Patented Oct. 24, 1944 2,360,905

UNITED STATES PATENT OFFICE

2,360,905

MANUFACTURE OF SULPHO-HALOGENATED ALIPHATIC MONOESTERS

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No Drawing. Application September 25, 1942, Serial No. 459,718

13 Claims. (Cl. 260—399)

This invention relates to the manufacture of sulpho-halogenated aliphatic monoesters and compositions containing the same.

In particular, it relates to the manufacture of synthetic sulpho-chlorinated-monoesters of fatty acids and compositions containing the same, especially compounded lubricants comprising a major amount of lubricating oil and a minor amount of such sulpho-chlorinated-monoesters, 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 sulpho-chlorinated-monoesters from glycerides of unsaturated fatty acids, such as lard oil and other fatty oils, with recovery of glycerine as a valuable byproduct.

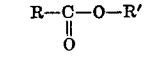
In our improved methods, fatty oils or glycerides containing unsaturated fatty acids are reacted with sulphur halogen compounds, advantageously sulphur chlorides, to form sulpho-halogen addition products and the sulpho-halogenated oils or glycerides are converted into sulpho-halogenated monoesters by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

The sulpho-halogenated monoesters so obtained are separated from the glycerine. They may be further refined, usually with lime and activated clay, to remove any deleterious byproducts, if present. Further, the sulpho-halogenated monoesters may be blended with mineral lubricating oils to obtain various compounded lubricants; the sulpho-halogenated monoesters being sometimes mixed with mineral oil prior to such refining. That is, the present invention achieves various improvements in making sulpho-halogenated monoesters 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 sulpho-halogenated monoesters of fatty acids and of lubricating oil compositions containing such sulpho-halogenated esters are well known. For instance, in Patent 2,179,062 to Smith and Cantrell, they have described and claimed improved lubricants comprising a mineral oil lubricating base and a minor amount of sulpho-chlorinated monoesters. As there shown, such lubricants have many advantageous properties and uses.

In that patent, Smith and Cantrell have specifically claimed lubricants containing sulpho-chlorinated sperum oil and like monoesters, particularly improved motor oils and like lubricants which are advantageous in lubricating cadmium-silver and other special alloy bearings without corroding said alloy bearings. As there pointed out, sperm oil, although often termed a fatty oil, is quite different from the ordinary fatty oils whcih are csters of glycerine, sperm oil being composed principally of fatty esters of monohydric alcohols. Further, the monoesters of sperm oil contain unsaturated aliphatic groups and are capable of reacting with sulphur chlorides to form simple addition products which are substantially neutral and are advantageous improvement agents for use in lubricating compositions. The superiority of such sulpho-halogenated monoesters, as a class, in making improved lubricants, is fully shown in Patent 2,179,062.

As disclosed and described in that patent, such sulpho-halogenated monoesters of fatty acids can be easily prepared by sulpho-halogenating unsaturated fatty or aliphatic esters having the formula

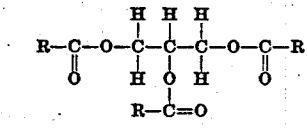


wherein R and R' represent straight chain aliphatic groups, at least one of said groups being unsaturated. In the methods there described, the said monoesters are reacted with sulphur chlorides to produce sulpho-chlorinated addition products which are substantially neutral compounds. As shown in said patent, the sulpho-chlorination of the monoesters may be advantageously effected by gradually adding sulphur chloride to the sperm oil (or like monoesters) and maintaining the reaction mixture between 40 and 120° F. until substantially all of the sulphur chloride has combined; the mixture usually being externally cooled to facilitate dissipation of the

exothermic heat of reaction. With the temperature maintained between 50 and 90° F. while the sulphur chloride is vigorously combining with the sperm oil, particularly good results were obtained. In such methods naturally occurring monoesters, such as sperm oil, etc. are ordinarily employed, as shown in Patent 2,179,062. However, as disclosed in that patent, synthetic unsaturated aliphatic monoesters, such as obtained by esterifying suitable fatty acids with appropriate alcohols, may likewise be reacted with sulphur chlorides to produce sulpho-chlorinated monoesters.

We have now found that such sulpho-halogenated monoesters of fatty acids can be prepared advantageously from glycerides of unsaturated fatty acids, such as fatty oils or mixture of such fatty oils, by new and improved methods yielding glycerine as a valuable byproduct, as well as excellent sulpho-halogenated monoesters 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 triglycerides. Generically, these triglycerides 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 or 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 of 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 two or three 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 present in addition to saturated fatty acid. Such mixed glycerides, upon hydrolysis, yield two or three different fatty acids. That is, ordinarily fats and fatty oils are not simple glycerides of a single fatty acid. 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 sulpho-halogenated monoesters may be obtained by processing commercial fatty oils and mixtures thereof according to our improved processes.

In our improved methods of making sulpho-chloro-monoesters, we first react the fatty oils or glycerides with sulpho-chloride, so as to obtain sulpho-chlorinated addition products, and then convert these sulpho-chlorinated glycerides into the desired sulpho-chloro-monoesters by reaction with monohydric alcohols, usually in the presence of a catalyst such as sulphuric acid. The sulpho-chloro-monoesters 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 we obtain valuable glycerine as a byproduct, as well as desirable sulpho-chloro-monoesters, both products being high grade materials.

In preparing the sulpho-chlorinated 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 mole of unsaturated fatty acid is useful in the present processes; triglycerides containing two or three moles of unsaturated fatty acids are also advantageous.

In particular, we find that fatty oils having iodine numbers ranging from 50 to 200 can be readily reacted with sulphur chlorides and then converted into sulpho-chloro-monoesters which are particularly advantageous improvement agents for lubricating oils. For example, lard oil having an iodine number of approximately 72 yields advantageous products when processed by our 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 monoesters of such acids, the sulphur and chlorine being added to the double bond of the unsaturated fatty acid. However, the final products obtained from lard oil contain relatively large amounts of monoesters of sulfo-chlorinated oleic acid. In fact, olein is typical of the glycerides of unsaturated fatty acids which are particularly useful and advantageous in the present processes. Moreover, we may also employ with advantage, other glycerides and mixtures of glycerides having iodine numbers ranging from 70 to 120, many of the commercial fatty oils having iodine numbers within this range. Other glycerine 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, soybean oil, corn oil, and other oils having relatively high iodine numbers and containing glycerides of fatty acids carrying two or three double bonds in the aliphatic chain thereof. That is, by selecting the fatty oils employed, or blending together various fatty oils or both, final products comprising mixtures of sulpho-chloro-monoesters and having particularly advantageous properties can be readily obtained.

Such fatty oils or oil mixtures containing glycerides of unsaturated fatty acids may be reacted with any of the usual sulpho-chlorides such as sulphur monochloride (S_2Cl_2), sulphur dichloride (SCl_2), etc. or mixtures thereof. Ordinarily, the commercial sulphur chlorides are used in the general practice of our invention. Substantially pure sulpho-monochloride has a light yellow color. The usual commercial sulpho-mono-chlo-

rides are yellowish-red, heavy liquids. Commercial sulphur dichloride is a dark brownish-red liquid. However, most commercial preparations are more or less mixtures of various sulphur chlorides in equilibrium with each other. They are primarily composed of sulphur dichloride and sulphur mono-chloride, depending upon the commercial source of the preparation, and other sulphur chlorides, such as sulphur tetrachloride (SCl_4) and sulphur tri-tetrachloride (S_3Cl_4) may also be present. Commercial sulphur chloride preparations having the following properties may be employed in the practice of this invention:

Specific gravity, 15°/15° C	1.6 to 1.7
Melting point ° C	−78 to −80
Boiling range ° C	59 to 139
Color	Light yellow to dark red
Sulphur per cent	31.1 to 47.4
Chlorine do	68.9 to 52.6

That is, any of the commercial sulpho-chloride preparations are useful for the present purposes, and by selecting a particular sulphur chloride or mixtures of sulphur chlorides, we can control the relative amounts of sulphur and chlorine combined in the fatty oils and in the sulpho-chlorinated monoesters obtained therefrom.

As is well known, sulphur chloride, such as sulphur monochloride and sulphur dichloride, readily react with fatty oils converting them into sulpho-chloro-glycerides. A wide variety of sulpho-chlorinated products can be obtained depending upon the reaction conditions employed. In general, we find that the sulpho-chlorinated products obtained by reacting 3 to 15 per cent of sulphur chloride by weight on the fatty oil are advantageous for the present purposes.

Further, we find it advantageous to employ certain controlled procedures in reacting the fatty oils with the sulphur chloride. For instance, we prefer to effect this reaction at temperatures between 40 and 180° F. with the temperature maintained between 50 and 90° F., while the sulphur chloride is vigorously combined with the fatty oil, we obtain sulpho-chlorinated glycerides which are particularly suitable for the present purposes. In making such materials, any suitable cooling means may be employed and vigorous agitation is used to prevent overheating. To further hold the temperature and reaction under control, the sulphur chloride is gradually added to the fatty oil; the rate of addition is such as will permit the mixture to remain within the preferred temperature range specified, either with or without external cooling, despite the exothermic heat of reaction. If no special cooling means is provided, the addition of the sulphur chloride will ordinarily require from 2 to 5 hours depending upon the amount used and the other factor, an additional period of 2 or 3 hours being allowed for the reaction to complete itself after all the said chloride has been added.

By adding the sulphur chloride to the lard oil or other fatty oil or mixture of oil, there is present during the initial reaction a large excess of the fatty glyceride. An excess of fatty oil is advantageous and favors the formation of simple addition products, while, at the same time, restraining the formation of undesirable side reaction products such as acid or acid-developing bodies, oil-insoluble products, etc. Further, any excess fatty oil remaining in the reaction mixture is subsequently converted into monoesters when the mixture is reacted with alcohol in the later stages of our processes, additional amounts of glycerine being liberated and recovered. The alcohol esters of the fatty acids, so derived from the excess fatty oil, are also useful improvement agents in lubricants. In fact, such monoesters are frequently combined with mineral oils in producing compounded lubricants.

Thus, in the practice of the present invention, we sometimes use an amount of sulphur chloride insufficient to completely saturate the double bonds of all the fatty acids present in the fatty oil. For instance, 3 to 15 per cent of sulphur chloride by weight on the fatty oil is satisfactory in many cases. With lard oil about 12 per cent of sulphur monochloride is sufficient to produce sulpho-chlorinated fatty oils useful for the present purposes. With other fatty oils or blended oils, the amount may be varied according to the particular fatty oil and sulphur chloride employed. With larger amounts of sulphur chloride more viscous products are obtained. Thus we may readily control the properties of the sulpho-chlorinated fatty oils and the products obtained therefrom, particularly their content of combined sulphur and chlorine, their viscosity, and other properties desired for the present purposes.

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

In preparing the sulpho-chlorinated fatty glycerides, the fatty oils are reacted with the desired amount of sulphur chloride at controlled temperatures, usually between 40 and 120° F. This may be advantageously done by preheating the fatty oil to about 300° F. until the water and other volatiles are removed, cooling the so-treated oil to between 40–50° F., and then gradually adding the sulphur chloride to the cooled oil, in small doses, at such a rate that the temperature, without external heating, is gradually increased to slightly below 100° F. by the time all the sulphur chloride has been added. The reaction mixture is then maintained at 90–100° F., by warming if necessary, until the reaction is complete. Then the reaction product is subjected to reduced pressure, usually about 100 mm. pressure, and heated to about 160° C. to remove any traces of unreacted sulphur chloride and volatile byproducts. After removal of such volatiles, the sulpho-chlorinated glycerides are cooled usually to approximately room temperature. The sulpho-chlorinated fatty oils so obtained are liquid materials and can be readily converted into sulpho-chloro-monoesters, as more fully described post.

In converting the sulpho-chloro-glycerides into the corresponding monoesters, the sulpho-chlorinated fatty oils are saponified and esterified

with monohydric alcohols, the sulpho-chloro-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 85 to 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 sulpho-chloro-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 sulpho-chloro-glyceride has been completely converted into sulpho-chloro-monoesters, the stirring is discontinued and the mixture stratified into two layers, an upper ester layer and a lower glycerine layer. The two layers are separated and may be refined as described post.

In forming the sulpho-chloro-monoesters, various alcohols may be reacted with the sulpho-chloro-glycerides and a wide range of sulpho-chloro-monoesters obtained. Advantageous products can be prepared using primary aliphatic alcohols, particularly the lower alkyl alcohols, such as methanol, ethanol, propanol, butanol and pentanol. Particularly good products are obtained with pentanol. Likewise, other alcohols may also be used. For instance, branch-chain aliphatic alcohols, such as isopropanol, isobutanol, etc. may be employed. Further, secondary aliphatic monohydric alcohols may be used as well as primary alcohols. In general, any monohydric alcohol may be reacted with the sulpho-chloro-glyceride to form useful sulpho-chloro-monoesters and liberate the glycerine. After this reaction is complete, the reaction mixture is permitted to stratify into an upper monoester 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 sulpho-chloro-monoesters have been separated from the glycerine layer, they are usually further refined, advantageously by clay contacting. In this procedure an appropriate amount of activated clay is added to the sulpho-chloro-monoesters, and the mixture is agitated until the clay absorbs the matter to be removed. Approximately two pounds of fine activated clay per gallon of sour oil (monoesters) is sufficient when the clay contacting is effected at elevated temperatures, say 275° F. The clay treated mixture is then filtered 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 sulpho-chloro-monoesters, 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 salts and excess lime may be settled or filtered off prior to clay treatment. However, complete removal prior to clay treatment is not essential and, in many cases, the lime 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 insolubles may be removed in one operation by filter pressing.

In recovering and refining the glycerine, the separated acid-glycerine layer may be processsed in several ways. As stated ante, this acid layer is usually neutralized with lime when sulphuric acid catalyst is used. In refining such byproduct glycerine, the glycerine also is mixed with an excess of hydrated lime, in the form of a slurry, and the mixture agitated until substantially neutral. The so-treated glycerine is 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 byproducts obtained in these processes are useful per se for many purposes.

From the foregoing description it will be evident that in the practice of our invention many and various embodiments thereof may be employed. In general, the several steps in our improved processes are interrelated and correlated to obtain high grade sulpho-chloro-monoesters from fatty oils with recovery of useful byproduct glycerine. In the main advantageous embodiments thereof, our improved processes include reacting sulphur chloride with fatty oils containing glycerides of unsaturated fatty acids to obtain sulpho-chloro-addition products thereof, reacting the sulpho-chloro-glycerides with monohydric alcohol in the presence of sulphuric acid to convert them into sulpho-chloro-monoesters, separating such monoesters from the glycerine, and refining the separated sulpho-chloro-monoesters usually with lime and clay. Likewise in recovering and refining the glycerine, the acid glycerine layer is heated with lime and otherwise refined to obtain pure glycerine. These and other embodiments of our 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 our invention.

Example I

This example illustrates one advantageous method of preparing sulpho-chloro-monoesters using commercial lard oil and sulpho-monochloride to produce sulpho-chloro-glycerides which are reacted with butanol; the lard oil and sulpho-monochloride having the following properties:

Commercial lard oil:

Specific gravity	0.915
Solidifying point ° C.	0
Saponification number	195–196
Iodine No.	56–74

Commercial sulphur monochloride (S_2Cl_2):

Molecular weight	135.03
Specific gravity	1.678
Freezing point ° C.	−80
Boiling point ° C.	135.6
Sulphur per cent	47.4
Chlorine do	52.6

The above commercial lard oil was a yellow semi-solid material obtained from lard oil by cold pressing. The commercial monochloride was a yellowish red liquid having a penetrating odor. These materials were reacted together and processed as follows:

Into a suitable vessel, equipped with means

for agitating and for cooling and heating the mixture, there were charged 880 pounds of the lard oil and then 88 pounds of the sulphur monochloride, gradually added in small proportion over a period of two hours, the temperature of the mixture being maintained at approximately 250° F. After all of the sulphur monochloride was added, the mixture was further agitated at approximately 250° F. for 14 hours.

To the sulpho-chloro-glycerides so obtained there were added 300 pounds of butanol containing 1 per cent of 93 per cent sulphuric acid, and the mixture agitated at 220° F. for 14 hours. After the reaction was complete the mixture was permitted to stratify into an upper ester and a lower glycerine layer and the glycerine layer withdrawn.

The ester layer was then admixed with 5 pounds of lime and agitated until substantially neutral. The neutral mixture was then admixed with 250 pounds of fine activated clay (2 pounds of clay per gallon of sour oil) and the mixture is agitated at 275° F. for 2 hours. After the clay contacting was completed, the mixture was filter pressed to remove the clay and other insolubles. The filtrate so obtained had the following properties:

Gravity, ° API	20.5
Viscosity, SUV:	
100° F	110
210° F	42.4
Flash, OC ° F	380
Fire, OC ° F	440
Pour ° F	+35
Sulphur per cent	5.57
Chlorine do	3.17

This filtrate was a mixture of butyl esters of the sulpho-chloro-fatty acids and was an excellent improvement agent for mineral lubricating oils and lubricants.

EXAMPLE II

This example illustrates one advantageous method of preparing sulpho-chloro-glycerides from commercial grades of lard oil and of sulphur monochloride, commercial materials having the following properties being employed:

Lard oil

Specific gravity, 60/60° F	0.915
Viscosity, SUV 100° F	210
Flash, OC ° F	555
Pour ° F	+20
Color, NPA	1.5
Neutralization number	1.9
Oleic acid eq. per cent	0.95
Saponification number	195
Iodine number	71

Sulpho-monochloride

Specific gravity, 29° C	1.678
Boiling range ° C	132–140
Color	Yellow-red
Sulphur per cent	47.4
Chlorine do	52.6

The above material were reacted together and processed as follows:

Into a suitable vessel equipped with means for agitating and for heating and cooling the oil and reaction mixture, there were introduced 880 pounds of the above lard oil and the oil was heated to 300° F. until any water and other volatiles present were evaporated. Then the oil was cooled to approximately 50° F. and 106 pounds of the commercial sulphur chloride (approximately 12 per cent by weight on the oil) were gradually added. The rate of introducing sulphur chloride was so controlled as to maintain the reaction temperature between 40 and 90° F., the exothermic heat of reaction being utilized to gradually bring the temperature to about 90° F. when all the sulphur chloride had been added. It required about 2 hours to so incorporate the sulphur chloride. Of course, the time required may be varied depending upon whether or not external cooling is employed. During this time, the reaction mixture was vigorously agitated to prevent any local overheating. After all the sulphur chloride had been added, the reaction mixture was maintained at 90 to 100° F. for a further period of 2 hours while the agitation was continued until the reaction was substantially complete.

The hot sulpho-chlorinated oil product so obtained was subjected to reduced pressure of approximately 100 mm. and heated to 180° F. under said pressure to remove any unreacted sulphur chloride and other volatiles. After the volatiles were so removed, the sulpho-chlorinated glycerides were cooled to approximately room temperature.

The sulpho-chlorinated lard oil so obtained had the following properties:

Gravity, degree API	20.5
Viscosity, SUV:	
100° F	110
210° F	42.4
Color, NPA	8.0
Chlorine per cent	3.2
Sulphur do	5.6
Neutralization number	3.7

In the above example, the amount of sulphur chloride may be varied from 6 to 14 per cent and other sulpho-chlorinated oils will be obtained which have properties rendering them advantageous for the present purposes; the smaller percentages of sulphur chloride produced oil products having somewhat lower viscosities and higher gravities. Likewise other commercial sulphur chloride and fatty oils may be employed in making these sulpho-chlorinated glycerides. With the reaction temperature maintained between 50 and 100° F., we obtained from any of the commercial fatty oils or mixtures of such oils sulpho-chlorinated oil products having good color and other properties.

The sulpho-chlorinated glycerides so obtained can be readily converted into sulpho-chloro-monoesters by reacting them with an excess of monohydric alcohol. For instance, excellent sulpho-chloro-monesters are obtained by reacting the sulpho-chlorinated glycerides with butyl alcohol.

In making butyl esters from the above sulpho-chloro-glycerides, 300 pounds of the sulpho-chlorinated lard oil were admixed with 85 pounds of acidulated butyl alcohol, prepared by mixing 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 1½ hours, and then maintained at this temperature for 4 hours while continuing the agitation. After the reaction was completed the stirring was discontinued and the mixture stratified into an ester layer and a glycerine-acid layer. The glycerine layer was withdrawn and 358 pounds of the sulpho-chloro-monoesters so-obtained were admixed with 15

pounds of lime and 40 pounds of activated clay and the mixture maintained at 275° F. with agitation for 3 hours. After this clay contacting, the sulpho-chloro-monoesters were filter pressed to remove the clay and other insoluble matter. The filtrate was an excellent improvement agent for mineral oils and lubricants.

The separated glycerine-acid layer weighed approximately 42 pounds and was further treated to recover the glycerine. In refining the glycerine layer, the procedure described in Example I was employed; the glycerine-acid mixture was limed and the so-treated glycerine was filtered, to remove the insolubles such as 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, methanol or isopropanol may be used to esterify the sulpho-chlorinated lard oil and produce excellent sulpho-chloro-monoesters. In the following Table I are given typical properties of the sulpho-chloro-monoesters obtained by reacting the sulpho-chlorinated lard oil with butanol, methanol and isopropanol, respectively, according to the procedure of Example II ante.

Table I

Alcohol used for esterification	Butanol	Methanol	Isopropanol
Clay-treated sulpho-chloro-monoesters:			
Gravity, °API	20.5	22.4	23.2
Viscosity, SUV, seconds—			
100° F.	110	109	102
210° F.	42.4	41.2	36.3
Flash, OC, °F.	380	390	380
Fire, OC, °F.	440	445	440
Sulphur, B, per cent	5.6	6.1	5.8
Chlorine, per cent	3.2	3.5	3.3

The sulpho-chloro-monoester compositions given in the above table are merely illustrative of certain embodiments of this invention, and other alcohol esters of sulpho-chloro-fatty acids can be prepared in like manner from other fatty oils, particularly those containing glycerides of unsaturated fatty acids.

Likewise, mixtures of fatty oils may be employed in our processes; two or more fatty oils being blended together to obtain mixtures of fatty glycerides advantageous for the present purposes. As stated ante, advantageous sulpho-chloro-monoesters can be obtained from fatty oils and mixtures of oils having an iodine number between 70 and 120.

Also, mineral oils, such as the usual grades of lubricating oils, may be incorporated with the sulpho-chloro-monoesters during the processing. Such oils may be advantageously admixed with the sulpho-chloro-monoesters prior to clay refining. In this way concentrates or lubricants can be directly obtained from the refining operations. The presence of the mineral oil facilitates precipitation and removal of byproducts which are insoluble in the final lubricant. For instance, in the embodiments illustrated in Examples I and II ante, 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 sulpho-chloro-monoesters then refined with clay to produce concentrated solutions, which are good lubricants and are useful to produce other lubricants containing small amounts of these improvement agents. We 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 II:

Table II

Description	A Pennsylvania type motor lubricant containing 3.0% of inhibitor described ante	A Pennsylvania type motor lubricant containing 3.0% of inhibitor described ante	A Texas type motor lubricant containing 3.0% of inhibitor described ante
Inspection:			
Gravity, °API	30.6	28.8	22.3
Viscosity, SUV—			
100° F.	495	1,537	510
210° F.	66	120	56
Flash, OC, °F.	455	535	405
Fire, OC, °F.	525	605	460
Pour, °C.	0	−5	−10
Color, NPA	3.5	4.0	4.5

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 sulpho-chloro-monoesters in a suitable base oil.

In general, sulpho-chloro-monoesters containing from 3.0 to 8.0 per cent of combined chlorine, by weight, are excellent improvement agents for mineral lubricating oils and lubricants and such advantageous improvement agents may 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 we claim is:

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

2. In the manufacture of sulpho-chloro-monoesters, the improved process which comprises heating sulpho-chlorinated fatty glycerides with a monohydric aliphatic alcohol in the presence of sulphuric acid until the sulpho-chlorinated fatty glycerides are converted into sulpho-chlorinated fatty monoesters of said alcohol and the glycerine is completely separated therefrom, and separately recovering the sulpho-chlorinated monoesters and glycerine so obtained, the said sulpho-chloro-monoesters 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 of lime and the neutral glycerine is filtered to remove the excess of lime and other insoluble matters.

4. The process of claim 2 wherein the sulpho-chloro-monoesters are refined with activated clay.

5. In the manufacture of sulpho-chloro-monoesters, useful as improvement agents for mineral lubricating oils and lubricants, the improved proc-

ess which comprises reacting sulphur chloride with a fatty oil containing glycerides of unsaturated fatty acids to form sulpho-chlorinated fatty glycerides and then converting said sulpho-chlorinated fatty glycerides into sulpho-chlorinated fatty monoesters by reacting the sulpho-chlorinated fatty oil with a monohydric aliphatic alcohol acidified with sulphuric acid to saponify the sulpho-chlorinated fatty glycerides and convert the same into sulpho-chlorinated fatty monoesters of said alcohol, separating the glycerine so liberated from said glycerides, and recovering and refining the sulpho-chlorinated fatty monoesters so produced to obtain substantially neutral sulpho-chlorinated monoesters useful as improvement agents for mineral lubricating oils and lubricants.

6. The process of claim 5 wherein said sulphur chloride is sulphur monochloride.

7. The process of claim 5 wherein said sulphur chloride is sulphur dichloride.

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

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

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 120.

11. The process of claim 5 wherein said fatty oil has an iodine number between 70 and 120.

12. In the manufacture of sulpho-chloro-monoesters from fatty oils and mixtures of fatty oils having an iodine number between 70 and 120 and containing glycerides of unsaturated fatty acids, the improved process which comprises reacting such fatty oils with sulphur chloride to form sulpho-chloro-addition products, reacting the sulpho-chlorinated fatty oils with a monohydric aliphatic alcohol in the presence of sulphuric acid to form sulpho-chloro-monoesters and liberate glycerine, separating the acid glycerine from the sulpho-chloro-monoesters, refining the separated sulpho-chloro-monoesters by contacting with activated clay and separating the refined sulpho-chloro-monoesters 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 and other insoluble matter.

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