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SULPHURIZATION OF ESTERS

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This invention relates to a process of sulphurizing esters of unsaturated aliphatic acids that contain at least ten carbon atoms. The invention also relates to new sulphurized products prepared from the esters.

The products of the invention are intended primarily for use as additives to lubricating oils and cutting oils. Sulphurized materials designed for this purpose should possess good solubility in the oils so as to make possible an important increase in the sulphur content of the oils. Also such materials should be light in color so as not to discolor the oils. Further, it is important that the additives should not impart to the oils undersirable characteristics such as a tendency to cause corrosion.

The esters which are employed as starting materials in the process of the invention are simple esters of unsaturated aliphatic acids that contain at least ten carbon atoms. They include esters of unsaturated higher fatty acids and esters of aliphatic acids containing a ring structure. In esters of the latter type the aliphatic unsaturated linkage may appear in a ring. Thus, the term "aliphatic" is used herein in its broad sense and includes cycloaliphatic as well as open chain compounds. In referring to simple esters it is meant that the esters contain but one ester group. The esters, therefore, are distinguished from ordinary vegetable and animal oils, which are triesters of glycerine.

It has been found in accordance with the present invention that an ester of the above class can be converted into a sulphurized product containing a high proportion of sulphur and being characterized by a light color and excellent solubility in mineral oils by reacting the ester with sulphur at a temperature of at least 300° F. in the presence of water and under a pressure of hydrogen sulphide. The products resulting from this process are considerably lighter in color than products prepared from the same starting materials by ordinary sulphurization processes using sulphur alone. The products make up a particularly valuable class of sulphurized materials as compared with materials obtained by the sulphurization of the usual vegetable and animal oils because they are less viscous and more soluble in mineral oils. Since the sulphurized products do not contain undesirable free carboxylic acid radicals, they possess advantages over products resulting from the sulphurization of free fatty acids.

From what has been said above, it will be recognized that any of a large number of esters are suitable for use as starting materials in the process. The esters may be naturally occurring compounds or compounds prepared synthetically and may be substantially pure or contain other compounds admixed therewith. The esters may be esters of any of the familiar unsaturated fatty acids containing at least ten carbon atoms, such as acids of the oleic series, linolic series, and linolenic series. Also the esters may be esters of unsaturated higher fatty acids containing substituents such as hydroxyl groups; e. g., the esters may be esters of ricinoleic acid. Where the esters are derived from, or may be regarded as derivatives of, unsaturated fatty acids it is preferred to employ esters of such acids which contain from 16 to 18 carbon atoms, particularly oleic acid. As examples of esters of aliphatic acids containing a ring structure, there may be mentioned esters of abietic acid. The esterifying radicals of the esters may be unsubstituted or substituted aliphatic (including cycloaliphatic) or aromatic radicals. Inasmuch as the primary function of the esterifying radical is believed to be the blocking of the carboxyl group in the acid, the specific nature of this radical is not of critical importance. For example, where aliphatic, the esterifying radical may be saturated or unsaturated and may contain substituents such as amino and hydroxyl groups; e. g., this radical may be an allyl, a hydroxy-ethyl, or an amino-ethyl radical. Valuable sulphurized products are obtained from esters in which the esterifying radical is an open chain aliphatic radical such as a methyl, ethyl, propyl, octyl, or cetyl radical. Additional examples of suitable esterifying radicals are the cyclohexyl and phenyl radicals. Representative esters which may be employed as starting materials in the process are the following: methyl oleate, ethyl oleate, cetyl oleate, methyl abietate, hydrogenated methyl abietate (containing one unsaturated linkage), and the methyl ester of corn oil fatty acids. Sperm oil, which is largely cetyl oleate, yields a particularly valuable product when employed as the starting material in the process.

In carrying out the present process in accordance with a preferred manner of proceeding, sulphur, water, hydrogen sulphide, and an ester of the above class are introduced into a reaction vessel. Although the order in which these materials are introduced into the vessel may be varied, it is generally convenient to mix the ester, water, and sulphur either in the reaction vessel or before introducing them into the vessel, and then, after closing the vessel, to introduce

the hydrogen sulphide through a suitable port. The reaction mixture is heated to a temperature of at least 300° F. preferably between 320° and 330° F. Sufficient hydrogen sulphide is employed to create a substantial pressure in the reaction vessel due to this compound. The mixture is maintained at the reaction temperature until substantially all of the free sulphur has entered into combination. Under the conditions specified this point is reached in a relatively short period of time. Thus, by maintaining the reaction mixture at a temperature of at least 300° F. for from one-half hour to two hours, the reaction is usually complete.

At the completion of the reaction, the sulphurized product may be recovered in any suitable manner, the particular method employed depending primarily upon the specific character of the starting material. It is usually advisable first to cool the reaction mixture so as to prevent over-reaction. This may be done before releasing the pressure in the reaction vessel. One convenient method for recovering the sulphurized product is to mix the reaction mixture with a water insoluble solvent for the sulphurized product and then to permit the resulting mixture to stand and form two layers. The water layer is drawn off and the solvent is removed from the sulphurized product by vaporization, preferably under reduced pressure conditions.

In this process it is important to control several conditions if products of particularly valuable properties are to be obtained. As brought out in the following discussion, the partial pressure of hydrogen sulphide in the reaction vessel affects the properties of the products. This pressure preferably is not permitted to drop below 50 pounds per square inch and may be as high as 300 pounds per square inch or higher. It has also been found that the amount of water used has an important effect upon the properties of the sulphurized products. Thus, if the water is used in an amount less than that corresponding to a weight ratio of water to ester of one to two, the color of the products is not as good as when the water is employed at least in this amount. Although a greater quantity of water appears to have no adverse effect upon the properties of the products, apparently no improvement results and therefore a greater quantity ordinarily would not be used. In general, it may be stated that the weight ratio between the water and the ester should be maintained from 1:2 to 2:1.

Although the invention is not limited to any theory of operation, it may be of advantage to point out that researches leading to the development of the invention have indicated that proceeding as above described prevents excessive polymerization due to linkage of double bonds. It appears that the dark color characteristic of ordinary sulphurized products is due at least in part to excessive polymerization of this type. When sulphur alone is used in sulphurization, hydrogen sulphide is evolved and this elimination of hydrogen sulphide produces unsaturation. The additional unsaturation places the compound being treated in condition to continue to polymerize by linkage or condensation through double bonds. By maintaining substantial hydrogen sulphide pressure, the evolution of hydrogen sulphide is prevented. The function of the water in the process is not clearly understood, but it apparently cooperates with the hydrogen sulphide to prevent excessive polymerization. When water is omitted, darker products result. Also the short period of time in which the present process may be carried out is an important factor in producing valuable sulfurized materials.

As will be apparent from a consideration of the following examples, as the temperature of the reaction mixture is raised the total pressure in the reaction vessel increases to a peak and then begins to decrease. Towards the end of the reaction, the pressure due to hydrogen sulphide is less than at a prior period during the heating, indicating that the hydrogen sulphide not only dissolves in the reaction mixture under the pressure conditions, but also undergoes some reaction with the material being sulphurized. That a reaction occurs is also borne out by the fact that in many cases the sulphurized products contain more sulphur than the amount of free sulphur used would lead one to expect.

As stated above the products prepared by the present process possess exceptional solubility in lubricating oils. They may be employed with advantage as additives to such oils to reduce the tendency of the oils to cause corrosion of hard metal bearings under extreme conditions, and to improve the extreme pressure characteristics and viscosity index of the oils. The addition of the sulphurized products to lubricating oils designed for lubricating Diesel engines improves the oils with respect to preventing ring sticking. The sulphurized products are also valuable for use as cutting oil additives.

In order that the invention may be understood more fully reference should be had to the following examples in which are described typical ways of practising the present process. It will be understood that these examples are given for illustrative purposes merely and are not intended as limitations of the invention.

Example I.—200 grams of winter-bleached sperm oil are agitated with 100 grams of water and 20 grams of sulphur. The resulting emulsion is poured into a reaction vessel having an internal volume of 600 cc. and capable of withstanding substantial pressures. The reaction vessel is closed and 20 cc. of liquid hydrogen sulphide is introduced through a suitable port; then, while agitating, the resulting reaction mixture is heated as rapidly as possible to temperatures within the range of 320° F. to 330° F. In ordinary equipment this requires 15 to 35 minutes. The temperature of the reaction mixture is maintained at 320° to 330° F. for 45 minutes, at which time substantially no free sulphur remains in the mixture. The reaction mixture is then cooled quickly by the action of cold water, the pressure in the vessel is released, and the reaction mixture is diluted with about an equal volume of methyl ethyl ketone. The resulting mixture is placed in a separatory funnel where a water layer and a layer composed of a methyl ethyl ketone solution form. The water layer is drawn off and the methyl ethyl ketone solution is filtered. The solvent is removed from the solution under vacuum, and the product is finally stripped with steam under vacuum to remove the last traces of solvent and hydrogen sulphide.

In carrying out the above process the total pressure in the reaction vessel varies between about 100 pounds and 350 pounds per square inch. Thus, at all times during the reaction period the partial pressure of hydrogen sulphide is substantially above 50 pounds per square inch. The sulphurized oil resulting from this process is a light-colored liquid which is excellently adapted for addition to lubricating oils of various types

without discoloring the oils, as is the case when ordinary sulphurized products are added to lubricating oils. The sulphurized sperm oil contains 10.5 per cent sulphur, whereas on the basis of the free sulphur used the maximum amount theoretically possible is 9.1 per cent. This indicates that the hydrogen sulphide acts to introduce sulphur into the product.

Example 2.—700 grams of winter-bleached sperm oil, 350 grams of water, 70 grams of sulphur, and 70 cc. of liquid hydrogen sulphide are charged to a reaction vessel capable of withstanding relatively high pressures and provided with external heating means. The vessel, after being closed, is heated so as to bring the reaction mixture rapidly to a temperature above 300° F. When the temperature of the reaction mixture reaches 205° F. the total pressure on the mixture is about 215 pounds per square inch. As the temperature increases from this point to 315° F., the pressure increases to about 315 pounds per square inch. The mixture is maintained at a temperature varying from 315° to 330° F. for a period of 45 minutes. During this period the pressure decreases somewhat although it does not drop below about 270 pounds per square inch. At the end of this period the mixture, which contains substantially no free sulphur, is removed from the reaction vessel. The reaction vessel is washed out with methyl ethyl ketone, and the washings are added to the mixture. Additional methyl ethyl ketone is added to bring the total volume up to about 1500 cc. An aqueous layer separates and is drawn off. The methyl ethyl ketone solution is filtered and vacuum steam stripped to remove the solvent. The stripped oil is filtered to yield a light straw-colored oil.

Example 3.—The process of this example is similar to that of Example 2, except that the reaction mixture is maintained at a temperature ranging from 300° to 320° F. for a period of 65 minutes. Also, the pressure during this period reaches a maximum of about 300 pounds per square inch and at the end decreases to about 255 pounds per square inch. The reaction mixture is worked up as described in Example 2 to yield a similar product.

Example 4.—The process of this example is also similar to that of Example 2. However, the reaction mixture is maintained at temperatures varying from 310° to 330° F. for a period of 45 minutes and the maximum pressure, which is reached at the beginning of this period, is about 305 pounds per square inch. After working up as described in Example 2, a sulphurized oil similar to that of Example 2 is obtained.

Example 5.—475 grams of ethyl oleate, 240 grams of water, 48 grams of sulphur, and 50 cc. of liquid hydrogen sulphide are charged to a reaction vessel of the type employed in Example 2. The reaction mixture is heated to 320° F., the heating period at a temperature over 300° F. being about 70 minutes. The pressure on the mixture reaches a maximum of 227 pounds per square inch and the final pressure is 175 pounds per square inch. The sulphurized product is recovered as described in Example 2. The product contains 10.8 per cent total sulphur, color value (Tag Robinson) 9, and a Saybolt Universal viscosity of 40.5 at 210° F.

Example 6.—700 grams of Mazola (the methyl ester of corn oil fatty acids), 350 grams of water, 70 grams of sulphur, and 70 cc. of liquid hydrogen sulphide are charged to a reaction vessel of the type employed in Example 2. The reaction mixture is heated to 320° F. The reaction is carried out at a temperature above 300° F. for a period of about 70 minutes. The pressure on the mixture reaches a maximum of 327 pounds per square inch and the final pressure is 210 pounds per square inch. The reaction mixture is worked up as described in Example 2 to yield a product having a good color and being suitable for use as a lubricating oil or cutting oil additive.

It will be understood that the conditions described in the examples may be varied. By substituting others of the class of esters herein defined, for example, those specifically referred to, for those employed in the examples, other valuable sulphurized products may be obtained. Generally, the amount of sulphur employed is the same as that used in sulphurization carried out with the use of sulphur alone. To some extent, however, the properties of the products may be varied in degree by using varying amounts of sulphur.

The time necessary to complete the sulphurization reaction may be determined in any particular case by analyzing withdrawn samples of the reaction mixture to detect the presence of free sulphur. When free sulphur is substantially absent in the reaction mixture, the reaction is complete. As stated above, the reaction requires not more than two hours and may take as little as 30 minutes. Preferably the reaction is effected in from 40 to 90 minutes. Although substantial reaction does not take place materially below 300° F., it is generally unnecessary to heat much above this point. Thus, it may be stated in general that a reaction temperature of 300° to 375° F. is satisfactory.

Where in the appended claims an ester of an aliphatic or fatty acid is referred to it will be understood that mixtures of such esters as well as compositions containing a substantial proportion of one or more of such esters is intended unless otherwise indicated.

Since changes may be made in the processes and products above described without departing from the scope of the invention, it will be understood that the above description is given for illustrative purposes merely and is not intended as a limitation of the invention.

We claim:

1. The process of manufacturing sulphurized products which comprises reacting a simple ester of an unsaturated aliphatic acid that contains at least ten carbon atoms with sulphur at a temperature of at least 300° F. in the presence of water and under a pressure of hydrogen sulphide.

2. The process of manufacturing sulphurized products which comprises maintaining at a temperature of at least 300° F. and under a pressure of hydrogen sulphide a reaction mixture containing sulphur, water, and a simple ester of an unsaturated aliphatic acid that contains at least ten carbon atoms, the weight ratio between the water and the said ester being at least 1:2, until substantially no free sulphur remains in the mixture, whereby said ester is converted into a sulphurized product having good color characteristics.

3. The process of manufacturing sulphurized products which comprises maintaining at a temperature of at least 300° F. and under a pressure of hydrogen sulphide of at least 50 pounds per square inch a reaction mixture containing sul-

phur, water, and a simple ester of an unsaturated aliphatic acid that contains at least ten carbon atoms, the weight ratio between the water and said ester being at least 1:2, until substantially no free sulphur remains in the mixture, whereby said ester is converted into a sulphurized product having good color characteristics.

4. The process of manufacturing sulphurized products which comprises reacting a simple ester of an unsaturated fatty acid containing at least ten carbon atoms, the esterifying radical of said ester being an open chain aliphatic radical, with sulphur at a temperature of at least 300° F. in the presence of water and under a pressure of hydrogen sulphide of at least 50 pounds per square inch.

5. The process of manufacturing sulphurized products which comprises maintaining at a temperature of at least 300° F. and under a pressure of hydrogen sulphide of at least 50 pounds per square inch a reaction mixture containing sulphur, water, and a simple ester of an unsaturated fatty acid containing from 16 to 18 carbon atoms, the esterifying radical of said ester being an open chain aliphatic radical, the weight ratio between the water and said compound being at least 1:2, until substantially no free sulfur remains in the mixture, whereby said ester is converted into a sulphurized product having good color characteristics.

6. The process of manufacturing sulphurized products which comprises reacting sperm oil with sulphur at a temperature of at least 300° F. in the presence of water and under a pressure of hydrogen sulphide of at least 50 pounds per square inch.

7. The process of manufacturing sulphurized products which comprises maintaining at a temperature of at last 300° F. and under a pressure of hydrogen sulphide of at least 50 pounds per square inch a reaction mixture containing sperm oil, sulphur, and water, the weight ratio between the water and the sperm oil being at least 1:2, until substantially no free sulphur remains in the mixture, whereby the sperm oil is converted into a sulphurized product having good color characteristics.

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