

UNITED STATES PATENT OFFICE

2,136,379

SULPHURIC ACID DERIVATIVES OF FATTY
ACID DIESTERS OF GLYCOLSLawrence H. Flett, Hamburg, N. Y., assignor to
National Aniline & Chemical Company, Inc.,
New York, N. Y., a corporation of New YorkNo Drawing. Application July 17, 1935,
Serial No. 31,864

25 Claims. (Cl. 260—458)

This invention relates to sulphuric acid derivatives of fatty acid diesters of glycols and to processes of making the same. As employed herein, the term "fatty acid" means aliphatic mono-

5 carboxylic acid.

The sulphated and sulphonated derivatives of glycerin esters (glycerides) of fatty acids have heretofore been employed in the arts and particularly in the art of treating and finishing textile materials; but owing to the ease with which they undergo hydrolysis or saponification, they are unsatisfactory for use in many connections. It has also been proposed heretofore to prepare sulphonation and sulphation derivatives of fatty acids in which the carboxyl and/or the sulphonic or sulphuric acid radicals are esterified by monohydric alcohols; but the latter products do not exhibit hydrotropic or detergent powers to a sufficient extent for many of the desired applications of said products in the arts. Moreover, the fatty acid esters of monohydric alcohols upon sulphonation tend to undergo hydrolysis or to effect the migration of the alkyl group from the carboxyl group in part or wholly to the sulphoxyl group.

25 I have found, by sulphating and/or sulphonating fatty acid diesters of glycols, which esters contain at least one fatty acid residue capable of reacting with a sulphonating agent (that is, which esters contain at least one double bond and/or at least one hydroxyl group in one or both of the fatty acid residues), that products are obtained having highly valuable properties. The products, which are herein referred to as "sulphuric acid derivatives of fatty acid diesters of glycols," are fatty acid diesters of glycols in which at least one of the fatty acid residues contains at least one sulphuric acid residue (a sulphate or sulphonate group in the form of the free acid or a salt thereof) and especially sulphate and/or sulphonate derivatives of esters of glycols having the general formula



in which G represents the residue of a glycol and
45 R and R' each represents the residue of a fatty acid, one or both of the residues R and R' containing at least one double bond and/or at least one hydroxyl group. Preferred products are sulphates and/or sulphonates of esters of the said type in which at least one of the residues represented by G, R and R' contains 8 or more carbon atoms. It will be understood that where in the specification and claims the term "residue of a fatty acid" is employed it refers to the part of a
55 fatty acid molecule other than the carboxyl group.

Also, it will be understood the term "residue of a glycol" refers to the part of the molecule of a simple or polyglycol other than the hydroxyl groups.

The said products are more resistant to hydrolysis or saponification than the products resulting from the sulphation and/or sulphonation of the glycerides of unsaturated and hydroxy fatty acids, and the said products are more stable against decomposition on standing than the products of sulphation and/or sulphonation of the said esters derived from monohydric alcohols (in which the carboxylic and/or sulphuric, or sulphononic, acid groups are esterified with monohydric alcohols). In view of the superior resistance of the said glycol esters of the fatty acids and their products of sulphonation and/or sulphation to hydrolysis, the amount of free fatty acids present in the products obtained in accordance with the present invention, or in treating compositions in which the said products are employed as active agents, is greatly reduced. Because of this fact and the advantageous hydrotropic and detergent properties of the said products of this invention, as well as their excellent stability toward salts, lime and acids, and their wetting, dispersing and penetrating action, these products are valuable agents and ingredients for the washing, scouring, wetting and other treatment of textile and related materials and in other connections where the said properties come into play.

As examples of specific glycols the esters of which may be employed in accordance with the present invention, there may be mentioned the various dihydric alcohols (alkan-diols) and their hydroxy alkyl ethers which contain only two free hydroxyl groups; as for example, the aliphatic dihydric alcohols ranging from ethylene glycol to the tetra-kosan-diols and higher (such as ethan-, propan-, butan-, pentan-, hexan-, heptan-, octan-, nonan-, and decan-diols, stearyl glycol, etc.), and the polyalkylene glycols (such as di- to hexa-ethylene glycols, ethylene propylene diglycol, and the like).

As examples of unsaturated and/or hydroxy fatty acids whose esters with the glycols may be employed in accordance with the present invention, there may be mentioned crotonic, tiglic, elaidic, erucic, brassidic, sorbic, oleic, linoleic, linolenic, glyceric, hydroxy caprylic, hydroxy myristic, mono- and di-hydroxy palmitic, mono- and di-hydroxy stearic, and ricinoleic acids, and the like.

The invention will be illustrated by the following specific examples in which the parts are by weight and the temperatures are in degrees centigrade.

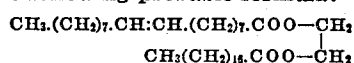
- 5 *Example 1.*—To 150 parts of ethylene dioleate (dioleic ester of ethylene glycol) there is slowly added, with good stirring, 74 parts of sulphuric acid monohydrate while maintaining the temperature at 0° to 5° C. After all of the sulphuric acid is added, the mixture is stirred until a sample is found to be completely soluble in water, which ordinarily requires about 2.5 to 3 hours. The mixture is then poured upon 300 parts of ice and allowed to stand until it separates into two layers. 10
- 15 The upper oily layer is separated and neutralized while maintaining a temperature not exceeding 10° C. by treatment with a 50 per cent caustic soda solution, the neutralized mass is saturated with common salt, and the resultant oil is separated and filtered. The crude product thus obtained is soluble in water and possesses wetting, emulsifying and detergent powers to a high degree. It consists principally of the sodium salt of the monosulphuric ester of ethylene dioleate. By 20
- 25 drying the product, as by evaporation at atmospheric or sub-atmospheric pressure, it may be obtained in a soap-like state or form.

- 30 *Example 2.*—The di-ricinoleic ester of ethylene glycol is employed in the process of Example 1 instead of the ethylene dioleate. A product is thus obtained which is a light brown oil, soluble in acid, neutral and alkaline, aqueous solutions and in alcohol.

- 35 *Example 3.*—A mixed product resulting from the esterification of 1 molecular equivalent of ethylene glycol with 2 molecular equivalents of a technical mixture of oleic and linoleic acids (obtained, for example, by saponification of the oil resulting from the removal of palmitin and 40 stearin from corn oil), said product containing in admixture ethylene dioleate, ethylene dilooleate and ethylene oleate linoleate, is subjected to the treatment described in Example 1 instead of the ethylene dioleate. The product thus obtained is 45 a light brown oil, soluble in acid, neutral and alkaline, aqueous solutions and in alcohol.

- 50 *Example 4.*—11.2 parts of sulphuric acid monohydrate are gradually added to 25 parts of triethyleneglycol dioleate, the temperature of the mixture (which is continuously agitated) being held throughout between 0° and 5° C. After the addition of the acid is complete (about 1 hour) the mixture is agitated for an additional 3 hours and is then neutralized by treating it with 15.8 55 parts of 50 per cent. sodium hydroxide solution. 10 parts of water are added and the mixture is filtered to remove sodium sulphate formed as a by-product. The mass is then left standing for about three days to crystallize out additional sodium sulphate and it is then again filtered. The resulting impure product is a light brown oil soluble in neutral, acid and alkaline, aqueous solutions, and in alcohol.

- 60 *Example 5.*—50 parts of ethylene oleate stearate having the following probable formula:



- are slowly added to 55 parts of well-stirred sulphuric acid monohydrate maintained at a temperature of 0°–5° C. When the addition of the ester is complete, the reaction mass is stirred until a sample of the mass becomes soluble in water, which ordinarily requires about 3 hours. 70
- 75 The mixture is then poured onto ice, common salt

is added, and the resulting oil layer is removed and neutralized by addition of the necessary quantity of a 50 per cent. solution of caustic soda. Salt is added to saturate the neutralized mass and the semi-solid product thus obtained is filtered off. The crude product, consisting principally of the sodium salt of the monosulphuric ester of ethylene oleate stearate, possesses excellent hydrotropic and detergent properties.

10 *Example 6.*—(A) A mixture of 282 parts of oleic acid, 53 parts of diethylene glycol and 30 parts of secondary amyl alcohol is heated to boiling under a reflux condenser. The condensed vapors are returned from the reflux condenser through a separation unit where the water formed by the 15 reaction is separated and removed from the solvent (amyl alcohol), the latter being permitted to flow back into the reaction vessel. When 18 parts of water have been separated and removed, a sample of the reaction mass is titrated with a standard caustic soda solution and if the titration shows that more than 5 per cent. of free acid is present, the refluxing is continued until a test sample shows that the esterification is at least 95 25 to 99 per cent. complete. The resulting product is comprised chiefly of diethylene glycol dioleate. It has a specific gravity less than that of water and a viscosity approximately that of glycerine.

(B) To 25 parts of the diethylene glycol dioleate obtained as the resulting product in Part (A) of this example, there is slowly added, with good agitation, 13 parts of sulphuric acid monohydrate, the temperature being maintained at 0° to 5° C. After all of the acid is added, the mixture is stirred and maintained at 0° to 5° C. for about 3 35 hours. The reaction mass, and a 50 per cent. aqueous solution of caustic soda, are each then slowly, separately and simultaneously added to 20 parts of alcohol maintained at a temperature of 0° to 5° C., the caustic soda solution being added 40 at such a rate as to maintain the resulting alcoholic solution in a slightly alkaline condition until near the end of the reaction at which time it is adjusted to neutrality and finished. The alcoholic reaction mixture is warmed to 50° C., filtered, and the filtrate evaporated to remove the 45 alcohol. The resulting product, which possesses fatty characteristics and is composed chiefly of the sodium salt of diethylene glycol dioleate monosulphate, is diluted with such an amount of water as to give a solution equivalent to approximately 38 per cent. of diethylene glycol dioleate. It possesses excellent hydrotropic, wetting and detergent properties.

55 In the above example (Part A), other solvents than secondary amyl alcohol may be used, for example, toluene, carbon tetrachloride, ethylene dichloride, and other solvents which are relatively insoluble or difficultly soluble in water.

60 The products obtained in accordance with the foregoing examples are in the form of oils owing to the presence of water which they contain and they are a light brown in color owing to the presence of impurities. If desired, they may be dried by any of the usual drying procedures for similar products, as for example, by evaporation on a rotary drum drier, to form a soap-like product of a similar brownish color.

65 The neutralization of the sulphonation mass in the presence of a water-miscible alcohol, as carried out in this example, is described and claimed in application Serial No. 126,736 of G. C. Toone, filed February 19, 1937.

70 *Example 7.*—100 parts of the sodium salt of the sulphuric ester of ethylene dioleate (prepared 75

for example as in Example 1) are heated with 122 parts of sodium sulphite and 40 parts of water in an autoclave at 160° C. for 3 hours. The reaction mass is cooled, mixed with 100 parts of water and dried on a rotary drum drier. The dried product, which comprises the sodium salt of the sulphonate of ethylene dioleate and inorganic salts, is extracted with alcohol and the alcoholic extract is dried on a drum drier. The product thus obtained is in the form of flakes which are white to light brown in color. It is the sodium sulphonate of ethylene dioleate substantially free from extraneous inorganic salts such as sodium sulphite and sodium sulphate. There is sometimes present a small amount of unchanged initial material. It possesses excellent wetting, emulsifying and detergent properties.

Other sulphonic acids of glycol diesters may be prepared in a similar manner from the corresponding sulphuric esters of glycol diesters.

Example 8.—Cleansing composition.

Two parts of the sodium salt of ethylene dioleate sulphate as prepared in Example 1 are dissolved in 1000 parts of a 1 per cent. common salt solution. Upon washing a white worsted cloth, which is fully soiled with mineral oil or tallow mixed with lamp black, in this solution at a temperature of 50° C., and subsequently rinsing the cloth thoroughly with water, it is recovered substantially free from contaminating materials and is white in color.

The cleansing solution may be prepared in any desired strength.

It will be realized by those skilled in the art that the invention is not limited to the details of the foregoing examples. Thus, the invention is generally applicable to the production of sulphates and/or sulphonates of glycol esters having the general formula:



in which G represents the residue of a glycol, and A and A' each represents the residue of a fatty acid, one or both of the residues A and A' containing at least one sulphonate and/or sulphate group in the form of the free acid or a salt thereof.

The details of the methods of preparation of the products of the present invention described in the foregoing examples also may be varied. Thus, other esters of glycols having the foregoing formula (I) may be subjected to sulphonation and/or sulphation, and especially those derived, on the one hand, from a glycol containing 2 or more carbon atoms, more particularly from 2 to 20 carbon atoms and especially from 2 to 6 carbon atoms, and, on the other hand, at least in part from a fatty acid capable of reacting with a sulphonating agent, more particularly one containing 10 or more carbon atoms and especially one containing from 16 to 18 carbon atoms. (Ranges herein given are inclusive of the limiting quantities.)

The glycol diesters employed in the preparation of the sulphuric acid derivatives of the present invention may be prepared by any suitable procedure, a number of which are well known. For example, the glycol (for example, commercial ethylene glycol) may be heated with the carboxylic acid or a mixture of carboxylic acids (for example, commercial oleic acid known as "red oil"), usually at the boiling temperature in the presence or absence of a small quantity of an esterification catalyst, such as a mineral acid and

in the absence or presence of an inert, water-insoluble, organic liquid suitable for removing water by distillation; or the glycol (for example, ethylene glycol) may be first heated with an amount of one carboxylic acid, which may be a saturated fatty acid, sufficient to produce a monoester of the glycol (for example, 1 mol of stearic acid) and then the monoester (for example, glycol mono-stearate) may be further esterified by heating it with another carboxylic acid (for example, oleic acid).

While, as indicated above, the present invention includes sulphuric acid derivatives of fatty acid diesters of glycols in which only one of the two fatty acid residues contains a double bond and/or a hydroxyl group and the other fatty acid residue is a saturated aliphatic hydrocarbon radical (as for example, CH_3 , $\text{C}_{12}\text{H}_{25}$, $\text{C}_{17}\text{H}_{35}$, etc.) the preferred products are sulphuric acid derivatives of fatty acid diesters of glycols in which each of the fatty acid residues contains at least one double bond or hydroxyl group.

Other sulphonating agents (which term generically includes sulphating agents) may be employed, as for example concentrated sulphuric acid, oleum, chlorosulphonic acid, sodium chlorosulphonate, the acid sulphuric esters of the mono- and poly-hydric alcohols, etc., and mixtures thereof. The treatment with the sulphonating agent may also be carried out with the aid of a sulphonation assistant, as for example, acetic anhydride, etc., and/or with the aid of a solvent or diluent, as for example, carbon tetrachloride, etc. The temperature at which the treatment with the sulphonating agent is carried out also may be varied. The particular sulphonation conditions, including temperature, employed will depend in part upon the specific properties desired of the final product. It appears that the more vigorous the sulphonating agent and the more elevated the temperature, the greater is the proportion of sulphonic acid derivatives and the lesser the proportion of sulphuric esters (sulphates) produced.

The products of the present invention may be prepared in the form of the free sulphonic acids and/or sulphates or in the form of their salts of metals, or of ammonia or of organic bases. In view of the ease of preparation of the alkali metal salts and the advantageous stability and solubility thereof in various aqueous solutions, they are ordinarily produced in the form of the alkali metal salts. It will be understood that where in the specification and claims a "sulphuric acid residue" is referred to, this term denotes generically one of the groups which in the form of the free acid have the formulas $-\text{OSO}_3\text{H}$ and $-\text{SO}_3\text{H}$; and that where in the specification and claims a "sulphuric ester group" is referred to, this term denotes the group which in the form of the free acid has the formula, $-\text{OSO}_3\text{H}$. As above indicated, in the compounds of the present invention containing one or more sulphuric acid residues, these groups may be in the free acid or salt form and are preferably in the form of alkali metal salts.

The products of the present invention are characterized by their excellent detergent, wetting and dispersing properties. They are accordingly useful in the washing and cleaning of textile and related materials, and as ingredients of preparations for the cleaning, wetting and other treatment of textile and related materials. They are also useful as ingredients of preparations intended

ed for use as insecticides, cosmetics and other compositions.

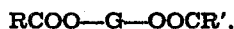
I claim:

1. A sulphuric acid derivative of a fatty acid diester of a glycol.

2. A sulphuric acid derivative of a fatty acid diester of a glycol, in which at least one of the fatty acid residues contains at least one sulphuric ester group.

3. A sulphuric acid derivative of a fatty acid diester of a glycol, in which one of the fatty acid residues contains at least one sulphuric ester group and the other fatty acid residue is unsulphonated.

4. A sulphuric acid derivative of a fatty acid diester of a glycol which diester corresponds with the general formula



in which G represents the residue of a glycol and R and R' each represents the residue of a fatty acid, at least one of the residues R and R' containing at least one member of the class consisting of the —OH group and the —C=C— linkage and at least one of the residues, G, R and R' containing at least 8 carbon atoms, and obtainable by subjecting a diester of the said type to sulphonation.

5. A sulphuric acid derivative of a fatty acid diester of a glycol in which at least one of the fatty acid residues contains at least 10 carbon atoms and at least one sulphuric acid residue.

6. A sulphuric acid derivative of a fatty acid diester of a glycol in which at least one of the fatty acid residues contains at least 10 carbon atoms, the glycol residue contains 2 to 6 carbon atoms, and at least one of the fatty acid residues contains a sulphuric acid residue.

7. A sulphuric acid derivative of a fatty acid diester of a glycol, in which each of the fatty acid residues contains at least 10 carbon atoms and at least one fatty acid residue contains a sulphuric ester group, said sulphuric acid derivative being obtainable by sulphonating a fatty acid diester of a glycol in which at least one fatty acid residue contains at least one member of the class consisting of the —OH group and the



linkage.

8. A sulphuric acid derivative of a fatty acid diester of a glycol, in which each of the fatty acid residues contains at least 10 carbon atoms, one fatty acid residue contains a sulphuric ester group, and the other fatty acid residue is unsulphonated, said sulphuric acid derivative being obtainable by sulphonating a fatty acid diester of a glycol in which at least one fatty acid residue contains at least one member of the class consisting of the —OH group and the



linkage.

9. A sulphuric acid derivative of a fatty acid diester of a glycol in which each of the fatty acid residues contains at least 10 carbon atoms and at least one of the fatty acid residues contains at least one sulphuric acid residue.

10. A sulphuric acid derivative of a fatty acid diester of a glycol in which each of the fatty acid residues contains at least 10 carbon atoms, at least one of the fatty acid residues contains at least one sulphuric acid residue, and the glycol residue contains 2 to 20 carbon atoms.

11. A sulphuric acid derivative of a fatty acid diester of a glycol in which each of the fatty acid residues contains 16 to 18 carbon atoms and the glycol residue contains 2 to 6 carbon atoms, at least one of the fatty acid residues containing a sulphuric acid residue.

12. A sulphuric acid derivative of a fatty acid diester of diethylene glycol in which both of the fatty acid residues contain 16 to 18 carbon atoms, at least one of the fatty ester groups containing a sulphuric acid residue.

13. A sulphuric acid derivative of a fatty acid diester of ethylene glycol in which both of the fatty acid residues contain 16 to 18 carbon atoms, at least one of the fatty acid residues containing a sulphuric ester group.

14. A sulphuric acid derivative of a fatty acid diester of ethylene glycol in which both of the fatty acid residues contain 16 to 18 carbon atoms, one of the fatty acid residues contains a sulphuric ester group, and the other fatty acid residue is unsulphonated.

15. A process which comprises reacting a sulphonating agent with a fatty acid diester of a glycol containing at least one fatty acid residue capable of reacting with the sulphonating agent.

16. A process which comprises reacting a sulphonating agent with a fatty acid diester of a glycol having the general formula



in which G represents the residue of a glycol and R and R' each represents the residue of a fatty acid, at least one of the residues R and R' containing at least one member of the class consisting of the —OH group and the



linkage and at least one of the residues G, R and R' containing at least 8 carbon atoms.

17. A process which comprises reacting a sulphonating agent with a fatty acid diester of a glycol in which both of the fatty acid residues are capable of reacting with the sulphonating agent.

18. A process which comprises reacting a sulphonating agent with a fatty acid diester of a glycol containing at least one fatty acid residue having at least 10 carbon atoms and capable of reacting with the sulphonating agent.

19. A process which comprises reacting a sulphonating agent with a fatty acid diester of a glycol containing 2 to 20 carbon atoms in which both of the fatty acid residues contain at least 10 carbon atoms and are capable of reacting with the sulphonating agent.

20. A process which comprises reacting a sulphonating agent with a fatty acid diester of a glycol containing at least one fatty acid residue containing at least one member of the class consisting of the —OH group and the



linkage.

21. A process which comprises reacting a sulphonating agent with a fatty acid diester of ethylene glycol in which both of the fatty acid residues contain a hydroxyl group and 16 to 18 carbon atoms.

22. A process which comprises reacting a sulphonating agent with a fatty acid diester of ethylene glycol in which both of the fatty acid residues contain a double bond and 16 to 18 carbon atoms.

23. A sulphuric acid derivative of diethylene glycol dioleate.

25. A sulphuric acid derivative of diethylene glycol dioleate, in which one of the oleic acid residues contains a sulphuric ester group and the other oleic acid residue is unsulphonated.

24. A sulphuric acid derivative of diethylene glycol dioleate, in which at least one oleic acid residue contains a sulphuric ester group.

LAWRENCE H. FLETT.

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CERTIFICATE OF CORRECTION.

Patent No. 2,136,379.

November 15, 1938.

LAWRENCE H. FLETT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 25, claim 4, for the formula " —C'—C'— " read $\text{—}\overset{\text{C}}{\underset{\text{C}}{\text{=}}}\text{—}$; and second column, line 2, claim 11, for the word "each" read both; line 10, claim 12, for "ester groups" read acid residues; and line 11, same claim, for "acid residue" read ester group; 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 27th day of December, A. D. 1938.

Henry Van Arsdale

(Seal)

Acting Commissioner of Patents.