

# UNITED STATES PATENT OFFICE

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## AMIDINE SALTS OF SULPHOSUCCINIC ESTERS

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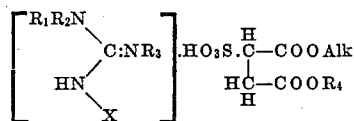
17 Claims. (Cl. 260—481)

This invention relates to amidine salts of esters of sulphosuccinic acid and to methods of preparing the same.

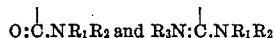
The alkyl esters of sulphosuccinic acid, and particularly the neutral and acid esters of this acid with aliphatic alcohols of 4 to 9 carbon atoms are remarkably effective wetting, penetrating and emulsifying agents when used in the form of their sodium salts. We have found that certain amidine salts of these esters of sulphosuccinic acid can be prepared by methods which will subsequently be described, and that these salts possess desirable surface active properties for certain fields of application. They are particularly useful for incorporation into photographic developing solutions and blueprint emulsions. In addition to their emulsifying properties they are also useful as demulsifying agents for breaking petroleum emulsions of the water-in-oil type when added to such emulsions in amounts of .01 to .005% by weight.

The amidine salts of sulphosuccinic acid esters are true addition products; that is to say, the free sulphonic acid of the sulphosuccinic acid group adds on to the organic base as does any other mineral acid. We believe that this addition takes place at one of the nitrogen atoms of the amidine, which undergoes a change of valence from 3 to 5, but this fact has not as yet been definitely established for any of the inorganic acid salts of any organic nitrogen base. Accordingly, we will use the customary method of representing addition products of this nature in describing our new compounds, this method consisting simply in showing the formula of the base in juxtaposition to the formula of the acid.

The amidine salts of sulphosuccinic acid esters of our invention may be represented by the type formula



in which Alk is an alkyl radical, and preferably an alkyl radical of 4 to 9 carbon atoms, R<sub>4</sub> is hydrogen or a similar alkyl radical, depending on whether the salt of the neutral or acid ester is formed, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals and X is a member of the group consisting of R<sub>1</sub>



The substituents R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> may be the same

or different in various compounds included within the scope of the invention and it should be understood that each symbol is intended to represent any member of the group defined.

5 An inspection of the above type formula will show that the amidine salts of our invention are salts of guanidine and its derivatives and substitution products, and particularly guanidine itself, guanylurea, biguanide, and their alkyl, hydroxyalkyl and aryl substitution products. These compounds are all organic bases, and are sufficiently basic to enable them to form salts with esters of sulphosuccinic acid.

10 Any guanidine base may be used for this purpose, such as guanidine itself, dimethyl or trimethyl guanidine, dibutyl guanidine, mono-, di- or triphenyl guanidine, ditolyl guanidine, or alkoxy substituted guanidines such as mono-, di- or triethanol guanidine and the like. Similarly, such guanylurea compounds as guanylurea itself, mono- or dimethyl guanylurea, diphenyl guanylurea, tetraethyl guanylurea, and triethanol guanylurea are organic bases which will form salts of sulphosuccinic acid esters.

15 Biguanide and such substituted biguanides as mono- and dimethyl and diethyl biguanides, diamyl biguanide, 1,5 diallyl biguanide, 1,1,5,5 tetramethyl biguanide, 1,1,2 trimethyl biguanide and 1,2,3 triphenyl biguanide will also form salts of esters of sulphosuccinic acid in accordance with the invention as will be illustrated in the following examples. It will be noted in these examples that the biguanides, unlike the other amidine bases included in the invention, will form both neutral and acid salts with dibasic mineral acids such as sulphuric acid. These two classes of salts will, in turn, form salts containing one and two molecular equivalents of sulphosuccinic ester for each mole of the biguanide compound, respectively. It should be understood that both classes of salts are included in the invention.

20 Many of the salts of the invention may be prepared simply by mixing a solution containing the free amidine base or its carbonate with a solution of an ester of sulphosuccinic acid. We have found, however, that the cost of production of these salts can be greatly reduced by a special method constituting a feature of the invention, which method employs a salt of the base and a salt of the sulphonic acid as starting materials. This reduction in cost is due to the fact that the amidine bases are more readily prepared in the form of their mineral acid salts, such as the neutral or acid sulphate, hydrochloride, hydrobromide, etc. The sulphosuccinates are also

most advantageously marketed in the form of their salts, and our improved process therefore starts with the two reagents in their most commercially attractive forms. According to this process we mix a solution of a mineral acid salt such as the sulphate or hydrochloride of an amidine corresponding to the above type formula with a solution of a salt of an ester of sulphosuccinic acid, using a salt of a metal which forms an insoluble precipitate with the mineral acid of the amidine salt. Thus, for example, if an amidine sulphate is used, the barium or lead sulphate will be employed, while the silver sulphate may be used with an amidine hydrochloride. When the two salt solutions are mixed an insoluble precipitate is formed and it is only necessary to separate the resulting compound from this precipitate by filtration, decantation or the like.

Our invention will be illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples described certain compounds constituting specific embodiments of the invention they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

#### Example 1

111 g. of sodium dioctyl sulphosuccinate ( $\frac{1}{4}$  mol) were dissolved in 400 cc. of ethyl alcohol and cooled to 4° C. in an ice bath. 13.3 cc. of 92% sulphuric acid ( $\frac{1}{4}$  molar equivalent) were slowly added, keeping the temperature at 4° C., and the mixture was allowed to stand at this temperature for one hour. The precipitated sodium sulphate was filtered off and washed with alcohol, whereby an alcoholic solution of dioctyl sulphosuccinic acid was obtained.

39 g. of guanidine carbonate were stirred into the sulphonic acid solution and the stirring was continued until the solution was neutral. The excess guanidine carbonate was filtered off and the alcohol evaporated from the filtrate, whereby 120 g. of white, waxy guanidine dioctyl sulphosuccinate were obtained.

The surface active properties of this salt were determined by the standard Draves wetting test which is based on a measurement of the sinking time of a standard cotton skein in various concentrations of the wetting agent at 25° C. The sinking times in seconds were as follows, the figures for the sodium salt being given for purposes of comparison.

	Conc. in grams per liter				
	0.5	0.35	0.25	0.2	0.15
Guanidine dioctyl sulphosuccinate	13.4	18.2	24.1	38.4	65.8
Sodium dioctyl sulphosuccinate	7.8	10.8	21.2	30.1	61.5

#### Example 2

1 mole of sodium dioctyl sulphosuccinate was dissolved in 1600 cc. of ethyl alcohol and cooled to 4° C. in an ice bath. The free sulphonic acid was liberated by addition of 78 cc. of 50% sulphuric acid followed by filtration of the precipitating sodium sulphate. 211 g. of diphenyl guanidine were then added and the mixture stirred until it had attained a pH of 6.5. The solution was then filtered and the alcohol evaporated on a steam bath.

630 g. of a slightly yellow oil, which solidified on cooling, were obtained. It was very soluble

in 50% aqueous alcohol, somewhat soluble in carbon tetrachloride and toluene, slightly soluble in solvent naphtha and aliphatic hydrocarbons, and insoluble in water and ether. A 4% solution in solvent naphtha was found to be effective as a mothproofing agent when applied to woolen cloth.

The xylyl guanidine salt of dioctyl sulphosuccinate was prepared in similar manner and found to be a thick, heavy syrup, insoluble in water but soluble to the extent of about 3% in solvent naphtha.

#### Example 3

360 g. of sodium diamyl sulphosuccinate were converted into the free sulphonic acid by addition of sulphuric acid as described in Example 1. Barium hydroxide was then added to the alcoholic solution of the free acid until the barium salt was formed.

2500 g. of copper sulphate containing 5 moles of water of crystallization were pulverized and added to 1286 g. of water. 2714 g. of 28% ammonium hydroxide were added to this mixture. 2000 g. of dicyandiamide were then introduced with thorough agitation and the mixture was placed in a pressure vessel which was closed and heated for 8 hours at 103° C.

The contents of the pressure vessel were filtered and washed with water until substantially free of the blue ammonia-copper complex and the wet filter cake was added to about 14 liters of 10% sulphuric acid. The mixture was heated to 80° C. to insure complete solution and was then filtered. On cooling, crystals of acid biguanide sulphate were obtained which were substantially pure and free from copper salt. A yield of 1200 g. of pure material was obtained.

100 g. of the acid biguanide sulphate were dissolved in aqueous alcohol and added to the alcoholic barium diamyl sulphosuccinate solution described above. The mixture was agitated and the precipitated barium sulphate was allowed to settle and filtered off with suction, and the filtrate was washed several times with 50% ethyl alcohol solution.

The combined filtrate and washings were evaporated to dryness on the water bath whereupon the biguanide salt of diamyl sulphosuccinate was obtained. It was a brown, waxy solid slightly soluble in water and very soluble in alcohol, and was found to have good emulsifying properties.

#### Example 4

194 g. of sodium dihexyl sulphosuccinate were converted into the free sulphonic acid as described in Example 1. 51 g. of guanylurea were added with stirring to the alcoholic solution and the alcohol evaporated off. The guanylurea salt of dihexyl sulphosuccinate was obtained as a white solid which could be dispersed in water to a thick gel and was easily soluble in alcohol. It had good emulsifying properties and was also a satisfactory demulsifying agent for breaking petroleum emulsions of the water-in-oil type when added in amounts of .01 to .005% by weight.

#### Example 5

100 g. of dicyandiamide and 125 g. of copper sulphate (5 H<sub>2</sub>O) were dissolved with 23% aqueous methylamine; the solution was placed in a pressure bottle and heated in a water bath at 92-94° C. for 5 hours. The reaction product was cerise colored; it was suspended in water, filtered and washed, whereupon 295 g. of moist

filter cake were obtained. The copper salt was dissolved in warm 10% sulphuric acid but it was found that even continued refrigeration did not yield any crystals. On addition of denatured alcohol, however, a thick crystal magma was obtained which was filtered and washed with alcohol. The pure dry acid methyl biguanide sulphate amounted to 124 g.

In a manner similar to the preparation of monomethyl biguanide sulphate there was obtained diethyl biguanide sulphate except that in this case the compound was obtained in beautiful large crystals on dissolving the copper compound in 10% sulphuric acid, and the addition of alcohol did not have to be resorted to.

208 g. of sodium diheptyl sulphosuccinate were dissolved in ethyl alcohol and the free acid liberated by addition of sulphuric acid. The sodium sulphate was filtered off at low temperatures and the solution neutralized with barium hydroxide. An equimolecular quantity of the acid methyl biguanide sulphate, prepared as described above, was then added, the mixture stirred and allowed to settle and the barium sulphate filtered off. When the filtrate was evaporated to dryness a light tan waxy solid was obtained which was soluble in aliphatic hydrocarbons, benzol and alcohol but only difficultly dispersible in water. It was the monomethyl biguanide salt of diheptyl sulphosuccinate. The diethyl biguanide salt was prepared in similar manner and possessed similar properties.

#### Example 6

84 g. of dicyandiamide, 111 g. of copper sulphate (5 H<sub>2</sub>O) and 272 g. of 25% aqueous solution of dimethylamine were mixed and put in a pressure bottle. The mixture was allowed to stand at room temperature for 2 days and then was found to have converted to the pink copper salt of dimethyl biguanide sulphate. No liquid was left in the bottle. The solid reaction product was suspended in water, filtered and washed in a Buchner funnel. The wet filter cake was dissolved hot at 80° C. in 600 cc. of 10% sulphuric acid and the hot solution was filtered to remove accidental impurities. On cooling dimethyl biguanide acid sulphate crystallized in shiny crystals.

The crystals were dissolved in aqueous ethyl alcohol and reacted with an alcoholic solution of the barium salt of dioctyl sulphosuccinate, using the procedure described in the preceding example. The dimethyl biguanide salt of dioctyl sulphosuccinate so obtained was similar in appearance to the product of Example 5, and had similar properties.

#### Example 7

30 g. of cyanourea were treated with 100 g. of alcoholic 33% methylamine solution for 2 hours in a sealed tube at 100° C. The resultant solution was concentrated in vacuo and 300 cc. of absolute alcohol were added as well as a few drops of concentrated sulphuric acid until no more precipitation occurred. The crystals were filtered and recrystallized from a small amount of water, considerable polymerized cyanourea remaining undissolved. Methyl guanylurea sulphate was finally obtained by adding ethyl alcohol to the filtrate and crystallizing. The crystals were dissolved in water and added to a 50% aqueous alcoholic solution of barium dioctyl sulphosuccinate, prepared as in Example 3. The precipitated barium sulphate was filtered off and

the filtrate evaporated to dryness. A soft waxy mass of the methyl guanylurea salt of dioctyl sulphosuccinate was obtained which was soluble in hot water, slightly soluble in aliphatic hydrocarbons, and possessed definite surface activity.

#### Example 8

84 g. of dicyandiamide, 111 g. of copper sulphate (5 H<sub>2</sub>O), 110 g. of n-monobutylamine and 100 g. of water were mixed. On mixing the first three components considerable heat was evolved and the mixture became dark bluish-black, stringy and almost resinous and so stiff that it could hardly be stirred; thereupon the water was added. The cool slurry became reddish. The mixture was heated in an open beaker in a water bath for four hours. The copper salt so obtained was suspended in water, filtered and washed with water, whereby 300 g. of salmon colored moist filter cake were obtained.

In order to obtain the salt in solid form the copper compound was suspended in water and hydrogen sulphide was passed in until all the copper was precipitated as copper sulphide. After filtration and evaporation in vacuo at 40-60° C. the butyl biguanide neutral sulphate was obtained as a waxy material in the form of scales with a nacreous luster.

The monobutyl biguanide salt of dioctyl sulphosuccinate was prepared by reacting an alcoholic solution of the sulphate with an alcoholic solution of the barium salt of the wetting agent. A brown, waxy solid soluble in alcohol and gasoline was obtained.

#### Example 9

210 g. of dicyandiamide, 310 g. of copper sulphate (5 H<sub>2</sub>O) and 480 g. of technical dibutylamine were mixed in the order given, a green thick mass resulting. It was placed in a pressure bottle and heated in the water bath at 96° C. for 7 hours. The dark green color changed to a dark red. The solid mass was suspended in water and filtered and the filter cake was then suspended in denatured alcohol in order to remove remaining dibutylamine which could not be removed by a water washing alone. The alcoholic filtrate was a dark bluish-black. After a second alcohol washing a very clean looking rose-colored copper salt of dibutyl biguanide sulphate was obtained.

The copper salt was suspended in water and hydrogen sulphide introduced, the copper sulphide was filtered off and the water evaporated in vacuo at 40-60° C. The resulting pasty mass was finally dried in a desiccator where it solidified entirely to flat crystals of dibutyl biguanide sulphate having a slightly yellowish tint.

The diamyl biguanide sulphate was also prepared by the same method.

The barium salt of dioctyl sulphosuccinate was prepared and dissolved in alcohol. The dibutyl and diamyl biguanide sulphates in alcoholic solution were reacted with separate portions of this solution, the barium sulphate filtered off from each, and the salts obtained by evaporating the alcohol on a steam bath. The two products were similar in characteristics, being waxy solids soluble in benzene, toluene and alcohol and dispersible in hot water to a thick gel. Their water dispersions showed good emulsifying and foaming properties.

#### Example 10

84 g. of dicyandiamide, 111 g. of copper sulphate (5 H<sub>2</sub>O) and 92 g. of monoethanolamine

were mixed. Considerable heat was evolved. 100 cc. of water were added and the mixture heated for several hours until the mass appeared uniform. It was then poured into 1400 cc. of water. The slurry was filtered and suspended in water, the copper precipitated with hydrogen sulphide and the solution evaporated in vacuo at 40-60° C. Lustrous crystals of monoethanol biguanide neutral sulphate were obtained.

The acid sulphate was obtained by dissolving the copper salt in 10% sulphuric acid, removing the copper with hydrogen sulphide and allowing to crystallize by slow spontaneous evaporation.

The ethanol biguanide salt of dioctyl sulphosuccinate was prepared from the corresponding barium salt by the procedure outlined in the preceding examples. It was a white waxy solid, soluble in water and ethyl alcohol and possessing definite wetting and emulsifying properties.

#### Example 11

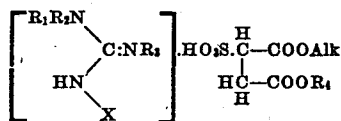
80 g. of copper dicyanamide, 150 g. of dimethylamine and 500 g. of water were heated in a pressure vessel at 120° C. for 24 hours. The resulting red copper salt was suspended in water, the copper precipitated with H<sub>2</sub>S and filtered off, and the sulphate formed by addition of concentrated sulphuric acid. It was separated from solution by crystallization after addition of alcohol and constituted a tetramethyl biguanide sulphate of the formula



The dioctyl sulphosuccinate salt of this base was formed by double decomposition with the barium compound in the usual manner. It was a brown waxy solid, soluble in alcohol but only slightly soluble in water.

What we claim is:

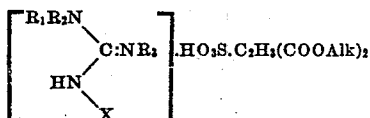
1. A salt of sulphosuccinic ester of the formula



in which Alk is an alkyl radical of 4 to 9 carbon atoms, R<sub>4</sub> is a member of the group consisting of hydrogen and alkyl radicals of 4 to 9 carbon atoms, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals and X is a member of the group

consisting of R<sub>1</sub>, O:CNR<sub>1</sub>R<sub>2</sub> and R<sub>3</sub>N:C.NR<sub>1</sub>R<sub>2</sub>.

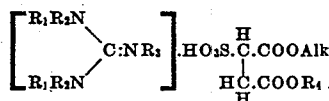
2. Salts of sulphosuccinic esters of the formula



in which Alk is an alkyl radical of 4 to 9 carbon atoms, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals and X is a member of the group

consisting of R<sub>1</sub>, O:CNR<sub>1</sub>R<sub>2</sub> and R<sub>3</sub>N:C.NR<sub>1</sub>R<sub>2</sub>.

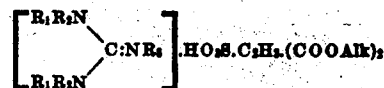
3. Salts of sulphosuccinic esters of the formula



in which Alk is an alkyl radical of 4 to 9 carbon atoms, R<sub>4</sub> is a member of the group consisting of hydrogen and alkyl radicals of 4 to 9 carbon

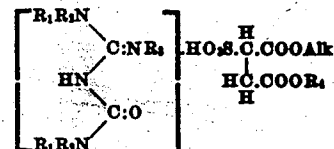
atoms and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

4. Salts of sulphosuccinic esters of the formula



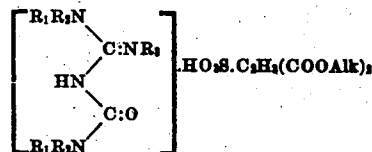
in which Alk is an alkyl radical of 4 to 9 carbon atoms and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

5. Salts of sulphosuccinic esters of the formula



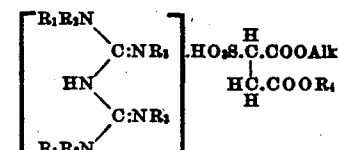
in which Alk is an alkyl radical of 4 to 9 carbon atoms, R<sub>4</sub> is a member of the group consisting of hydrogen and alkyl radicals of 4 to 9 carbon atoms, and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

6. Salts of sulphosuccinic esters of the formula



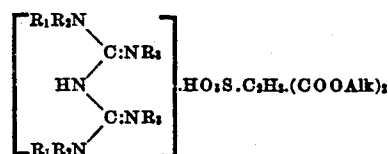
in which Alk is an alkyl radical of 4 to 9 carbon atoms, and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

7. Salts of sulphosuccinic esters of the formula



in which Alk is an alkyl radical of 4 to 9 carbon atoms, R<sub>4</sub> is a member of the group consisting of hydrogen and alkyl radicals of 4 to 9 carbon atoms and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

8. A salt of sulphosuccinic ester of the formula



in which Alk is an alkyl radical of 4 to 9 carbon atoms and R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

9. A guanidine salt of a dialkyl sulphosuccinate.

10. A guanylurea salt of a dialkyl sulphosuccinate.

11. A biguanide salt of a dialkyl sulphosuccinate.

12. A methyl biguanide salt of a dialkyl sulphosuccinate.

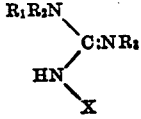
13. Guanidine dioctyl sulphosuccinate.

14. Diphenyl guanidine dioctyl sulphosuccinate.

15. An alkyl biguanide salt of dioctyl sulphosuccinate.

16. A method of preparing an amidine salt of a sulphosuccinic ester which comprises mixing a solution of an amidine sulphate with a solution of a barium salt of a sulphosuccinic ester and separating the barium sulphate formed by the double decomposition.

17. A method of preparing amidine salts of sulphosuccinic esters which comprises mixing a solution of a mineral acid salt of an amidine of the formula



in which  $R_1$ ,  $R_2$  and  $R_3$  are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals and  $X$  is a member of the group

5 consisting of  $R_1$ ,  $O:C:NR_1R_2$  and  $R_3N:C:NR_1R_2$  with a solution of a salt of an alkyl sulphosuccinate, which salt contains a metal forming an insoluble precipitate with the mineral acid of the amidine salt, and separating the resulting compound from the inorganic precipitate.

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