Patented Oct. 24, 1933 1,932,179

UNITED STATES PATENT OFFICE

1,932,179

SULPHURIC ACID DERIVATIVES OF CARBOXYLIC ARYLIDES

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No Drawing. Application May 27, 1932, Serial No. 614,032, and in Germany April 12, 1929

13 Claims. (Cl. 260—124)

The present invention relates to the production of assistants for the textile and related industries and particularly of wetting, cleansing, softening and dispersing agents.

We have found that excellent assistants for the textile and related industries and particularly wetting, cleansing and dispersing agents are obtained by reacting an aliphatic, that is aliphatic open chain and cycloaliphatic, saturated compound, which contains the group



in which X is either OH (acid), O.R1 (ester),



(anhydride R1 being an aliphatic radicle) or halogen, and R contains from 5 to 15 carbon atoms with an aromatic primary or secondary amine, which is free from aliphatic alcoholic and chromophorous groups, the resulting arylides being then reacted with sulphonating agents to form either sulphonic acids or sulphuric esters, or mixtures of both, or products which contain both sulphuric ester and sulphonic groups, if the arylides are free or only contain an insufficient quantity of sulphuric ester and/or sulphonic acid radicles. The acid components of the arylides do not include mixed aliphatic aromatic acids but may be chosen from any saturated aliphatic acids containing from 6 to 16 carbon atoms especially from those of oils or fats of vegetal, i. e. animal or vegetable origin. Instead of the free acids, their anhydrides or halides or the oils or fats themselves (esters) may be employed. Similarly, the synthetic high molecular fatty acids obtainable by the oxidation of paraffin wax and similar high molecular hydrocarbons by means of gaseous oxidizing agents may be employed or saturated resinic or naphthenic acids; lower aliphatic carboxylic acids containing at least 6 carbon atoms, such as caproic acid, may also be employed. Further specific examples of the acids are for example heptylic, caprylic, nonylic, caprinic, lauric, myristic and palmitic acids as well as the corresponding hydroxycarboxylic acids, such as hydroxy-louric acid, or mixtures of such acids. The said acids may also contain other substituents such as nitro or amino groups.

The said aromatic amines may be chosen from aniline, di-phenylamine, benzidine, biphenyl amines or from naphthylamines and like aromatic amines. In any case these amines must not contain aliphatic alcoholic groups since otherwise esters might be obtained instead of the desired amines, and the amines must be free from chromophorous groups since otherwise colored compounds might be obtained which cannot be used for the purposes intended. The said bases may be employed in the free state or also in the form of their salts when alkaline agents are present during the formation of the arylides. As already stated the acid components may contain one or more sulphonic acid or sulphuric ester groups and the aromatic amines may contain sulphonic groups and in these cases the subsequent sulphonation may be dispensed with; the arylides containing a lower number of sulphuric ester or sulphonic groups are usually suitable as washing and scouring agents and their solubility in water may be increased by introducing further sulphonic acid groups, or of sulphuric ester groups if the acid radicles contain hydroxyl groups. Thus, for example, the carboxylic acids may be converted into arylides with the aid of amino sulphonic acids as for example sulphanilic acid and the like; on the other hand the carboxylic acids may contain sulphuric ester and/or sulphonic groups as for example hydroxy-stearic sulphonic acid or its methyl ester (obtainable by sulphonating oleic methyl ester with chlorsulphonic acid in the presence of ethyl ether and subsequent washing with alkali), the sulphuric ester of hydroxy-stearic methyl ester (obtainable by acting with dimethyl sulphate on the sodium salt of hydroxy-stearic sulphuric ester which latter can be obtained by acting on oleic acid with sulphuric acid at about 20° C.), dihydroxy-stearic sulphuric ester (obtainable from ricinoleic acid and the like).

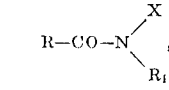
Generally speaking it is advisable to take higher amines, such as naphthyl amines for the conversion when lower carboxylic acids, such as caproic acid or another acid containing up to 10 carbon atoms are employed, and higher carboxylic acids or their derivatives, such as lauric acid and myristic oil, when a lower amine, such as aniline, is used. Particularly suitable are in many cases arylides which have been prepared from higher carboxylic acids, or their derivatives, and from the higher aromatic amines. Stearic acid or still higher carboxylic acids are not employed since products prepared therefrom show an insufficient solubility and sensitivity to precipitation by lime compounds. Arylides from lower acids and lower amines may be usefully employed as wetting agents in baths of a rather high content of electrolytes such as are used for many purposes of the textile industries.

The action and results of the treatment with

sulphonating agents depend on the arylides to be worked and on the conditions of the treatment. Sulphuric esters, for example, can be obtained from arylides containing hydroxyl groups as pointed out above. For the production of sulphuric esters the reaction may be carried out with concentrated sulphuric acid or also with stronger sulphonating agents, such as fuming sulphuric acid, sulphur trioxide or chlorsulphonic acid, which latter agents or mixtures thereof with sulphuric acid are usually preferred. The reaction may be carried out in the presence of diluents, such as carbon tetrachloride, trichlor ethylene, nitrobenzene, acetic acid and the like which usually allow of reducing the temperature of working, and/or in the presence of agents removing water, such as anhydrides or chlorides of organic or inorganic acids. At least one molecular proportion of sulphonating agent is usually employed with each molecular proportion of the arylide concerned, but in the aforesaid case of acting on compounds containing hydroxyl groups with strong sulphonating agents, such as sulphur trioxide or chlorsulphonic acid or with mixtures of milder sulphonating agents with the strong sulphonating agents or with agents removing water, the quantity of the strong sulphonating agents, or of the agents removing water should not exceed one molecular proportion for each hydroxyl group. In most cases, the temperature employed during the reaction should not considerably exceed 40° C. when more than one molecular proportion of sulphonating agent is employed for each molecular proportion of arylide.

If, however, sulphonic acids are to be produced and when the primary reaction products do not already contain one or more sulphonic groups, the temperature of a sulphonation by means of sulphuric acid monohydrate must exceed 40° C., a temperature of about 100° C. being preferably chosen, since otherwise sulphuric esters might be formed if hydroxyl groups be present or no reaction takes place. When stronger sulphonating agents, such as fuming sulphuric acid, sulphur trioxide or chlorsulphonic acid or mixtures of mild sulphonating agents with these or with agents removing water be employed for this sulphonation of compounds containing one or more hydroxyl groups, the quantity of these strong sulphonating agents or of the agents removing water must exceed one molecular proportion per each hydroxyl group present. It is obvious that variations of the conditions described may lead to the production of mixtures of products of the said different types. When working with considerable quantities of strong sulphonating agents sulphonic radicles may be introduced into an aliphatic radicle of such an arylide together with a sulphonation of the nucleus.

The products according to the present invention correspond to the general formula



wherein R—CO denote a radicle of an aliphatic, that is an open chain aliphatic or cycloaliphatic, saturated carboxylic acid containing from 6 to 16 carbon atoms, R_1 denotes an aromatic mono- or polynuclear radicle free from aliphatic and chromophorous groups, whereas X denotes hydrogen or a radicle of the kind denoted by R_1 or the same as R_1. In any case R or R_1, or both, will contain at least one sulphonic acid radicle, or R will contain a sulphuric ester radicle and R_1 may then contain one or more sulphonic acid radicles. As another possibility R may contain both a sulphuric ester radicle and a sulphonic acid radicle, as may happen for example by a condensation of a hydroxy-fatty acid sulphonic acid with an amine, or amine sulphonic acid, and subsequent treatment with a sulphonating agent. The number of carbon atoms in R—CO cannot be chosen below 6, since, otherwise, the products would not substantially show the desired properties.

The resulting products are distinguished by excellent wetting properties, in neutral, acid or also alkaline baths. The products are also not precipitated by the constituents of hard water. Consequently the products according to the present invention constitute highly valuable assistants for all the branches of the textile and allied industries. Anilides prepared from hydroxyl-bearing fatty or resinic acids, and treatment with a sulphonating agent may or the condensation of higher primary aromatic amines with carboxylic acids containing sulphonic or sulphuric ester groups may generally find useful application especially as wetting agents, whereas arylides prepared from fatty acids free from hydroxyl groups, and sulphonation, are particularly valuable washing, scouring, softening and emulsifying agents, as well as the products prepared by the condensation of high molecular saturated carboxylic acids and aromatic primary amines containing sulphonic groups. The secondary arylides are particularly stable even in alkaline baths, have a high emulsifying and levelling power and a far reaching power for dispersing water-insoluble or difficultly water-soluble solid substances, such as alkaline earth metal soaps, water-insoluble dyestuffs or other water-insoluble coloring materials, fats, waxes and the like.

The arylides according to the present invention may be employed as such or in conjunction with other wetting or emulsifying agents, such as soaps, products of the type of Turkey red oils, sulphonic acids of aromatic and especially of polynuclear compounds or their salts, hydroxyalkyl amines, quaternary ammonium bases or their salts, or with protective colloids, such as glue, gelatine or vegetable mucilages or gums. Salts as for example soda, sodium bicarbonate, waterglass, common salt, neutral or acid sodium sulphate may be added, or organic solvents, such as monocresyl ethylene glycol ether, trichlorethylene or bleaching agents, such as perborates, percarbonates, para-toluene sulphonic chloramide sodium. The said agents are employed in quantities depending on the desired purpose and several of them may be added conjointly. Thus, for example, the quantity of these additions may be the same as that of the arylides or considerably higher depending on the purposes of emulsifying, wetting, washing, cleaning or dispersing solid water-insoluble materials in water. In baths for the treatment of textiles the quantity of the sulphonated arylides may be as low as a few per cent or even a few per thousand of the whole liquors.

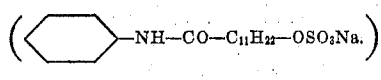
All the products according to the present invention must be free from nitro and auxochromic groups, since otherwise they would be inoperative for the different purposes of their application and should preferably contain at least 12 carbon atoms.

The present application is a continuation in part of the application Ser. No. 441,717, filed April 4, 1930.

The following examples will further illustrate how the said invention may be carried out in practice, but the invention is not restricted to these examples. The parts are by weight.

Example 1

100 parts of α-hydroxy-lauric anilide (obtainable by heating α-hydroxy-lauric methyl ester and aniline until the distillation of methyl alcohol has ceased) are mixed at about 35° C. with 200 parts of concentrated sulphuric acid and are then treated with 75 parts of fuming sulphuric acid containing about 23 percent of SO_3. The reaction mixture is then incorporated with water containing some ice, neutralized with caustic soda solution and subjected to extraction with ethyl alcohol, if a separation from Glauber's salt be desired. The product recovered from the alcoholic solution consists mainly of the sodium salt of lauric anilide sulphuric ester



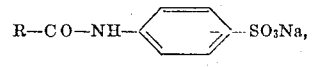
A similar product can be obtained from di-phenylamine in the place of aniline.

Example 2

1000 parts of a mixture of saturated fatty acids containing mainly from 12 to 15 carbon atoms and obtained by the liquid phase oxidation of paraffin wax with the aid of air while warming to say 150° C. and separating the acids from unattacked initial material, are heated under reflux with 2000 parts of aniline for 17 hours to from 180° to 190° C., the water formed during the reaction being continuously distilled off. The remainders of free aniline are then distilled off in vacuo and the residue is dissolved in 4,750 parts of sulphuric acid monohydrate. 2200 parts of fuming sulphuric acid containing 23 per cent of sulphur trioxide are then introduced into the solution at about 10° C. and the mixture is stirred for about 20 hours at 20° to 25° C. The reaction product is then poured onto a mixture of ice and common salt and filtered. The product may be employed as such or after neutralization with caustic soda, if desired after removal of the mineral acid salts. It possesses a high resistance to acid and a high scouring power superior to that of soaps and is not precipitated from aqueous solutions by means of alkaline earth metals.

Example 3

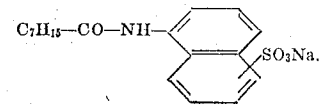
500 parts of coconut oil fatty acid anilide (from acting with the mixture of the fatty acids of coconut oil on aniline) are fused and introduced at 20° C. into 1000 parts of sulphuric acid monohydrate; 1000 parts of fuming sulphuric acid containing 23 per cent of SO_3 are then introduced at from 30° to 35° C. and the mixture is stirred at this temperature for 4 hours. The product, which is a mixture of the sulphonic acid sodium salts of the anilides of the different acids of the coconut oil and thus corresponds to the general formula



is poured onto ice, rendered neutral with caustic soda and inspissated.

Example 4

14 parts of α-naphthyl-amine are dissolved in 10 parts of pyridine, whereupon 30 parts of caprylic chloride are added while cooling. After warming to about 98° C. for ½ hour under reflux the product is washed with aqueous acetic acid and dried. 20 parts of the caprylic naphthyl amide are dissolved in 19 parts of sulphuric acid mono-hydrate, 40 parts of fuming sulphuric acid containing 23 per cent of SO_3 are added and the whole is warmed to from 50° to 60° C. until a sample is soluble in water. The reaction mixture is poured onto ice, rendered neutral with caustic soda and inspissated. The product corresponds presumably to the formula



Example 5

20 parts of undecylic toluidide are dissolved in 40 parts of sulphuric acid monohydrate and then stirred at from 100° to 120° C. with 40 parts of fuming sulphuric acid containing 23 per cent of SO_3 until the product is water-soluble, whereupon the latter is poured onto ice, neutralized with aqueous caustic soda solution and inspissated.

Example 6

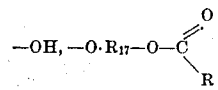
25 parts of saturated naphthenic di-phenylamide, obtainable by acting on a solution of diphenylamine in pyridine with naphthenic chloride (prepared by acting with phosphorus trichloride on commercial saturated napthenic acid) are mixed with 20 parts of sulphuric acid monohydrate at from 10° to 15° C., whereupon 50 parts of fuming sulphuric acid containing 23 per cent of SO_3 are added and the whole is heated to about 98° C. until a sample is soluble in water. The reaction mixture is poured onto ice, neutralized with aqueous caustic soda and inspissated.

What we claim is:

1. The process for the production of carboxylic arylides containing sulphuric derivative radicles which comprises reacting an aliphatic saturated compound containing the grouping



in which X is either halogen

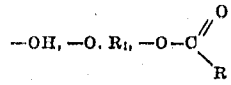


R being an aliphatic saturated radicle containing from 5 to 15 carbon atoms and R being an aliphatic saturated radicle, which radicles may possess sulphuric ester or sulphonic acid groups, with an aromatic amine free from aliphatic alcoholic and chromophorous groups, but containing at least one hydrogen atom connected to a nitrogen atom which amine may contain sulphuric derivative groups, and if the above initial reacting components do not contain sulphuric ester or sulphonic acid groups, reacting the resulting arylide with a sulphonating agent.

2. The process for the production of carboxylic arylides containing sulphuric derivative radicles, which comprises reacting an aliphatic saturated compound containing the group

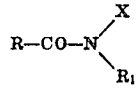


in which X denotes



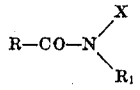
or halogen, R being an aliphatic saturated radicle containing from 5 to 15 carbon atoms and R_1 being an aliphatic saturated radicle, with an aromatic amine free from aliphatic alcoholic and chromophorous groups but containing at least one hydrogen atom connected to a nitrogen atom, the resulting carboxylic arylide being then reacted with a sulphonating agent.

3. Carboxylic arylides corresponding to the formula



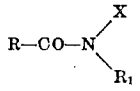
in which R—CO denotes an aliphatic saturated radicle containing from 6 to 16 carbon atoms, R_1 denotes an aromatic radicle of the benzene or naphthalene series free from aliphatic alcoholic and chromophorous groups and X denotes hydrogen or a radicle as denoted by R_1, at least a hydrogen atom of R or R_1 being substituted by a sulphonic acid group or at least a hydrogen atom of R being substituted by a sulphuric ester group.

4. Carboxylic arylides corresponding to the formula



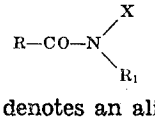
in which R—CO denotes an aliphatic saturated radicle containing from 6 to 16 carbon atoms, R_1 denotes an aromatic radicle free from aliphatic alcoholic and chromophorous groups and X denotes hydrogen or a radicle as denoted by R_1, at least a hydrogen atom of R or R_1 being substituted by a sulphonic acid group or at least a hydrogen atom of R being substituted by a sulphuric ester group.

5. Carboxylic arylides corresponding to the formula



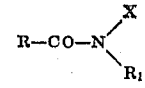
in which R—CO denotes an aliphatic saturated radicle containing from 6 to 16 carbon atoms, R_1 denotes an aromatic radicle free from aliphatic alcoholic and chromophorous groups and X denotes hydrogen or a radicle as denoted by R_1, at least a hydrogen atom of R being substituted by a sulphuric ester group and a hydrogen atom of R_1 being substituted by a sulphonic acid group.

6. Carboxylic arylides corresponding to the formula



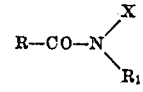
in which R—CO denotes an aliphatic saturated radicle containing from 6 to 16 carbon atoms, R_1 denotes an aromatic radicle free from aliphatic alcoholic and chromophorous groups and X denotes hydrogen or a radicle as denoted by R_1, at least one hydrogen atom of R or R_1 being substituted by a sulphonic acid group.

7. Carboxylic arylides corresponding to the formula



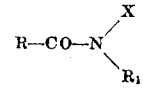
in which R—CO denotes an aliphatic saturated radicle containing from 6 to 16 carbon atoms, R_1 denotes an aromatic radicle free from aliphatic alcoholic and chromophorous groups and X denotes hydrogen or a radicle as denoted by R_1, at least one hydrogen atom of R and one hydrogen atom of R_1 being substituted by sulphonic acid groups.

8. Carboxylic arylides corresponding to the formula



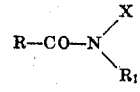
in which R—CO denotes an aliphatic saturated radicle containing from 6 to 16 carbon atoms, R_1 denotes an aromatic mono-nuclear hydrocarbon radicle and X denotes hydrogen or a radicle as denoted by R_1, at least a hydrogen atom of R or R_1 being substituted by a sulphonic acid group or at least a hydrogen atom of R being substituted by a sulphuric ester group.

9. Mixtures of carboxylic arylides corresponding to the formula



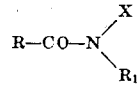
in which R—CO denotes the radicles of the fatty acids of coconut oil, R_1 denotes an aromatic mono-nuclear hydrocarbon radicle and X denotes hydrogen or a radicle as denoted by R_1, at least a hydrogen atom of R or R_1 being substituted by a sulphonic acid group or at least a hydrogen atom of R being substituted by a sulphuric ester group.

10. Mixtures of carboxylic arylides corresponding to the formula



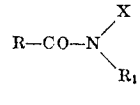
in which R—CO denotes the radicles of the fatty acids of a liquid phase oxidation of paraffin wax with the aid of air while warming, R_1 denotes an aromatic mono-nuclear hydrocarbon radicle and X denotes hydrogen or a radicle as denoted by R_1, at least a hydrogen atom of R or R_1 being substituted by a sulphonic acid group or at least a hydrogen atom of R being substituted by a sulphuric ester group.

11. Carboxylic anilides corresponding to the formula



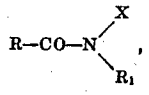
in which R—CO denotes the radicles of the fatty acids of coconut oil, R_1 denotes phenyl and X denotes hydrogen or a radicle as denoted by R_1, at least a hydrogen atom of R or R_1 being substituted by a sulphonic acid group or at least a hydrogen atom of R being substituted by a sulphuric ester group.

12. A mixture of carboxylic arylides corresponding to the formula



in which R—CO denotes the radicles of the fatty acids of coconut oil, R_1 denotes a phenyl sulphonic acid radicle and X denotes hydrogen.

13. A mixture of carboxylic anilides corresponding to the formula



in which R—CO denotes the radicles of fatty acids containing from 12 to 15 carbon atoms, R_1 denotes a phenylsulphonic acid radicle and X denotes hydrogen.

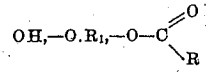
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Certificate of Correction

Patent No. 1,932,179. October 24, 1933.

FRITZ GUENTHER ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 47, for "hydroxy-louric" read *hydroxy-lauric*; page 3, lines 127–130, claim 1, strike out the formula and insert instead:



and line 132, for "R" read R_1; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of May, A. D. 1934.

[SEAL]

BRYAN M. BATTEY,
Acting Commissioner of Patents.