

UNITED STATES PATENT OFFICE

2,522,476

COMPOSITIONS CONTAINING AND PROCESS
FOR PREPARING STABILIZED UNSATU-
RATED FATTY OILSJones I. Wasson, Union, N. J., assignor to Stand-
ard Oil Development Company, a corporation
of DelawareNo Drawing. Application July 19, 1947,
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6 Claims. (Cl. 252—48.6)

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This invention pertains to compositions containing stabilized unsaturated fatty oils and to methods for preparation thereof. More specifically, the invention pertains to a method whereby the oil solubility, the resistance to oxidation, rust inhibiting characteristics, and pour point depressing properties of certain fatty oils and their derivatives, may be improved so that they may be more effective when combined with mineral oil compositions. The invention pertains further to the products of the methods mentioned above and particularly to fatty oils and derivatives having improved solubility in mineral oil, increased rust inhibiting qualities, and increased resistance to oxidation.

It is known that certain unsaturated fatty oils such as cotton seed oil, corn oil, castor oil, rapeseed oil, linseed oil, and the like have desirable oiliness properties which make them useful in lubricants. Some of these oils, however, oxidize so rapidly that they cannot be used for general lubricating processes since they would form gums and other undesirable products which are highly objectionable, especially in the lubrication of internal combustion engines.

In addition to the tendency toward oxidation mentioned above, certain of these oils have limited solubility in mineral oil. Castor oil, for example, is soluble only to a very limited extent in ordinary mineral oils of lubricating oil viscosity grades. Hence the amount of castor oil that may be blended with mineral lubricating oil is definitely limited.

Many compounds containing unsaturated fatty oil radicals, for example those containing oleyl radicals, have noteworthy rust inhibiting properties. Here again, however, the limited oil solubility possessed by some of these compounds seriously limits their use in mineral oil as rust preventive agents. A notable example is the partial ester, pentaerythritol mono oleate, which has outstanding rust inhibiting properties but which is sparingly soluble in mineral oil and therefore cannot be used in concentration of more than 1.5 to 2.0%. Other unsaturated acid esters of pentaerythritol may be used, preferably those derived from the mono-unsaturated acids having 16 to 22 carbon atoms.

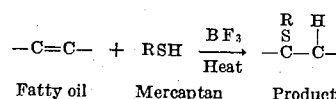
It is an object of my invention to treat oils, esters and partial esters, of the general character referred to above, in such a manner as to utilize their respective advantages while at the same time improving them with respect to the particular deficiencies which have been mentioned. Thus it is an object of my invention to increase

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the oil solubility of certain fatty oil compounds and derivatives and a further object is to stabilize compounds or at least to partially stabilize them against oxidation. The latter preferably is accomplished by saturating unsaturated bonds possessed by the various compounds included in the above general classification. Still a further object of my invention is to produce new and useful compounds or compositions containing desirable and hitherto unknown properties and to accomplish the foregoing in a novel manner.

It is well known that certain unsaturated fatty oils such as cottonseed oil, corn oil, linseed oil, and the like oxidize very readily when exposed to the air. In fact this property is utilized when certain of these compounds, notably linseed oil, soya bean oil, and the like, are used as vehicles for paints, varnishes, and related coating compositions. Notwithstanding the known excellent oiliness properties of some of these compounds for use in lubricants, they have not been very widely used in the past because of their extreme tendency toward rapid oxidation. Hydrogenation and other treatments to reduce their unsaturation have been practiced in many cases but the various treatments to which these oils have been subjected have not, in general, rendered them suitable for use in lubricants. On the other hand, certain other unsaturated oils, of which castor oil is a notable example, have been used by themselves as lubricants but have not been used in combination with mineral oil because of their limited solubility, as indicated above. Here again treatments of various types have been suggested to improve resistance to oxidation, miscibility with mineral oils, and the like, but the various processes of the prior art have not been entirely satisfactory.

I have found that the various oils just referred to will react readily with mercaptans in the presence of a metal halide catalyst at moderately elevated temperatures. By the selection of suitable mercaptans a side chain may be added on to the fatty oil molecule at a double bond according to the following general reaction.



A suitable catalyst is boron fluoride though other metal halides may be used if desired.

The same general reaction as just described is applicable to esters and partial esters containing relatively long fatty oil radicals of the unsaturated type. Thus the compound, pentaerythritol

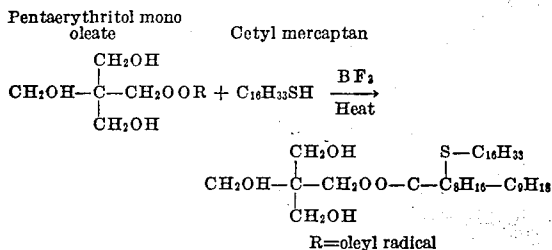
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mono-oleate, may be reacted with a suitable mercaptan, of suitable type as will be explained, in the same general manner as indicated above. Other partial esters that may be similarly employed include glycerol mono or dioleate, glycol mono-oleate, trimethylol propane mono-oleate, pentaerythritol mono-oleate-mono acetate, the mono-oleate ester of partially dehydrated sorbitol, and the like.

While various mercaptans may be used, the alkyl mercaptans are preferred and where oil solubility is an important consideration it is preferred to use a mercaptan of fairly long chain length. Therefore, a mercaptan having a general formula RSH , where R is an alkyl radical having from 6 to 20 or more carbon atoms, is considered particularly effective. Higher mercaptans may be used but their high cost and limited availability restrict their use. The most desirable materials appear to be those mercaptans containing from 10 to 20 carbon atoms. Lauryl ($C_{12}H_{25}SH$) and cetyl ($C_{16}H_{33}SH$) mercaptans are particularly suitable because of their ready availability.

The reaction between an ester such as pentaerythritol mono oleate and cetyl mercaptan proceeds rather readily at a temperature of $300^{\circ}F$. using BF_3 as a catalyst. Other conventional Friedel-Crafts catalysts such as stannic or stannous chloride or aluminum chloride may be used as the catalyst. Various other metal halides, for example zinc chloride, may also be used, but boron fluoride is particularly convenient to use because of its gaseous form. A small amount of the catalyst BF_3 may be bubbled through the composition before or during reaction, recovery being simpler than in the case where solid catalysts are used. While a reaction temperature of about $300^{\circ}F$. appears to be convenient and desirable, the reaction may be carried out at temperatures as low as about $50^{\circ}F$. or at any temperature from 50° up to $325^{\circ}F$. or more. The rate of reaction, of course, varies with the temperature. Hence it is generally desirable to operate at a temperature of at least $100^{\circ}F$. and preferably somewhat higher.

As indicated above, the treatment of a partial ester, such as pentaerythritol mono oleate, with an alkyl mercaptan is effective to increase the oil solubility of the final product over that of the original mono oleate. The excellent rust inhibiting properties of the partial esters of this general character are not adversely affected by their saturation with a mercaptan whereas their oil solubilities are appreciably enhanced.



As indicated above, the mercaptan, for example cetyl mercaptan, is added on to the oleyl radical at the double bond. The reaction product is several times more soluble in mineral oil than the original pentaerythritol mono oleate which normally is only sparingly soluble.

The reaction just described can be utilized in the case of any partial ester having an ethylenic type unsaturation such as a double bond where

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the mercaptan can be added on to the molecule.

While the above description has made special reference to partial esters such as the mono oleate, it will be understood that other esters having similar unsaturated fatty acid radicals may be similarly treated. These include partial esters of such acids as linoleic, ricinoleic, and the like. Likewise, the length and character of the mercaptan chain can be varied considerably, use being made of either the normal, secondary, or in some cases, but less desirably, the tertiary types of mercaptan compounds. As a matter of fact, certain of the alkaryl or aralkyl mercaptans also may be used so long as they contain a sufficient chain length or molecular configuration to impart the requisite oil solubility to the final compound. If oil solubility is unimportant the lower mercaptans are quite satisfactory.

Aside from the properties mentioned above certain of the long chain unsaturated esters and partial esters, particularly partial esters of the general character of pentaerythritol mono oleate, are found to have good pour point depressing properties when used with mineral lubricating oils. Thus the reaction product of pentaerythritol mono oleate and cetyl mercaptan, heated together in the presence of a suitable catalyst, e. g. tin chloride (SnCl_4), shows very excellent pour point depressing properties as indicated in the following table. In this table the reaction product was the only additive used in the two types of mineral oil indicated.

Pour point results

Base Oil	Per Cent Additive	Pour Point, $^{\circ}F$.
Penn. 180 Neutral.....	None	+30
Penn. 180 Neutral.....	1.0	-20
Penn. 180 Neutral.....	2.0	-35
Mid-Cont. Neutral.....	None	+30
Mid-Cont. Neutral.....	2.0	less than -35

¹ Pentaerythritol mono oleate cetyl mercaptan reaction product. Pentaerythritol mono oleate by itself has no pour point depressing characteristics.

The degree of reaction between fatty oils, fatty acids, and fatty oil derivatives such as the partial esters mentioned above, on the one hand, and mercaptans on the other hand, may be varied considerably depending upon the particular materials chosen, the catalyst used, the reaction temperature, and the degree to which the reaction is permitted to go. Apparently as reaction continues the fatty oils which normally have drying properties become increasingly soluble in mineral oil and at the same time become more and more stable against oxidation. Thus, for example castor oil which is normally insoluble in mineral oil, after reaction with cetyl mercaptan in the presence of BF_3 for an hour at $300^{\circ}F$. has been found readily soluble in large proportions. A sample of sparingly oil soluble cottonseed oil reacted with the same mercaptan in a similar manner became readily miscible with mineral oil, and heat treating of the reaction product showed that the tendency of such cottonseed oil to polymerize readily had been almost entirely overcome.

A suitable test procedure for determining rust preventing properties is as follows:

Sand blasted panels of hot rolled steel are dipped into samples of the compositions to be tested, then maintained vertically in a box for 16 hours under ordinary room conditions to allow the rust preventive film to reach an equilibrium condition. Compounds containing petrolatum or

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waxes are applied at room temperatures. The coated panels are then placed in an upright position in a humidifier chamber maintained at 100-120° F. where they are subjected to continuous moisture condensation. The test pieces are spaced in the cabinet in such a manner that they do not come in contact with each other. The time, in hours, for a panel subjected to these conditions to develop initial evidence of rusting is observed and recorded as the resistance life of the coating composition.

In another test, cottonseed oil was heat thickened for 62 hours at 250° to 270° F. The product of this treatment had a viscosity of 1500 S. S. U. at 210° F. and was quite insoluble in mineral oil. This material was thereafter reacted with 25% by weight of cetyl mercaptan at 300° F. for one hour. As a catalyst, 1% by weight of stannic chloride was used. The resulting product was quite soluble in lubricating oil.

In testing the rust preventing properties of fatty oil partial ester-mercaptan reaction products, a striking contrast was found between the solubilities of the untreated ester and the ester-mercaptan product. Thus a 2% solution of pentaerythritol mono oleate in a 120 grade aviation oil had a life of 100+ hours when subjected to a humidity cabinet test at 120° F. Although this blend contained only 2% of the ester it was very cloudy and unstable showing that the solubility limit was very close if not actually exceeded. On the other hand, blends of the same oil base containing as much as 5% of the ester-mercaptan reaction product were found to be clear and stable. In the humidity cabinet test a 2% blend of the reaction product in the same oil also had a life of 100+ hours showing that the rust inhibiting characteristics of the ester were unimpaired. In other tests blends containing various quantities from 2% up to 5% of the mercaptan reaction product showed the same satisfactory life tests and remained entirely clear showing that solubility limits had been materially extended.

By the general method described herein above, valuable fatty oil type blending agents may be produced using commonly available fatty oils, particularly vegetable oils, which have hitherto been considered generally less satisfactory than the now more costly and scarce animal fats and oils. Normally, in carrying out my improved process, a temperature of 300° F. or from 120° to 350° F. and the reaction time of an hour or so prove quite satisfactory. As a rule the catalyst required ranges from about ½ to 1% by weight based on the total weight of the reaction products, although the invention is not limited by the amount of catalyst employed. Preferably, theoretical quantities of the respective reaction ingredients are utilized and the material is agitated during the entire reaction period. After the reaction has been completed the product is washed with water and dried, for example on a steam chest. If necessary, a solvent such as naphtha may be used to thin out the product, especially if

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heavy emulsification results. Thereafter the naphtha is stripped out either on a steam chest or by distillation.

Where solubility is relatively unimportant a very short chain mercaptan such as methyl, ethyl or propyl mercaptan may be used, these having the advantage of being quite economical and being readily available from crude oil refining processes. The higher mercaptans required for good oil solubility are more expensive. The tertiary mercaptans may be used but generally are somewhat objectionable as they have a tendency to release hydrogen sulfide gas. Hence, it is commonly preferred to use either primary or secondary mercaptans.

I claim:

1. The method of stabilizing against oxidation and improving the rust inhibiting effect of a partial ester of a polyhydric alcohol and a long chain unsaturated fatty acid which consists of heating said ester with an alkyl mercaptan having 6 to 20 carbon atoms per molecule in the presence of a Friedel-Crafts metal halide catalyst to a temperature of 50° to 300° F. to at least partially saturate said fatty oil component.

2. As a new composition of matter the reaction product of pentaerythritol mono oleate with a cetyl mercaptan, said reaction being carried out in the presence of a Friedel-Crafts catalyst and at a temperature between about 100° and 325° F.

3. The method recited in claim 1 wherein said metal halide catalyst is boron tri fluoride.

4. The method recited in claim 1 wherein said metal halide catalyst is stannic chloride.

5. A composition of matter consisting essentially of a mineral base oil of lubricating grade containing 0.5 to 10% of the reaction product of pentaerythritol mono oleate and an alkyl mercaptan having 6 to 20 carbon atoms, said reaction being carried out at a temperature of 50° to 300° F. in the presence of a metal halide to attach the mercaptan to a double bond of said oleate radical.

6. A composition consisting essentially of mineral base lubricating oil containing about 0.1 to 10% of the reaction product of a C₁₈ unsaturated fatty acid partial ester of a polyhydric alcohol reacted with an alkyl mercaptan of 10 to 20 carbon atoms in the presence of a Friedel-Crafts catalyst and at a temperature between about 100° and 325° F.

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