Patented Sept. 26, 1939

2,174,127

UNITED STATES PATENT OFFICE

2,174,127

SULPHATED ACYLOINS AND PROCESS OF PRODUCING THEM

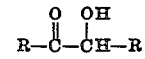
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No Drawing. Application December 13, 1937, Serial No. 179,618

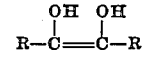
8 Claims. (Cl. 260—458)

This invention relates to sulphated chemical compounds, their preparation, and use. Particularly it relates to sulphation products of acyloins, their preparation and applications as wetting, dispersing, deterging and emulsifying agents, as dye bath assistants and in general as textile assistants.

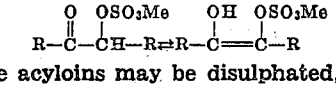
Applicants are aware that sulphated alcohols are old in the chemical art, but it is believed that acyloins with their particular configuration and properties have not been sulphated heretofore. On being sulphated acyloins may react in accordance with either of two tautomeric structures, the keto-alcoholic structure



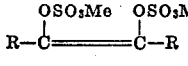
or the di-enolic structure



Consequently a sulphate ester may possess either of the following structures or both



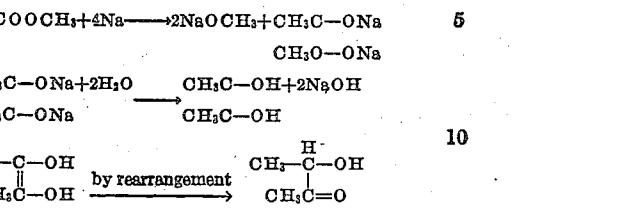
Also, the acyloins may be disulphated, in which case it is thought that the product has the second configuration



Developments in the textile industry have created a demand for improved agents of the class generally referred to as textile assistants. It, therefore, is the general object of this invention to provide a new and useful group of such materials, and procedure for their manufacture; further objects will be evident from the description of the invention.

It has been discovered that a new group of chemical compounds of particular use in the textile arts can be obtained by subjecting acyloins to the action of mild sulphating agents to produce the mono and di-sulphate esters.

Acyloins themselves may be prepared conveniently by the procedure of U. S. Patent 1,996,471 of April 2, 1935. That process consists in reducing an aliphatic acid ester or a mixture of such esters in xylene by means of a suspension of finely divided sodium in xylene. The sodium derivative of the dienol is decomposed with acid and the resulting acyloin is separated from the xylene by fractional crystallization. The following equations in which methyl acetate is the starting material are taken from U. S. Patent 1,996,471. They are given in the patent as typically illustrative of the steps in known procedure for preparation of acyloins.



Another description of the preparation of acyloins may be found on page 2303, vol. 57, of the Journal of the American Chemical Society. The citations are given merely for informative purposes and it is to be understood that applicants' sulphation process applies to acyloins no matter how obtained.

In the sulphation of acyloins a wide range of sulphating agents may be used but it is preferred to employ chlor-sulphonic acid or chlorsulphonic acid with ether or other suitable diluent. Concentrated sulphuric acid modified with commonly used inhibitors, such as potassium acid sulphate gives good results. Among other particular sulphating agents that may be mentioned as satisfactory for our purposes are:

Sodium chlor-sulphonate
Aminosulphonic acid
Pyridine-sulphuric-anhydride
Dimethylaniline-sulphuric-anhydride
Pyridine-sodium pyrosulphate
Acetyl sulphuric acid
Lower alkyl sulphates
Sulphuric anhydride dissolved in ether, etc.

The degree of sulphation is dependent chiefly on the nature of the acyloins sulphated, the choice and amount of sulphating agent used, time of sulphation, agitation, amount of solvent used and temperature. Temperatures of 0–10° C. are employed ordinarily, but with certain inhibitors in the sulphating acid it is possible to operate at somewhat higher temperatures and shorten the time of sulphation.

The following examples, which are not to be construed as limitative, illustrate the sulphation of particular acyloins by procedure within the scope of the invention:

Example I

To 30 grams of capryloin (prepared by the sod-

ium reduction of methyl caprylate) in 100 cc. of anhydrous ether was added a solution of 15 grams chlorsulphonic acid (110% excess of calculated quantity necessary for mono sulphation) in 15 cc. of anhydrous ether. The acid solution was gradually added over a period of 30 minutes, the temperature being maintained at 0–10°, by means of an ice bath. When the acid had all been added, the sulphation mass was stirred one-half hour longer, then neutralized in a mixture of 200 cc. of ice and 25 grams 50% caustic soda solution. The solution was evaporated to dryness and the sulphate ester extracted with methanol. The methanol solution was diluted with water, extracted twice with petroleum ether and the extracted solution evaporated to dryness on the steam bath under moderate vacuum. The monosulphation product was a white solid, soluble in water with foaming. It possessed excellent wetting-out properties.

Example II

To 20 grams of caproin, prepared by the sodium reduction of methyl caprate ($CH_3OOC_{10}H_{19}$) in 100 cc. of anhydrous ether was added a solution of 8.5 grams of chlorsulphonic acid in 10 cc. of anhydrous ether. The solution was stirred one half hour during which time the originally cloudy solution cleared. The sulphation mass was poured into 200 cc. of ice and neutralized to pink with phenolphthalene with 10% caustic soda. The solution was evaporated, the solid taken up in methanol diluted with water, purified by petroleum ether extraction, and the solution evaporated to dryness. The product was the mono sulphation product of caproin. It dissolved in water to give a solution which foamed.

Example III

To 20 grams of capryloin in 100 cc. of anhydrous ether were added 20 grams of chlorsulphonic acid. The acid was added over a period of 30 minutes and then stirred for an additional 30 minutes. The sulphation mass was neutralized by drowning in an ice-caustic soda solution. The solution was evaporated to dryness, taken up in methanol and purified as in the preceding examples. The product is thought to be the di-sulphation product of capryloin.

Example IV

20 grams of mixed acyloins prepared by reducing the esters of fatty acids derived from the oxidation of petroleum and containing an average of twenty carbon atoms were dissolved in 100 cc. of anhydrous ether and sulphated with 15 grams of chloro-sulphonic acid. When a test drop was found to be soluble in water the sulphation mass was added to a mixture of 200 grams of ice and 25 grams of 50% caustic soda solution. The neutralized solution was evaporated to dryness and extracted with methanol. The methanol solution which contained the sulphated acyloin was diluted with water, the unsulphated acyloin extracted with petroleum ether, and the methanol-water solution evaporated to dryness. A yellow waxy product having wetting out properties was obtained.

Example V

30 grams of mixed acyloins prepared as in Example IV but containing an average of sixteen carbon atoms were sulphated and treated as in Example I. The product was found to have excellent wetting properties.

Example VI

30 grams of mixed acyloins prepared by reducing the esters of mono-carboxylic fatty acids derived from the oxidation of oleic acid were sulphated and treated as in Example IV. The product obtained was a waxy solid with good wetting power.

While the examples relate to comparatively few starting materials many other straight chain acyloins can be used such as acetoin, butyroin, valeroin, myristoin, lauroin; mixed acyloins as acet-lauroin from methyl acetate and methyl laurate, butyrcaproin from methyl butyrate and methyl caprate, acyloins of mixtures of acids as coconut oil acids, lard oil acids, rape seed oil acids; branched chain acyloins as iso butyroin, iso butyrlauroin from methyl iso butyrate and methyl laurate; unsaturated acyloins as oleoin butyr-oleoin from butyric and oleic methyl laurate; unsaturated acyloins as oleoin butyr-oleoin from butyric and aleic methyl esters. Also acyloins from cyclic acids such as the naphthenic acids, phenyl acetic acid and phenyl butyric acid can be used.

In foregoing examples sodium salts of sulphated acyloins have been disclosed but salts of other bases can be used, such as those of potassium, lithium, magnesium, ammonium, trimethylamine, triethanolamine and pyridine. For certain purposes it may be necessary or at least advantageous to use a salt other than the sodium salt. Of course, the free acid can be used when desirable.

The acyloin sulphation products comprise a new class of compounds which are water soluble and are highly useful in the textile and other industries. By using different acyloins and degrees of sulphation the properties of the sulphate esters can be greatly varied. The lower acyloin sulphation products e. g. acetoin sulphate, butyroin sulphate, and isohexion sulphate are good printing paste assistants and mercerizing assistants; the sulphation products from higher acyloins i. e. containing a radical of eight or more carbon atoms such as capryloin, acet-oleoin, acet-myristoin serve well as wetting agents; sulphation products of coconut oil acid acyloins, butyr-stearoin, caprolauroin make good detergents. Sulphation products from stearoin and myristoin are useful as dry cleaning soaps. Acyloin sulphation products can also be used in making emulsions of the oil in water type, in making edible emulsions, and as wetting and spreading agents for insecticides and fungicides. They can be used in solid form or as aqueous solutions alone or mixed with other materials such as sodium carbonate, borax, sodium silicate, etc. In the following listings there are shown specifically many further uses in which various sulphated acyloins can be employed with benefit.

A. Treatment for the processing and improvement of natural or synthetic textile materials involving:
1. Cleansing vegetable and animal fibers when removing fatty or oily materials.
2. Carbonization.
3. As an addition to flax wetting baths.
4. Fulling.
5. Sizing.
6. As an addition when sizing is removed from textile materials.
7. Impregnating.
8. Bleaching.
9. Mordanting.

10. As an addition to soap in an acid or hard water bath.
11. Mercerizing lye liquors.
12. Improvement of absorption capability of fibrous materials particularly when subjected to a treatment for finishing, softening, stiffening, coloring or special chemical treatment such as waterproofing or mildew-proofing.
13. Delustering or lustering.
14. Degumming.
15. Kier boiling.
16. Scouring.
17. Stripping.
18. Felting.
19. Oiling or lubricating.
20. Weighting or loading.

B. Dyeing processes:
1. Dyeing in neutral, acid or alkaline baths.
2. Reserving cotton in acid baths.
3. Dyeing with developed dyes.
4. Dyeing of animal fibers with vat dyes.
5. Dyeing cellulose acetate fibers with insoluble dyes.
6. Dyeing and printing with aniline black.
7. Dyeing of leather.
8. In printing pastes to assist in the dispersion of the dye or dye component and in the penetration into the natural or synthetic fiber.

C. Dyes and coloring:
1. For making pastes of dyes or dye components.
2. For the production of pigments of azo, basic acid vat, and sulphur dyes in a finely divided condition.
3. For the production of finely divided inorganic pigments.

D. Miscellaneous uses:
1. For converting liquid or solid substances normally insoluble in water, such as hydrocarbons, higher alcohols, other oxygen containing compounds, fats, oils, waxes, resins, pitches and pitchy substances into clear solutions or stable emulsions or dispersions.
2. As cleansing agents particularly in hard water and where a fatty or oily film resists the ordinary cleansing media.
3. In tanning.
4. In softening and treating baths for hides and skins, particularly the fat liquor treatment.
5. In flotation processes including minerals and oils such as the recovery of fixed oil from the oil sands.
6. In tooth pastes, tooth powders and dentifrices generally.
7. In the treatment of paper pulp and cellulosic materials generally.
8. In latex solutions and adhesives containing latex and related substances.
9. As a mold lubricant for use in the manufacture of rubber and other molded or moldable products.
10. For the breaking of petroleum emulsions which occur in nature or are formed during the refining of petroleum.

E. General:
1. The reagents may be used in pure or standardized form.
2. They may be used in conjunction with the known processing or treating agents.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to specific embodiments thereof except as defined in the appended claims.

We claim:

1. The process of preparing surface active substances which comprises reacting acyloins with a sulphating agent at a temperature in the neighborhood of 0° C. until sulphation is at least partially complete.

2. The process of preparing surface active substances which comprises reacting acyloins dissolved in an inert organic solvent with a sulphating agent at a temperature in the neighborhood of 0° C. until sulphation is at least partially complete.

3. The process of preparing surface active substances which comprises reacting acyloins dissolved in an inert organic solvent with chlorsulphonic acid dissolved in an inert solvent at a temperature in the neighborhood of 0° C. until sulphation is at least partially complete.

4. The process of preparing surface active substances which comprises reacting acyloins dissolved in an inert organic solvent with a sulphating agent at a temperature in the neighborhood of 0° C. until sulphation is at least partially complete, neutralizing the reaction mixture, and separating the sulphated product by extraction with a solvent.

5. The process of sulphating capryloin dissolved in an inert organic solvent with a sulphating agent at a temperature in the neighborhood of 0° C. until sulphation is at least partially complete, neutralizing the reaction mixture and separating the sulphated product by extraction with a solvent.

6. Sulphated acyloins.

7. Sulphated capryloin.

8. New products useful as textile assistants included in the group consisting of sulphated acyloins and water-soluble organic and inorganic salts thereof.

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