operation the temperature is also controlled to insure complete refining. Advantageously, the temperature employed is between 250° and 275° F. However, the temperature should be held below 300° F. At higher temperatures discoloration of the oil occurs and overheating offsets the improvement in color obtained by this clay treatment.

The sour oil, after separation of the acid sludge, is admixed with a suitable amount of acid-washed clay, such as those commonly used in refining mineral oils and known commercially as Filtrol. The oil-clay mixture is warmed to approximately 275° F. and agitated until the clay has adsorbed the undesirable impurities. Usually from 1 to 30 per cent of such acid-washed clay is sufficient for this purpose. With the sulphurized oils prepared with the amounts of sulphur and acid-treated as described ante, approximately 20 per cent of clay is ordinarily satisfactory. A further advantage of employing the higher temperatures in acid-treating the sulphurized sperm oil is that only a slight heating of the sour oil is necessary to increase its temperature after admixture with the clay; the sour oil being here raised from 220° to 275° F.

In the clay treatment agitation at the said temperatures for about three hours is usually sufficient to adsorb the undesirable impurities present in such sour oil compositions. After the impurities have been fixedly adsorbed by the clay, the agitation is discontinued and the refined oil separated and recovered. Advantageously, this is accomplished by filter pressing the hot mixture. Also, the clay may be settled out of the refined oil composition.

Sometimes the acid treatment may be omitted, if an extremely light color is not required. That is, a clay treatment alone may be used to remove the deleterious impurities and improve the color and other properties of these oil compositions. Usually, in such instances, a single treatment with clay is employed. However, by using longer treatment with large amounts of clay or by repeated treatment with clay, products having a color and other properties approaching that secured by the combination of acid and clay treatment sometimes can be obtained.

When the refining is by clay treatment alone, the procedure given ante is slightly modified. In such instances, the cooling of the sulphurized sperm oil is so adjusted as to obtain an oil composition having a temperature of approximately 275° F. This being an advantageous temperature for clay treating, the clay may be directly added to the so-cooled oil composition. Further, if desired, the clay treatment can be effected in the same reaction vessel. In such advantageous procedures, the sperm oil is sulfurized as before and, upon completion of the sulfurization, the circulation of the cooling medium is discontinued. While continuing the agitation sufficient mineral oil is added to cool the mixture to the said temperature, say approximately in a ratio of 1:3 parts of mineral oil to sulphurized oil. The exact ratio depends upon several factors, such as the specific heats of the oils, natural radiation, and whether a pre-cooled mineral oil or one at ordinary temperature is added.

There is added approximately 30 per cent of the acid-washed clay by weight on the sulphurized sperm oil content of the so-diluted oil as soon as the sulphurized oil composition has been cooled to the desired temperature. During this time the agitation is continuous, but now a suitable heating medium, such as steam, is circulated in lieu of the previous cooling medium. The heating and agitation are continued until the clay fixedly adsorbs the undesirable impurities, about three hours being required. Then the mixture, while still hot, is filter pressed to remove the so-separated impurities and excess clay. On filtering the hot mixture the refined sulphurized sperm oil is readily separated from the suspended solid materials, it being extremely thin and mobile. In this operation the mixture is ordinarily pumped through the filter presses under substantial pressure. Thus the separation is rapid and smaller amounts of the hot oil composition remain adsorbed in the filtered clay. The filter cake may be extracted with a light paraffinic naphtha which dissolves the oil composition without disturbing the adsorbed impurities. As pointed out ante, paraffinic hydrocarbons have a precipitating action upon such undesirable impurities of these compositions.

The oil composition so recovered may be separately collected or it may be recycled and used in diluting another batch of reaction mixture containing sulphurized sperm oil. In fact, recycling may be employed to advantage in certain modifications of the present processes. For instance, the desirable oil constituents in the separated clays obtained during refining may be completely extracted by suitable means and the extract given an acid treatment to remove any impurities also extracted in such complete treatment of the spent clay. The sour oils from the acid treatment being introduced with the cold diluted oil in a subsequent clay treating operation, an acid refining may sometimes be used as a collateral operation to the main refining procedures and a part of the desirable products recycled in this manner. By using a rather light highly paraffinic mineral oil for such treatment of spent clay, this light oil solution may be employed as a diluent for cooling the reaction mixture of sulphurized materials. In any of these ways, the loss of valuable sulphurized sperm oil in either the acid sludge or spent clay may be reduced to a minimum.

Thus, various diluents may be employed in the present process and their amounts varied according to the exact combination of steps employed.

In fact, sometimes it is advantageous to omit the use of diluents entirely and directly refine the sulphurized sperm oils. In such instances, a combination acid and clay treatment is ordinarily used. In that modification of the present invention, the circulated cooling medium is lowered in temperature or is circulated more rapidly, after the sulphurization is complete, to bring the temperature to that desirable for the acid refining. With undiluted sulphurized esters the higher temperatures are employed for acid-treating, to maintain the sulphurized oil in as mobile condition as possible. As stated before, this produces hard, solid acid sludges which can be removed by filtration. After removal of the sludge by filtration, the sour oil is clay-treated as before.

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 an advantageous method of sulphurizing sperm oil, employing a commercial sperm oil having the following properties:

Gravity, °A. P. I.	29.0
Specific gravity, 60°/60° F.	0.8816
Viscosity, S. U. V., seconds:	
70° F.	171
100° F.	100
130° F.	71
210° F.	43.3
Flash, O. C., °F.	505
Pour point, °F.	35
Color, Saybolt	−5
Neutralization number	0.14
Saponification number	130.9
Iodine number	87

By the following procedure such oil is sulphurized under controlled conditions, using approximately 12 per cent sulphur by weight on the oil.

Into a direct-fired, open-top grease kettle, equipped with suitable cooling coils, we charge 8057 pounds of said sperm oil (1097 gal.). The oil is gradually heated to 340° F. in about 2 hours, while stirring. While continuing the stirring, 1098 pounds of sulphur flour (approximately 1 lb. of sulphur per gallon of oil) is rapidly added to the pre-heated oil over a period of 30 minutes. As soon as the reaction becomes vigorous, the heating is discontinued. The heat of reaction quickly raises the temperature to between 360° and 385° F., where it is maintained for one hour by sufficient cooling. After the sulphur has combined, the mixture is cooled to 275° F. for further treatment with clay, as shown in Example 2.

After all the sulphur dissolves, the viscosity changes as follows:

Minutes	Viscosity, S. U. V. at 210° F., seconds
15	90
30	105
45	116
60	125

In this way there is obtained 8955 pounds of sulphurized oil; the percentage yield by weight being approximately 98 per cent of the materials charged.

The sulphurized oils so obtained are of high quality and have the following properties:

Gravity, °A. P. I.	16.4
Specific gravity, 60°/60° F.	0.9567
Pounds per gallon	7.967
Pour, °F.	+60
Sulphur, B., per cent	9.28
Viscosity, S. U. V. at 210° F., sec.	135
Color, N. P. A. (dilute)	8.5
Neutralization number	0.58

Example 2.—The following example illustrates an advantageous embodiment of the clay refining procedure as applied to an undiluted, partially cooled sulphurized sperm oil such as that obtained in Example 1.

While continuing the agitation of the partially cooled sulphurized sperm oil there is added 1791 pounds of commercial acid-treated clay having fineness between 200 and 300 mesh. The mixture is maintained at 275° F. for approximately three hours. At the end of that time substantially all of the deleterious impurities are adsorbed by the clay. The mixture is then pumped to a suitable filter press and the hot refined sulphurized oil is separated from the excess clay and adsorbed impurities.

In the following table the properties of the sulphurized sperm oil before and after refining are given, together with the properties of a prior type of sulphurized sperm oil such as disclosed in Example 1, of application Serial No. 60,355, mentioned ante.

Properties	New type		Old type
	Before refining	After refining	
Gravity, °A. P. I.	16.4	16.6	14.1
Specific gravity	0.9567	0.9554	0.9718
Pounds per gallon	7.967	7.956	8.093
Viscosity, S. U. V. at 210° F., sec.	135	125	242
Pour, °F.	+60	+60	+45
Color, N. P. A.	8.5 (dil.)	4.5	Dark
Sulphur, B., percent	9.28	9.28	11.10
Neutralization number	0.58	0.48	0.63

In the above example, the filter cake may be treated by suitable means to recover the residual sulphurized sperm oil absorbed therein. Advantageously, the filter cake may be broken up and stirred into a relatively large volume of highly paraffinic mineral oil having the following properties:

Gravity, °A. P. I.	33.1
Specific gravity, 60°/60° F.	0.8597
Viscosity, S. U. V., seconds:	
100° F.	180
130° F.	98
210° F.	46
Viscosity index	108
V–G constant	.800
Flash, O. C., °F.	420
Fire, O. C., °F.	490
Pour, °F.	0
Color, N. P. A.	1.25
Sulphur, per cent by weight	.05
Carbon residue	.02
Copper strip test	Passes

After thoroughly agitating, the so-washed clay is permitted to settle. Then the mineral oil solution of recovered sulphurized sperm oil is siphoned off from the settled solids. This mineral oil solution may be advantageously employed as a diluent in quenching the hot sulphurized reaction mixture obtained in the sulphurizing procedures. When so recycled, it is ordinarily employed as a diluent to prepare intermediate compositions for acid refining.

Example 3.—This example illustrates those modifications of the present invention wherein the sulphurized sperm oil is quenched by dilution with a mineral oil and the intermediate product so obtained is acid-treated prior to the clay treatment. The following procedure is typical of the acid-refining procedures. The sulphurized sperm oil here refined is prepared by the procedure of Example 1, wherein the hot sulphurized mixture is quenched and cooled to 150° F. by adding to 1000 pounds of the hot oil 1000 pounds of pre-cooled paraffinic mineral lubricating oil, the mineral oil being sufficiently cooled to give the desired temperature when the oils are admixed. The paraffinic mineral oil employed has the following properties:

Gravity, °A. P. I.	33.1
Specific gravity, 60°/60° F.	0.8597
Viscosity, S. U. V., seconds:	
100° F.	180
130° F.	98
210° F.	46
Viscosity index	108
V–G constant	0.800
Flash, O. C., °F.	420
Fire, O. C., °F.	490
Pour, °F.	0
Color, N. P. A.	1.25
Sulphur, percent by weight	0.05
Carbon residue	0.02
Copper strip test	Passes

In lieu of that mineral oil, the solution of recovered sulphurized sperm oil obtained by washing the clay as set forth in Example 2 may be employed as the diluent.

To the intermediate oil mixture so obtained, while maintained at 150° F., there is added 50 pounds of 98 per cent sulphuric acid, ordinary commercial grade. This is approximately 10 pounds of acid per barrel of oil composition. The mixture is thoroughly stirred until uniform and then the mixture is heated to between 180° and 200° F., while continuing the agitation for approximately one hour. The agitation is then discontinued and the acid sludge permitted to settle out. The stratified acid sludge is usually withdrawn and so removed represents approximately 10 per cent of the oil composition being refined. The sour oil so obtained may be readily refined with clay.

Example 4.—The sour oil so obtained in Example 3 is clay refined by the procedure given in Example 2. Being a dilute sulphurized sperm oil, a suitable adjustment is made in the amount of acid-washed clay employed. Here, too, an excess of clay is employed; the clay also neutralizes the sour oil. To insure neutralization of such acid oil compositions, small amounts of lime are sometimes added. Approximately 15 per cent by weight of acid-washed clay on the oil composition satisfactorily refines the intermediate oil composition obtained in Example 3. If the diluent there employed is the mineral oil solution of recovered sulphurized sperm oil, a somewhat larger amount of clay may be employed, say 20 per cent. With the larger amount of clay a very thorough refining is obtained and the refined intermediate oil composition obtained has a very light color, being usually about 3 N. P. A.

The following table gives the properties of the

refined intermediate oil composition obtained by the combined acid and clay treatment of Examples 3 and 4; the same properties of the blended intermediate before acid refining and of the original sulphurized mixture are also given for purposes of comparison.

Properties	Sulphurized mixture original	Blended intermediate before acid refining	Refined intermediate acid and clay refined
Gravity, ° A. P. I	16.4	24.4	25.3
Specific gravity, 60°/60° F	0.9576	0.9076	0.9024
Pounds per gallon	7.967	7.558	7.514
Viscosity, S. U. V. at 210° F., seconds	135	71.1	67.9
Pour, ° F	+60	+45	+45
Color, N. P. A	8.5 (dil.)	4.75 (dil.)	3.5
Sulfur, percent	9.28	5.06	4.67
Neutralization number	0.58	0.26	0.5

The above refined solution of sulphurized oil in paraffinic motor oil is an excellent intermediate for preparing a wide range of commercial lubricants. A typical illustration of its use in making lubricating compositions is given post.

The combination acid and clay refining procedures may be employed also with advantage to sulphurized sperm oils prepared by Example 1, which have been diluted with mineral oils derived from a naphthenic base oil. When naphthenic lubricating oils derived from such a base by solvent extraction are employed, the preliminary acid treatment is further advantageous, particularly when effected at the higher temperatures. In this way intermediates are obtained which, when further diluted with more lubricating oil, particularly a similar solvent-extracted lubricating oil, produces motor oils and other lubricants having improved resistance to sludging.

The following example illustrates the use of the refined intermediate oil compositions containing the substantially pure sulphurized sperm oil dissolved in a mineral oil.

Example 5.—This example illustrates the preparation of an improved motor oil useful for lubricating alloy bearings, etc.

This improved motor oil is prepared by dissolving 1.8 per cent by weight of the refined intermediate oil composition of Example 4, in a paraffinic lubricating oil having the same properties as that employed in Example 3 to quench the hot sulphurized sperm oil. The paraffinic motor oil here employed is a S. A. E. 10 grade oil.

The motor oil produced from the refined intermediate contains 0.9 per cent of substantially pure sulphurized sperm oil. It is stable to light, has a very light color, and possesses an extremely high resistance to sludging.

Its properties in detail are as follows:

Properties	Oil containing new type sulphurized oil
Gravity, °A. P. I	32.9
Specific gravity, 60°/60° F	0.8607
Viscosity, S. U. V., seconds:	
100° F	184
130° F	100
Viscosity index	107
V-G constant	0.801
Flash, O. C., °F	430
Fire, O. C., °F	495
Pour, °F	−5
Sulphur, B., percent	0.15
Carbon residue	0.03
Neutralization number	0.02

This motor oil has extreme pressure characteristics. When tested by the Almen Test the following results were obtained:

Almen test	Untreated mineral lubricating oil	Oil containing new type sulphurized oil
Journal speed, R. P. M	600	600
Rubbing speed, feet per minute	40	40
Lever load, pounds	10	18
Torque, lb. ft./10	12	24
Unit load, lb./sq. in	5,000	9,000
Lubricant temperature, °F.:		
Initial	79	79
Final	105	137

The excellent character of this improved motor oil for lubricating special alloy bearings is clearly shown by the results obtained with the accelerated corrosion test ordinarily used to determine the suitability of lubricants for such alloys.

Special oxidation and corrosion test	Mineral lubricating oil	Improved lubricant
Time oxidized, hours	48	48
Oil bath temperature, °F	347	347
Air rate, cubic centimeters per hour	2,000	2,000
Oil volume, cubic centimeters	300	300
Oxidized oil:		
Gravity, °A. P. I	31.1	32.3
Viscosity, S. U. V., seconds:		
100° F	212	200
210° F	48	47
Viscosity index	107	103
Carbon residue, percent	0.39	0.26
Neutralization number	1.34	0.40
Sludge, percent	0.01	0.39
Cadmium-silver bearing:		
Weight before test, g	37.1528	36.3571
Weight after test, g	36.7515	36.3591
Change in weight, g	−0.4013	+0.0021
Weight loss, percent	1.08	Nil.
Appearance	Etched.	Good.

The improved intermediates produced by the present methods are useful in making other lubricating oils and lubricants having extreme pressure characteristics. My blending the refined intermediate with sufficient additional mineral lubricating oil, either those derived from paraffinic or naphthenic stocks to give compositions containing between 2 and 10 per cent of the rapidly sulphurized sperm oil, there are obtained lubricating oils having excellent properties and general utility for lubricating metals wherein the lubricant is subjected to high pressure, that is relatively high bearing loads. The so improved motor oils are useful in the various engines equipped with ordinary bearings, also.

In fact, these improved intermediates may be blended with other ingredients, in addition to the mineral oils, to produce a wide range of improved lubricants. By employing other suitable ingredients, greases, marine engine oils, locomotive driving journal compounds, steam cylinder lubricants, etc., may be readily prepared. That is, the intermediate oil compositions obtained by the present improved methods may be employed in preparing any of the particular lubricating compositions set forth in the said co-pending application, Serial No. 60,355.

Moreover, the present improved methods, as stated ante, are highly advantageous in preparing lubricants for special alloy bearings. Those compositions prepared by the present methods from paraffinic base lubricating oils, such as illustrated in Example 5, are very stable in storage

even when exposed to the action of light for long periods. Under such conditions there is no separation or insoluble matter. The oil compositions prepared entirely from lubricating oils derived from naphthenic base stocks show a marked improvement as to their sludging characteristics. That is, motor oils prepared by the present methods wherein a lubricating oil obtained by solvent extraction of naphthenic stocks is employed, both in diluting the hot sulphurized mono-esters and in the blending operations, are very advantageous in lubricating special alloy bearings in modern automobile engines. They are particularly stable in storage and have a relatively long life in the engine. Further, they have a marked resistance to sludging. Thus the lubricant requires less frequent change or replenishment in such engines when this type of improved motor oil is employed.

Also, by the present method blended oils may be readily and advantageously prepared. For instance, a refined intermediate comprising a sulphurized sperm oil dissolved in a lubricating oil derived from napththenic stock, and refined by a combined acid and clay treatment, may be advantageously further diluted and blended with a paraffinic lubricating oil. The intermediate having been thoroughly refined, the paraffinic oil may now be incorporated without giving rise to any tendency towards separation of in solubles when the oil composition is exposed to light for long periods. On the other hand, an intermediate oil composition comprising the sulphurized oil dissolved in paraffinic lubricating oil, and obtained by clay refining alone, may be advantageously diluted and blended with the naphthenic type lubricating oils. In either of the above types of motor oils or lubricants containing blended mineral oil bases, the lubricating oil derived from a paraffinic base or from a naphthenic base may be present as a major component of the lubricant.

The improved intermediates produced by the present methods are useful in making other lubricating oils and lubricants having extreme pressure characteristics. By blending the refined intermediate with sufficient additional mineral lubricating oil, either those derived from paraffinic or naphthenic stocks to given compositions containing between 2 and 10 per cent of the rapidly sulphurized sperm oil, there are obtained lubricating oils having excellent properties and general utility for lubricating metals wherein the lubricant is subjected to high pressure, that is, relatively high bearing loads. The so improved motor oils are useful in the various engines equipped with ordinary bearings, also.

In fact, these improved intermediates may be blended with other ingredients, in addition to the mineral oils, to produce a wide range of improved lubricants. By employing suitable other ingredients, greases, marine engine oils, locomotive driving journal compounds, steam cylinder lubricants, etc., may be readily prepared. That is, the intermediate oil compositions obtained by the present methods may be employed in preparing any of the particular lubricating compositions set forth in the said co-pending application Serial No. 60,355.

However, the present improved methods, as stated ante, are highly advantageous in preparing lubricants for special alloy bearings. Those compositions which are prepared by the present methods from paraffinic base lubricating oils, such as illustrated in Example 5, are very stable in storage, even when exposed to the action of light for long periods. Under such conditions there is no separation of insoluble matter. The oil compositions prepared entirely from lubricating oils derived from napththenic base stocks show improvement as to their sludging characteristics. That is, motor oils prepared by the present methods, wherein a lubricating oil obtained by solvent extraction of naphthenic stocks is employed in diluting the hot sulphurized mono-esters and in the blending operations, are very advantageous in lubricating special alloy bearings in modern automobile engines. They are particularly stable in storage and have a relatively long life in the engine. Further, they have improved resistance to sludging. Thus the lubricant requires less frequent change or replenishment in such engines when this type of improved motor oil is employed.

Also, by the present method, blended oils may be readily and advantageously prepared. For instance, a refined intermediate comprising a sulphurized sperm oil dissolved in a lubricating oil derived from naphthenic stock, and refined by a combined acid and clay treatment, may be advantageously further diluted and blended with a paraffinic lubricating oil. The intermediate having been thoroughly refined, the paraffinic oil may now be incorporated without giving rise to any tendency towards separation of insolubles when the composition is exposed to light for long periods. On the other hand, an intermediate oil composition comprising the sulphurized oil dissolved in paraffinic lubricating oil, and obtained by clay refining alone, may be advantageously diluted and blended with the naphthenic type lubricating oils. In either of the above types of motor oils or lubricants containing blended mineral oil bases, the lubricating oil derived from a paraffinic base or from a naphthenic base may be present as a major component of the lubricant.

The following example illustrates another advantageous method of making improved sulphurized sperm oil comopsitions by the present invention.

Example 6.—In this example, the sperm oil is sulphurized by the procedure of Example 1, with a smaller amount of sulphur, approximately 7 per cent by weight on the sperm oil being employed.

After the sulphur has combined, the hot sulphurized sperm oil is withdrawn from the reaction vessel and pumped into a relatively large volume of mineral lubricating oil, contained in a vessel suitable for the acid treatment. In so quenching, the mineral oil is employed in approximately the ration of 3:1 by weight on the hot sulphurized sperm oil. By so quenching the hot sulphurized sperm oil, an oil composition is obtained (an intermediate for refining) which is at approximately the temperature desired for acid treatment. The sulphurizing vessel is flushed with mineral oil, using an amount about equal in weight to the sulphurized sperm oil, and then the washings are combined with the main body of oil composition, the composition so obtained being then adjusted to approximately 20 per cent of sulphurized oil and having a temperature of about 150° F. In so quenching and diluting the sulphurized sperm oil, there is employed a lubricating oil obtained by solvent-extracting a mixed base stock.

This solvent-extracted oil has the following properties:

Gravity, °A. P. I.	27.8
Viscosity, S. U. V., seconds:	
100° F.	345
130° F.	160
210° F.	54.1
Flash, O. C., °F.	425
Fire, O. C., °F.	495
Color, N. P. A.	3.0

After this solution is brought to approximately 150° F., there is added 5 pounds of 80 per cent sulphuric acid per 100 pounds of oil composition. The mixture is agitated and gradually brought to between 200° and 225° F., and maintained at such temperatures for about one hour. The agitation is stopped and the temperature held at about 225° F. until the acid sludge is hardened and most of it settles out of the oil composition. The stratified oil composition (sour oil) is drawn off and is filter pressed while still hot.

The hot filtrate is then mixed with 10 pounds of acid-washed clay per 100 pounds of sour oil. The mixture is agitated and heated to approximately 275° F., being held at that temperature for three hours. The hot mixture is then filter pressed. The filtrate so obtained is a valuable intermediate oil composition. It is a refined material substantially free from the impurities deleterious in lubricating compositions. The refined intermediate so obtained may be converted into valuable motor oils for special alloy bearings. To prepare such improved motor oil, the refined intermediate is dissolved in sufficient of the same lubricating oil (solvent-extracted oil) employed ante to produce a finished solution containing approximately 0.8 per cent of refined sulphurized sperm oil. This improved motor oil has improved resistance to deterioration, in addition to lubricating alloy bearings without substantial corrosion of the same. That is, the improved motor oil has a relatively long life in lubricating engines equipped with such bearings.

The above refined intermediate may also be converted into improved motor oils by dissolving it in other lubricating oils. A different lubricating oil derived from a naphthenic base or mixed base stock may be employed so that the mineral oil component of the finished lubricant is a blended mixture of two or more lubricating oils. In this way, the final lubricant may contain oils of different S A E classification, for instance S A E 30 and S A E 40. Thus by the present invention, a fine adjustment of the properties of the finished lubricant can be readily obtained for the conversion of the intermediate oil composition into the finished lubricant. In fact, paraffinic motor oils may be likewise employed to dissolve the above refined intermediate and a further adjustment in the characteristics of the finished lubricant obtained. The highly paraffinic motor oil mentioned in Example 2 is advantageous for this purpose.

In most of the above procedures, the major constituent of the final lubricant is incorporated after the refining has been completed. Thus the selection of the mineral oil employed to dissolve the refined sulphurized sperm oil or the refined intermediate oil compositions should be carefully selected. The mineral oil being the major constituent of the final lubricant, its properties more or less impart the dominating characteristics of the finished lubricant. However, it is primarily the improved sulphurized sperm oil or refined intermediate oil composition which produces the improvements here obtained. In other words, the mineral lubricating oils employed in the methods of the present invention are improved by the refined sulphurized oil compositions incorporated in the same.

What we claim is:

1. In an improved method of making sulphurized oil compositions from mono-esters of fatty acids, the improvements which comprises sulphurizing the fatty mono-ester at temperatures between 360 and 450° F. to produce sulphurized esters containing minor amounts of by-products deleterious in lubricating composition and subsequently removing the said by-products by mixing the sulphurized esters with an acid washed clay, agitating the mixture until said clay absorbs the products deleterious in lubricating compositions and recovering the refined sulphurized esters from said mixture.

2. The process of claim 1 wherein the fatty mono-ester is sperm oil.

3. The proces of claim 1 wherein the sulphurization is effected between 360° and 400° F., and the sulphurized esters are quickly cooled to below 300° F. to check the side reactions.

4. The process of claim 1 wherein the mono-ester is pre-heated to about 340° F., finely divided sulphur is added as rapidly as it dissolves, the heat of reaction being dissipated by positive cooling to maintain the reaction mixture below 400° F.

5. The process of claim 1 wherein the sulphurized mono-esters are diluted with mineral oil prior to said treatment with acid lined clay.

6. The process of claim 1 wherein the sulphurization is effected between 360° and 385° F., and the hot sulphurized mono-esters are quickly cooled by adding sufficient mineral oil to lower the temperature below 300° F.

7. The process of claim 1 wherein an excess of acid washed clay is added to the said sulphurized esters and the added clay and absorbed impurities are separated from the so-refined sulphurized mono-esters by filter pressing.

8. The process of claim 1 wherein the removal of the said deleterious by-products is effected by a combined acid and clay treatment, the sulphurized mono-ester being given an acid treatment to separate an acid sludge prior to said treatment with clay.

9. The process of claim 1 wherein the refined sulphurized mono-esters are subsequently dissolved in sufficient mineral lubricating oil to obtain improved lubricants.

10. In the manufacture of improved oil compositions from sperm oil, the steps which comprise pre-heating the sperm oil to approximately 340° F., rapidly adding finely divided sulphur to the pre-heated oil as fast as the sulphur dissolves therein, effecting the sulphurization at temperatures between 360° and 400° F., the reaction mixture being cooled to maintain the temperature below 400° F., and quickly cooling the sulphurized sperm oil to below 300° F. after substantially all of the sulphur has combined, and subsequently admixing the sulphurized sperm oil with an acid-washed clay, agitating the mixture until said clay adsorbs the by-products deleterious in lubricating compositions, and recovering the refined sulphurized sperm oil from said mixture.

11. The process of claim 10 wherein the hot sulphurized sperm oil is diluted with mineral oil to quickly cool the mixture to below 300° F., and wherein the hot oil composition is admixed with

clay, the mixture agitated at temperatures between 250° and 275° F. until the said by-products are adsorbed and then separating the refined oil composition from the excess clay and adsorbed material by filtration.

12. The process of claim 10 wherein the hot sulphurized sperm oil is quickly cooled to between 150° and 225° F., the so-cooled composition is admixed with acid and maintained at said temperatures until acid-removable impurities are separated, and removing the acid sludge from the so-refined oil composition, the sour oil composition so obtained being subsequently refined with clay.

13. The process of claim 10 wherein the hot sulphurized sperm oil is quenched with a mineral oil from a naphthenic oil base and the refined oil composition so obtained is subsequently diluted with a paraffinic mineral oil to obtain an improved lubricant having a mixed mineral oil base.

14. The process of claim 10 wherein the hot sulphurized sperm oil is quenched with a mineral oil from a paraffinic oil base and the refined oil composition so obtained is subsequently diluted with a naphthenic mineral oil to obtain an improved lubricant having a mixed mineral oil base.

15. The process of claim 10 wherein the refined sulphurized sperm oil so obtained is subsequently dissolved in a mineral lubricating oil to produce improved lubricants stable to light and resistant to sludging.

16. In the manufacture of improved sulphurized sperm oils, the step which comprises rapidly sulphurizing sperm oil at a temperature between 360 and 400° F., mixing the sulphurized sperm oil with sulphuric acid, heating the mixture between 150° and 225° F., and separating the acid sludge from the refined sulphurized sperm oil.

17. In the manufacture of improved sulphurized sperm oils, the steps which comprise rapidly sulphurizing the sperm oil at a temperature between 360 and 400° F., mixing the sulphurized sperm oil with a clay capable of adsorbing the impurities deleterious in lubricating compositions, agitating the mixture at temperatures between 250° and 275° F., and recovering the refined sulphurized sperm oil.

18. In an improved method of making sulphurized oil compositions, the process which comprises rapidly sulphurizing sperm oil at a temperature between 360 and 400° F., acid refining the sulphurized sperm oil, clay treating the sour oil so obtained, recovering the so-refined oil, and dissolving the refined oil in a mineral oil to obtain improved lubricants.

19. The process of claim 18 wherein the sulphurized sperm oil is diluted with a mineral oil prior to acid refining.

HERSCHEL G. SMITH.
TROY LEE CANTRELL.

CERTIFICATE OF CORRECTION.

Patent No. 2,179,063. November 7, 1939.

HERSCHEL G. SMITH, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 42, for "and" read any; page 7, first column, line 30, for the words "in solubles" read insolubles; line 49, for "given" read give; page 8, second column, line 23, claim 3, for "proces" read process; line 35, claim 5, for the word "lined" read washed; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of December, A. D. 1939

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.