ESTERS OF SULPHODICARBOXYLIC ACIDS

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This invention relates to new esters of aliphatic
sulphodicarboxylic acids and to a new method of
producing such esters.

5 Esters of sulpho saturated and unsaturated
aliphatic dicarboxylic acids such as, for example,
methoxy, di-methoxy succinic, sulphochlorosuccinic,
sulphoacetic, sulphopyrrocarboxic, sulphoglutaric,
sulphosuberic, sulphosebacic, sulphomaleic, sul-
phumaric, sulphodimethyl succinic, sulphometh-
amic, sulphophenylsuccinic, sulphonylglutaric, and
other sulphonic dicarboxylic acids of the aliphatic
series have never been prepared hitherto. These esters,
particularly in the form of their alkaline metal form,
are of great importance in industry by reason of their
extraordinarily wetting powers in various aqueous
and organic solutions emulsions or suspensions. They
are also of importance as detergents, emulsifying agents, and the like.

15 A list of a few typical uses for the esters of the
present invention are the following: emulsifying
agents; aids in carbonizing; washing agents;
dye assistants; dispersing agents in making emul-
sions and dispersions of various chemicals, such
as emulsions of hydrocarbons of various groups of
the aliphatic and aromatic series; terpene
emulsions; wetting compositions in emulsified
form; dispersing agents in making emulsified
germicides; color lakes; dye preparations; boring
oil; drilling oils; emulsions of various animal and
vegetable fats and oils; greasing compositions in
emulsified form; lubricating compositions contain-
ing vegetable or animal fats and oils; solvents
for fats in emulsified form; wetting compositions
containing oils in emulsified form; wire-drawing
oils in emulsified form; printing inks; writing
inks; insecticidal preparations in emulsified form;
emulsified dressing compositions containing va-
rious substances such as shellacs, gums, natural
and synthetic resins, fats and oils; emulsified fat
liquoring baths; emulsified finishing compositions;
emulsified soaking compositions containing
nest's-foot oil or other oils to be used as
beaver fat liquors; emulsified waterproofing composi-
tions; automobile polishes; cleansing compo-
sitions containing soaps; compositions for clea-
ning paint and metal surfaces; degreasing and
greasing compositions in emulsified form; de-
tensive and scouring compositions; furniture pol-
ishes in emulsified form; metal polishes in emul-
sified form; scouring compositions for wood-
work, linoleum, rugs, and the like; shoe creams
and polishes in emulsified form; waterproofing
compositions in emulsified form for treating mis-
cellaneous fibrous and other compositions of
matter; coating compositions for oicloth and
linoleum; asphalitic paints and varnishes; emul-
sified paints and varnishes; pigment emulsions;
shellac emulsions; emulsified preparations used
for the treatment of paper and pulp products;
sizing compositions in emulsified form containing
rosin, casein, starches and the like; waxing com-
positions in emulsified form; creams in emulsified
form; emulsified shampoos; lotions; latherless
shaving creams; various emulsified perfumes and
cosmetics; emulsions containing petroleum or
heavy petroleum distillates; emulsified cutting
oils for lathe and screw-press work; kerosene
emulsions; naphtha emulsions; soluble greases
in emulsified form; soluble oils in emulsified
form; for lubricating textile machinery; various
emulsified textile oils; rubber compositions in
emulsified form; special emulsified preparations
used for coating, protecting, decorating and other
surface treating of rubber mechanism; hand-
cleaning compositions in emulsified form; various
emulsified cleansing and scouring compositions
containing soap; dressing compositions in emul-
sified form; dispersions used for degreasing and
washing raw wool; emulsified preparations for
degumming silk; emulsions for soaking and
emulsified mercerizing baths; special lubricating
compositions used in weaving, knitting, warping
and winding; emulsions for fire extinguishers;
emulsions for the preservation and impregnation
of wood; and emulsions for mordanting.

The esters may be prepared by esterifying the
sulpho acids, which acids may be prepared either
by sulphonating the unsulphonated saturated
acid or by adding a sulphite or bisulphite to the
50 corresponding unsaturated acid or its salts. An-
other method of producing the sulpho acid is to
35 treat the halogenated saturated acid with a
relatively pure product from a crude unsaturated
acid. This is of particular importance in conjunction with the pro-
cess of new esters as new chemical compounds
is not concerned with the particular method by
which the esters are prepared, in a more specific
aspect an improved process of comparing the
esters is included. This process consists in ester-
ifying the corresponding unsaturated acid and
adding a bisulphite to the ester. This process
presents marked advantages over the alternative
process of esterifying the already prepared sul-
pho acid, since the unsaturated acid is prac-
tically in all cases more easily esterified and in the
form of the ester can be readily purified where
it is desired to produce a relatively pure product
from a crude unsaturated acid. This is of par-
maker important in conjunction with the pro-
duction of esters of sulphosuccinic acid because the raw material, maleic and fumaric acids, can be readily obtained in a somewhat crude form as a byproduct from the manufacture of phthalic anhydride, by the catalytic oxidation of naphthalene. As the esters of sulphosuccinic acid can be manufactured very cheaply and show extraordinary properties as wetting agents and emulsifying agents and are commercially of prime importance, the preferred process is of special economic value in conjunction with the production of esters of sulphosuccinic acid.

The esters of the sulphoaliphatic dicarboxylic acids are of the most various types. Thus, for example, esters of low molecular alcohols such as methyl and ethyl and propyl alcohols, are very soluble in water in the form of their alkaline metal salts, and form excellent detergents. Esters of higher molecular alcohols show increasing powers as wetting agents, but in general with a decreasing solubility in water in the form of their alkaline metal salts. Thus the butyl esters show considerable increased wetting powers over the propyl ester and the diaryl esters show extraordinarily high wetting powers and still have excellent solubility in water. These amyl esters may be single esters such as normal amyl, isooamyl, or secondary amyl esters; or mixed amyl esters may be obtained by esterifying with the mixture of amyl alcohols obtained by the hydrolysis of halogenated pentane fraction of natural gas and sold under the trade name of "Pentosol". Even higher wetting power is obtained with esters of the various octyl alcohols, such as, for example 2 ethyl hexyl alcohol and capryl alcohol.

Alcohols of still higher molecular weight are of importance as wetting agents and particularly as emulsifying agents where the solubility in water is not of prime importance. Typical examples are, lauryl esters and stearyl esters. The esters may be prepared from the pure alcohols or for most purposes it is sufficient to use the technical grade of mixed alcohols obtained from the reduction of various fats and fatty acid mixtures.

In addition to the monohydric paraffin alcohols, various ether alcohols are of importance such as, for example, the ethers of ethylene glycol, for instance, the methyl, ethyl, butyl, amyl, ethers, etc., which are readily obtainable in the trade. The ethers of diethylene glycol such as the methyl, ethyl or butyl ethers are likewise of importance and produce esters which are valuable wetting agents and detergents. The invention is in no sense limited to esters of aliphatic monohydric alcohols but includes also esters of cyclic alcohols and phenols which are of importance for many purposes. Thus, for example, benzyl esters, esters of phenol, cresols, xylenols, naphthalenes and the like, are included in the invention. Alcoholic alcohols such as cyclohexanol, methylhexanol, likewise form esters having important and useful properties. Esters of various terpene alcohols are also included, such as borneol, fenchyl alcohol, menthol, and the like, can be prepared and are included.

Heterocyclic alcohols also form esters with desirable properties. Examples of typical heterocyclic alcohols are furfuryl alcohols, tetrahydrofurfuryl alcohol, and the like. Alcohols of various types may also be used.

In addition to the esters in which two molecules of the same alcohol unite with the carboxyl groups of the dicarboxylic acid, a series of very important esters can be obtained in which one carboxyl group unites with one alcohol and another carboxyl group unites with a different alcohol. These mixed esters are particularly important where it is desired to obtain some of the valuable wetting and emulsifying properties of high molecular alcohols, such as, for example, lauryl and stearyl alcohols, without sacrificing too great an extent to the water solubility of their alkaline metal salts. Thus, for example, the mixed ethyl-lauryl and methyl-stearyl esters of a sulpho acid such as sulphosuccinic or sulphadipic acid possess many of the properties of the monoalcohol esters but are considerably more soluble in water. Obviously of course, the number of mixed esters which can be produced is extraordinarily large and only a few typical members are given in the specific examples of the invention to follow. The technique of producing mixed esters is substantially the same for all of the mixed esters and a wide variety may be produced and all are included in the present invention. While most of the mixed esters of greatest importance are those in which one alcohol is high molecular and the other low molecular, it should be understood that the invention is in no sense in this particular modification to mixed esters in which one alcohol is high molecular and the other low. Thus, for example, very desirable mixed esters may be obtained in which the two alcohols are of comparable molecular weight. Such esters are, for example, mixed amylolctyl mixed ethoxy ethamyl and the like. It is thus possible to produce esters which have desirable properties of two different alcohols embodied in the same product.

Certain mixed esters of a complex nature are also obtainable, for example by esterifying ethylene oxide or similar alkyene oxides such as propylene or butylene oxide with acids such as malic acid and then adding the sulpho group or by esterifying the sulphodcarboxylic acid directly with ethylene oxide.

While some of the most important esters of the present invention are those with monohydric alcohols such as the ones enumerated above, important esters can also be obtained with polyhydric alcohols. Thus, for example, an ester may be obtained with glycerine which is water soluble in the form of its alkali or ammonium salt. Ethylene glycol and other glycols such as propylene and butylene glycol produce new esters having desirable properties, not obtainable with the glycols of the aliphatic type but instead of hydroxyl group may only be united with the sulphodcarboxylic acid. Thus, for example, a monoglyceril ester of sulphosuccinic acid may contain a free hydroxyl group. If desired, this may be esterified with another acid. A further series of mixed esters are obtained when the acid ester of a monohydric alcohol or sulphodcarboxylic acid is caused to unite with one or more hydroxyls of a polyhydric alcohol. A large number of these mixed esters can be produced, some of which are resins of various types, and for the most part they show solubility in water in the form of the alkali metal or ammonium salts. Such esters of polyhydric alcohols which show resinous characteristics are applicable to resinous coating compositions which are to be applied in aqueous solution and open up a considerable field to synthetic resin compositions which was hitherto to more or less closed.

Instead of esterifying a compound which is 75
purely a mono or polyhydric alcohol, esters can of course be produced from other compounds which contain hydroxyl groups. Thus, for example, ricinoleic acid or castor oil can be esterified with a sulphodicarboxylic acid to form a further series of esters having very important wetting powers, particularly when the wetting agent has to be used in alkaline solution. Such esters are, of course, also included in the invention.

The most common esters of the present invention are those in which the sulphonic group of the acid is a single sulphonic group. It is, of course, possible to esterify di and polysulpho acids with the production of corresponding di and polysulpho esters, and such esters are of course included.

Most of the commercially useful esters are employed in the form of their alkali metal, usually sodium salts. For some purposes, however, it is undesirable to have an alkali metal present in the compound and very effective products are obtained in the form of salts with ammonia or other important properties which render their utilization, as for example, triethanolamine mono, di or trimethyl or ethyl amine, etc. It is also possible to form salts of alkaloids and other organic basis capable of salts formation with the sulphonic group. Thus, for example, salts with pyridine, nicotine, cinchona alkaloid and the like may be prepared and have the important advantage that they are readily applied in the form of aqueous dispersions because of the high wetting power of the esters of the sulpho acid. This permits the active organic base to be distributed in an aqueous material instead of a nonaqueous material, and is of importance in aiding the use of nicotine or pyridine as an insecticide or cinchona alkaloids as mothproofing agents since they can be applied in aqueous dispersions instead of solutions in organic material which for some purposes is a more desirable method of application. The application of certain basic dyes in the form of their salts with the sulpho esters is also important and such salts are likewise included.

The esters of the present invention possess two important properties which render their use as wetting agents, detergents or emulsifiers of particular importance. The first is their property of operating in hard water by reason of the great solubility of their calcium and magnesium salts.

The second property is their remarkable resistance to decomposition in respect they show great superiority to nearly all wetting agents which have been developed up to the present time.

Because of the large number of esters which can be prepared according to the present invention, only a few are illustrated in the following specific examples, it being understood that these are typical examples of the large number of esters included in the present invention. In the specific examples various processes of producing the esters have been illustrated. It should be understood that the invention is not limited to such illustrations. Thus, for example, if a particular ester is described in a specific example as produced by a particular process, this does not limit this ester to production by the illustrated process as, in general, the esters can be produced by any of the available processes which have been briefly described and which will be illustrated in greater detail in the specific examples.

**Example 1**

1 mol. of sulphomaleic acid in the form of its monosodium or potassium salt is distilled with 2,028,091 sulphuric acid being added as an esterification catalyst. The distillate is fractionated under a reflux, water or aqueous methyl alcohol is withdrawn from the system from the bottom of the fractionating column and the operation is continued until a conversion of 98% or higher is obtained. The mixture is then neutralized with caustic soda or, if desired, with sodium carbonate and the excess alcohol is recovered by distillation. The residual aqueous solution is evaporated to dryness and forms a white, rubbery acid having a definite melting point and showing a very great solubility in water. The product is the sodium or potassium salt of dimethyl sulphomaleate.

**Example 2**

1 mol. of normal diamin maleate having a boiling point from 146 to 148° C. at 2 mms. is mixed with 1.08 mols. of sodium bisulphite and the whole agitated at 100° C. with water in the proportion of 100 parts by weight of 4-5 mols. of methyl alcohol, a small amount of catalyst. The distillate is fractionated under a reflux, water or aqueous methyl alcohol is withdrawn from the system by dissolving in an organic solvent such as benzene, filtering and evaporating the benzene. The product, which is diamin sulphosuccinate, is a transparent soapy solid which can be ground with some difficulty to a white powder. It is very soluble in water, benzol, alcohol or gasoline. It is a wetting agent of great power and an excellent detergent, particularly because its calcium salt shows almost as much solubility as the sodium salt.

**Example 3**

340 parts of diocyl tumerate (boiling point 180 to 190° C. at 4 mms.) is prepared by the esterification of fumaric acid with 2 ethyl hexanol and is mixed with 109 parts of sodium bisulphite and sufficient water to form a 50% solution. The addition of sodium bisulphite is carried out as described in Example 2 and the product purified in the same way. The resulting sodium salt of diocyl sulphosuccinate is a transparent rubbery mass which cannot be ground to a powder. It is soluble in water and the common organic solvents, and shows a wetting power even greater than the diamin sulphosuccinate.

Instead of recovering the diocyl sulphosuccinate as described in Example 2, it may be salted out by any suitable salt such as sodium chloride or sodium sulphate. Some of the salt may be precipitated or retained by the diocyl succinate and this is unobjectionable since the addition of a certain amount of salt increases the wetting power of this ester. The salt may have no wetting power itself or the salt from another wetting agent such as, for example, the sodium salt of isopropyl napthalene sulphonic acid may be added. Such mixed wetting agents are very useful for certain purposes.

The triethanol amine salt can be prepared by reacting with triethanol amine hydrochloride and is likewise water soluble. Similarly salts can be prepared with pyridine, nicotine, or cinchona alkaloid.

**Example 4**

372 parts of the commercial mixed lauryl alcohols are mixed with 242 parts of the disodium salt of sulphosuccinic acid, 50 parts of sulphonic acid and 440 parts of toluene. The mixture is distilled until approximately 36 parts of water
have collected in the distillate, whereupon the mixture is neutralized and dried, giving a mixture of the sodium salt of dilluryl sulphocarbonate and sodium sulphate. The product is a white, rubbery substance slightly soluble in water, readily soluble in most organic solvents and giving a soapy solution of high emulsifying power.

**Example 5**

340 parts of dicapryl maleate are agitated with 109 parts of sodium bisulphite, dissolved in 100 parts of water until the reaction mixture is soluble in water. Preferably the agitation is under slight pressure and at about 100°C, as in the case of Example 2. The mixture is dried and purified by solution in organic solvents as in Example 2, and the product which is dicapryl sodium sulphocarbonate is a transparent, rubbery substance which is considerably more soluble in water than the dioctylsorbers. The corresponding ammonium salt can be readily prepared and is likewise very soluble in water. Instead of purifying the dicapryl sulphocarbonate as described in Example 2, it may be salted out, as is described in Example 3 and the presence of some additional salt improves the wetting power of the ester.

**Example 6**

242 parts of the disodium salt of sulphocarboxylic acid are mixed with 462 parts of fenchyl alcohol and 500 parts of monochlorobenzene. 50 parts of sulphuric acid are added and the mixture is slowly distilled until the theoretical quantity of water produced by the esterification has collected in the distillate. The mixture is neutralized with caustic soda and steam distilled to remove the excess fenchyl alcohol and monochlorobenzene. The remaining solution is then evaporated to dryness and constitutes the difenchyl sodium sulphocarbonate which is a white powder, moderately soluble in water and in organic solvents.

**Example 7**

256 parts of the disodium salt of alpha sulphopyrroctoracaric acid which may be obtained by the action of sodium sulphite on itaconic, citraconic or mesaconic acid are mixed with 270 parts of the ethyl ether of ethylene glycol and sufficient sulphuric acid to combine with the sodium attached to the carboxyl group of the pyrroctoracaric acid and to liberate a little free sulphonic acid. The mixture is distilled until esterification is complete, the acid neutralized and the excess ethyl ether of ethylene glycol removed by steam distillation. The residual sludge is then evaporated to dryness and forms a jelly-like mass of sodium diethoxyethyl sulphopyrroctorate. The compound is very soluble in water and shows good wetting powers.

**Example 8**

Maleic acid is esterified with the butyl ether of ethylene glycol and 386 parts of the ester thus produced are sulphonated with sodium bisulphite as described in Example 2. The product, which is the sodium salt of the dibutoxydiethyl-ene glycol sulphonocarboxylic, is very similar to that of Example 7.

**Example 9**

294 parts of crystalline dicyclohexyl glutarate are produced by esterifying glutaric acid with cyclohexanol, are mixed with 110 parts of sodium bisulphite as a 50% aqueous solution, the mixture being agitated at 100–110°C. until the whole is water soluble. Thereupon 500 parts of water are added to the mixture, heated, filtered and allowed to crystallize. The resulting cyclohexyl ester of sulphoglutaric acid is quite crystalline, the substance having no definite melting point and is readily soluble in water.

**Example 10**

248 parts of monosodium salt of sulphoacidic acid are esterified with 324 parts of benzyl alcohol using the procedure described in Example 6 but adding only 1 part of sulphuric acid to liberate a small amount of the free sulphonic acid to act as the catalyst. The product after removing any excess alcohol, is the sodium salt of dibenzyl sulphoacetate, being a white powder soluble in water.

**Example 11**

282 parts of the diphenyl ester of mesaconic acid (melting point 66–67°C) which may be obtained by heating mesaconic acid dichloride with sodium phenolate in toluene, are agitated for 24–48 hours with 104–208 parts of sodium bisulphite as a 50% water solution. The agitation preferably takes place under pressure at some what above 100°C, and is continued until the mixture is completely soluble in water, whereupon toluene is added and the mixture distilled until all the water is removed. The residual toluene is filtered and the toluene evaporated leaving a white solid residue of sodium diphenyl sulphopyrroctorate. The product is readily soluble in water from which it may be crystallized on long standing.

**Example 12**

284 parts of the dimaleic ester of tetrahydrofurfuryl alcohol are agitated at 100–110°C. with 100 parts of sodium bisulphite in the form of a 50% aqueous solution. The product is then purified as described in Example 2 and is an amorphous white solid possessing no definite melting point, being exceedingly soluble in water and organic solvents. The product is the sodium salt of the diethylhydrofurfuryl ester of sulphocarboxylic acid.

**Example 13**

Sulphosuberic acid is prepared by sulphonating sueric acid, and 276 parts of the monosodium salt are pyrolysed with a methyl isobutyl carbinal. The excess alcohol is distilled off and the product which is the diester of sodium sulphosuberic acid with methyl isobutyl carbinal is a white solid which is very soluble in water.

**Example 14**

326 parts of the disodium salt of sulphobenzo acid is esterified with excess butyl alcohol and slightly more than 1/3 mol. of sulphuric acid for every molecule of the disodium sulphobenzoate. The excess butyl alcohol is distilled off and the dibutyl sodium sulphobenzoate is recovered as a white powder which is soluble in water.

**Example 15**

Distearyl maleate is prepared by esterifying a technical alcohol containing stearyl alcohol as its main constituent with maleic anhydride, the esterification being carried out in a toluene solution. The crude product is recrystallized with benzol, and 124 parts of the ester are heated at 100°C. for 24 hours with 42 parts of sodium bisulphite and 40 parts of water, vigorous agitation being maintained during the heating. The product is...
then isolated and purified as in Example 2 and is a white, soapy powder, very slightly soluble in water. It constitutes the sodium salt of diesterly sulphosuccinate.

Example 16
Maleic acid is esterified with oleyl alcohol in the same manner as described in Example 15. 124 parts of the ester are then heated at 100° C. for about 24 hours with 42 parts of sodium bisulphite in 40 parts of water, vigorous agitation being continuously maintained. The sodium salt of dioleyl sulphosuccinate is then isolated as described in Example 2 and is a white soapy powder having a slight solubility in water.

Example 17
98 parts of maleic anhydride are heated with 40 parts of ethyl alcohol for about 1 hour, forming the acid ethyl ester of maleic acid. Thereupon 270 parts of stearyl alcohol are added together with sufficient sulphuric acid to act as a catalyst. Then 250 parts of toluene are added and the mixture slowly distilled until conversion to the ethyl stearyl maleate is complete. 250 parts of the 50% water solution of sodium bisulphite are then added and the mixture is agitated at 100° C. until a dried sample is soluble in water. The product, which is the sodium salt of ethyl stearyl sulphosuccinate is a white powder showing a moderate solubility in water. The solubility is very much greater than the diesterly ester and the product is usable as a wetting agent for various aqueous dispersions.

Example 18
142 parts of ethylene glycol maleate are agitated with a 50% aqueous solution containing 158 parts of sodium bisulphite. The agitation is maintained at 100° C. until the reaction mixture dissolves in water. Thereupon 1500 parts of monochlorobenzol are added and the water removed by azoetric distillation. The dried mixture is filtered and the filtrant evaporated, leaving a tough gummy solid which is fairly soluble in water and which constitutes the sodium salt of glycol sulphosuccinate.

Example 19
Ethylene oxide and maleic acid are heated together to form a complex ester. 180 parts of this reaction product are agitated at 100° C. with 150 parts of sodium bisulphite. The reaction proceeds rapidly and as soon as it is complete the mixture is evaporated to dryness and the product is separated from excess bisulphite by dissolving in boiling alcohol, filtering and evaporating the filtrate. The ester of sulphosuccinic acid obtained is a glassy mass which is soluble in water, the solubility depending to some extent on the character of the ethylene oxide maleic acid reaction product.

Example 20
98 parts of maleic anhydride are heated with 130 parts of octyl alcohol at 120° C. producing the acid octyl maleate. 228 parts of this acid ester are then poured into a solution of 126 parts of sodium sulphite in 1000 parts of water and the mixture stirred at 50° C. for some minutes until a clear solution is obtained. This solution may be used as such or it may be evaporated to dryness, a white, amorphous, somewhat sticky product remaining, which is the disodium salt of mono-octyl sulphosuccinate. The product is easily soluble in water.

Example 21
92 parts of glycerine and 98 parts of maleic anhydride are heated at 120° C. for 2 hours. The mixture is cooled to 80° C. and poured into a solution of 104 parts of sodium bisulphite in 200 parts of water. The resulting mixture is then agitated for 2 hours at 80° C. and evaporated to dryness. A brittle, glassy mass which is the sodium salt of glycerol sulphosuccinate is obtained. It can be easily ground to a white powder and is very soluble in water.

If ammonia bisulphite is used, the corresponding ammonium salt is produced which is equally soluble in water.

Example 22
124 parts of ethylene glycol are heated at 120° C. for 2 hours with 98 parts of maleic anhydride and the diglycol maleate so obtained is poured into a solution of 104 parts of sodium bisulphite in 150 parts of water. The mixture is agitated at 60° C. until an acidified sample liberates no SO₂ whereupon the solution is evaporated to dryness and the product may be ground to a white powder which is exceedingly soluble in water. The product obtained is the sodium salt of diglycol sulphosuccinate.

Example 23
184 parts of glycerine are heated to 120° C. for 1 hour with 98 parts of maleic anhydride. 204 parts of acetic anhydride are slowly added, the temperature being maintained at 120° C. After all of the anhydride has been added the heating is continued for 2 more hours and then the mixture is cooled at 100° C. whereupon 110 parts of sodium bisulphite in 150 parts of water are added and the mixture agitated in a closed vessel at 110° C. for 8 hours, or until the mixture is completely water soluble. Thereupon the mixture is evaporated to dryness and a semitransparent gummy mass is obtained which is readily soluble in water. It is the sodium salt of the glycerine ester of sulphosuccinic and acetic acids.

Example 24
92 parts of glycerine and 283 parts of oleic acid are heated to 200° C. for 12 hours. The mixture is cooled to 120° C. and 196 parts of maleic anhydride are added whereupon the heating is maintained for 3 hours and then 400 parts of normal amyl alcohol and 1/2 part of sulphuric acid are added. The mixture is distilled until substantially 36 parts of water have collected in the distillate, at which time the esterification is complete. The excess amyl alcohol is removed by steam distillation and the residual oil is agitated at 100° C. for 24 hours with 250 parts of sodium bisulphite. The solution is then evaporated to dryness and a soft resin is obtained which is readily soluble in water. This would be probably as the following formula:

\[
\begin{align*}
\text{CH}_2\text{OOC-CH}_2\text{Na} & \quad \text{Na}_2\text{SO}_4 \\
\text{CH}_2\text{OOC-CH}_2\text{OH} & \quad \text{COOCNa} \\
\text{CH}_2\text{OOC-CH}_2\text{CH} & \quad \text{COOCNa} \\
\text{Na}_2\text{SO}_4 &
\end{align*}
\]

Example 25
148 parts of phthalic anhydride are heated with 88 parts of a primary amyl alcohol at about 100° C. for 2 hours. The acid amyl phthalate obtained is then mixed with 92 parts of glycerine and the mixture heated at 120° C. for four hours. The phthalic anhydride unites with one hydroxyl of
the glycerine and the remaining hydroxyls of the glycerine are then esterified with 98 parts of maleic anhydride by heating at 120°–140° C. for several hours. The ester thus obtained is then sulphonated with 104 parts of sodium bisulphite as described in previous examples and recovered in the usual manner. The glycerine ester of sulphosuccinic acid and acid amyl phthalate is obtained as a powder and is readily soluble in water.

Instead of phthalic anhydride other dibasic acids may be used such as succinic acid, chloro-maleic acid, tartaric acid and the like.

**Example 26**

184 parts of glycerine are heated with 148 parts of phthalic anhydride at 130° C. for 4 hours. Thereupon 196 parts of maleic anhydride are added in 1000 parts of tetraline. The mixture is slowly distilled until approximately 54 parts of water have been collected in the distillate. Then the mixture is cooled to 80° C. At this stage mixed phthalic maleic ester of glycerine is obtained. 208 parts of sodium bisulphite dissolved in 300 parts of water are added and the mixture agitated at 80° C. until a sample is completely water soluble. The tetraline is removed by steam distillation and the aqueous solution remaining filtered and dried, the residue is ground and constitutes a glyceryl phthalate sulphonate being a white powder very soluble in water.

Instead of using phthalic anhydride mono-basic acids such as benzoic acid or benzoylbenzoic acid can be employed in which case, of course, the proportion of maleic acid is increased.

**Example 27**

2 mols. of castor oil are esterified with 3 mols. of maleic anhydride resulting in a neutral ester in which the six hydroxyl groups of the castor oil unite with the six hydroxyl groups of the maleic acid. This neutral ester is then treated with 3 mols. of sodium bisulphite to transform it into the corresponding sulphosuccinate. The product is not readily soluble in water but can be rendered soluble by sulphonation with sulphuric acid.

**Example 28**

An ester of maleic acid and castor oil is prepared but instead of using 2 mols. of castor oil only 1 mol. is used. After transformation into the sulphosuccinate by means of bisulphite, the product can be sulphonated with sulphuric acid or can be treated with caustic alkali to increase its water solubility.

What I claim is:

1. An ester of an aliphatic dibasic acid having the formula

   \[ \text{COOX} \]

   in which \( R \) is an aliphatic carbon chain containing at least one sulphonated group but free from other substituents, and \( X \) is hydrogen or an alcohol or phenol radical not connected by a carbon to carbon bond with \( R \), at least one \( X \) being such an alcohol or phenol radical.

2. An ester of an aliphatic dibasic acid having the formula

   \[ \text{MeSO} + \text{COOX} \]

   in which \( R \) is an aliphatic carbon chain containing at least one sulphonated group but free from other substituents, and \( X \) is hydrogen or an alcohol or phenol radical not connected by a carbon to carbon bond with \( R \), at least one \( X \) being such an alcohol or phenol radical, and \( Me \) is hydrogen or a base.

3. An ester of an aliphatic dibasic acid having the formula

   \[ \text{COOX} \]

   in which \( R \) is an aliphatic carbon chain containing at least one sulphonated group, but free from other substituents, and \( X \) is an alcohol or phenol radical not connected by a carbon to carbon bond with \( R \).

4. An ester of an aliphatic dibasic acid having the formula

   \[ \text{COOX} \]

   in which \( R \) is an aliphatic carbon chain containing at least one sulphonated group, but free from other substituents, and \( X \) is an alcohol or phenol radical.

5. An ester of an aliphatic dibasic acid having the formula

   \[ \text{COOX} \]

   in which \( R \) is an aliphatic carbon chain containing at least one sulphonated group, but free from other substituents, and \( X \) is an alcohol or phenol radical and \( Y \) is a different alcohol or phenol radical.

6. An ester of an aliphatic dicarboxylic acid having the following formula

   \[ \text{MeSO} + \text{COOX} \]

   in which \( R \) is a carbon chain free from mercapto groups, \( Me \) is a base, \( X \) is an alcohol or phenol radical and \( Y \) is a different alcohol or phenol radical.

7. An ester according to claim 2 in which \( Me \) is an organic amine base.

8. An ester of a sulphosuccinic acid in which at least one carboxyl group is united with the radical included in the group consisting of alcohols, phenols.

9. An ester of sulphosuccinic acid in which each carboxyl group is joined to a radical included in the group consisting of alcohols, phenols.

10. An ester according to claim 9 in which alcohol or phenol radicals attached to the different carboxyl groups are different.

11. A diamyl ester of sulphosuccinic acid.

12. A diester of sulphosuccinic acid and an octyl alcohol.

13. A method of producing an ester of a saturated sulphoaliphatic dicarboxylic acid which comprises producing the ester of the corresponding unsaturated aliphatic dicarboxylic acid and reacting the ester with a bisulphite.

14. A method of producing an ester of sulphosuccinic acid which comprises subjecting an ester of an acid included in the group consisting of maleic acid and fumaric acid to the action of a bisulphite.

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