United States Patent Office **3,254,080**
Patented May 31, 1966

3,254,080

PROCESS FOR THE PREPARATION OF N,N-DI-SUBSTITUTED DITHIOCARBAMIC ACID ESTERS

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No Drawing. Filed May 10, 1961, Ser. No. 109,010
Claims priority, application Germany, June 8, 1960, D 33,501
3 Claims. (Cl. 260—247.1)

This invention relates to an improved process for producing N,N-di-substituted dithiocarbamic acid esters and to a process of producing a mixture of N,N-di-substituted dithiocarbamic acid esters and thiol alkane sulfonic acids.

N,N-substituted dithiocarbamic acid esters which contain a sulfo group in the non-acidic esterification component (alcohol moiety) are known products which, in the form of their water soluble salts, are used as additives in electroplating baths and produce ductile and full bright metal deposits (U.S. Patent No. 2,849,351). These compounds, which may also contain the effective atom configuration several times in the molecule, that is those compounds which may be derived from secondary amines having more than one secondary amine group or compounds having more than one di-substituted dithiocarbamic acid group, are usually prepared by reacting secondary aliphatic, cycloalphatic or araliphatic amines in the presence of an alkali with carbon disulfide and subsequently reacting the N,N-di-substituted dithiocarbamic acid salts obtained thereby with salts of halogen alkane sulfonic acids or with inner anhydrides of analogous hydroxy sulfonic acids (sultones).

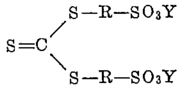
Another known group of compounds which, as additives in electroplating baths, favorably influence the quality of metal electrodeposits are the subject matter of U.S. Patent No. 2,830,014. These are salts of nitrogen-free mercapto alkane sulfonic acids whose mercapto group may also be etherified. Such compounds are preferably employed in conjunction with full brightening agents of the previously described type, whereby specific leveling effects are produced and the metal electrodeposits undergo a further improvement.

It is an object of the invention to produce N,N-di-substituted dithiocarbamic acid esters having a sulfo group in the alcohol moiety starting from trithiocarbonic acid esters.

It is a further object of the invention to produce simultaneously a mixture of an N,N-di-substituted dithiocarbamic acid ester having a sulfo group in the alcohol moiety and a salt of a thiol-alkane sulfonic acid starting from trithiocarbonic acid ester.

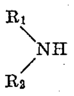
These and other objects of the invention will become more apparent as the description thereof proceeds.

We have now found that salts of N,N-di-substituted dithiocarbamic acid esters which contain a sulfo group in the non-acidic esterification component (alcohol moiety) can be produced simultaneously, that is in a single reaction step, with the salts of mercapto alkane sulfonic acids, by reacting trithiocarbonic acid esters which have a sulfo group attached to the non-acidic esterification component, that is compounds of the general formula



$$S{=}C\begin{matrix}S-R-SO_3Y\\ S-R-SO_3Y\end{matrix}$$

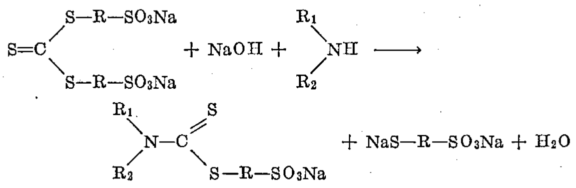
wherein R represents a low molecular weight alkane radical having from 1 to 7 carbon atoms and Y represents a water solubilizing radical selected from the group consisting of alkali metal and organic base, with one equivalent of an alkali metal hydroxide and one equivalent of a secondary aliphatic, cycloaliphatic or araliphatic amine whose substituents may be identical to or different from each other, substituted or interrupted, or also connected to each other through carbon or hetero atoms and which may also contain more than one secondary nitrogen atom. Secondary amines which are suitable for this reaction have the formula



$$\begin{matrix}R_1\\ R_2\end{matrix}NH$$

wherein R_1 and R_2 may be the same or different and are radicals selected from the group consisting of alkyl having from 1 to 22 carbon atoms, alkenyl having from 3 to 22 carbon atoms, hydroxyalkyl having from 2 to 22 carbon atoms, cycloalkyl having from 5 to 6 carbon atoms, alkylcycloalkyl having from 7 to 22 carbon atoms, alkylcycloalkenyl having from 7 to 22 carbon atoms, phenylalkyl having from 7 to 22 carbon atoms, dialkylaminoalkyl having from 4 to 22 carbon atoms, and, when taken together, alkylene having 4 to 5 carbon atoms and alkyloxyalkyl having 4 carbon atoms. Among the secondary amines are the following, for example: dimethylamine, diethyamine, dibutylamine, dioctadecylamine, dioleylamine, diethanolamine, dicyclohexylamine, dimethylcyclohexylamine, dinaphthenylamine, dibenzylamine, methylbenzylamine, ethylcyclohexylamine, piperpidine, morpholine, piperazine, N,N'-diethyl-ethylene diamine, N,N,N'-triethylethylene diamine and the like.

The reaction according to the process of the present invention proceeds practically quantitatively in accordance with the following reaction equation:



$$S{=}C\begin{matrix}S-R-SO_3Na\\ S-R-SO_3Na\end{matrix} + NaOH + \begin{matrix}R_1\\ R_2\end{matrix}NH \longrightarrow \begin{matrix}R_1\\ R_2\end{matrix}N-C\begin{matrix}{=}S\\ S-R-SO_3Na\end{matrix} + NaS-R-SO_3Na + H_2O$$

where R, R_1 and R_2 have the above assigned values.

The preparation of trithiocarbonic acid esters with sulfonic groups in the alkyl radicals, which are required as starting materials for the above reaction, is well known and may be accomplished technically in very simple fashion. They are most conveniently obtained by reacting sodium trithiocarbonate, which is readily formed from equivalent amounts of carbon disulfide and sodium sulfide in water, with salts of halogen alkane sulfonic acids, such as bromoethane sulfonic acid, bromopropane sulfonic acid, etc., or especially by reacting these salts with inner anhydrides of hydroxy alkane sulfonic acids, such as 1,3-propane sultone, 1,4-butane sultone, etc. or with their substitution products.

The reaction of the salts of the disulfonic acids thus obtained with an equivalent amount of alkali metal hydroxide and secondary amine, according to the process of the invention, is effected in aqueous solution by stirring for several hours at a temperature between about room temperature and about 100° C. As a rule, however, temperatures above 50° C. are not require. The separation of the salts of N,N-disubstituted dithiocarbamyl-S-alkanesulfonic acids thus formed, provided they do not separate out of the reaction mixture because of their low solubility, may be accomplished by salting out, preferably with the aid of sodium chloride. The mixture of the two components, after neutralization with sulfuric acid, can also be isolated by evaporation and used in this form in electroplating processes.

If the salt of a thioether alkane-sulfonic acid is desired to be obtained in place of the salt of a mercapto alkane-sulfonic acid, the etherification of the mercapto group with the aid of halogen compounds or other agents for etherifying a mercapto group may be accomplished in the same reaction mixture after termination of the above reaction.

The etherification reaction proceeds by addition of a stoichiometric amount of the etherifying agent to the aqueous reaction mixture and stirring several hours at a temperature between about room temperature and about 100° C., preferably at about 50° C. The salt of the N,N-di-substituted dithiocarbamyl-S-alkane-sulfonic acid may be separated from the salt of the thioether alkane-sulfonic acid by fractional crystallization or the water can be evaporated from the reaction mixture to obtain an electroplating composition comprising about an equimolecular mixture of the salt of the N,N-disubstituted dithiocarbamyl-S-alkane-sulfonic acid, and the salt of the thioether alkane-sulfonic acid.

The etherifying agent can be a halogen compound of the formula R_3X where X represents a halo group such as chlorine and bromine and R_3 represents a radical selected from the group consisting of alkyl, having from 1 to 22 carbon atoms, alkenyl having from 3 to 22 carbon atoms, cycloalkyl having from 5 to 6 carbon atoms, alkylcycloalkyl having from 7 to 22 carbon atoms, phenylalkyl having from 7 to 22 carbon atoms, sulfoalkyl having from 2 to 22 carbon atoms. Among such compounds are ethyl chloride, benzyl chloride, bromoethane sulfonic acid, etc. Other etherifying agents such as the inner anhydrides of hydroxy alkane sulfonic acids having from 2 to 7 carbon atoms can be used such as 1,3-propane sultone.

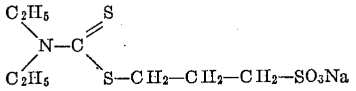
It is known from investigations by Holmberg (see Journal fur Praktische Chemi (2) volume 71, page 286; volume 81, page 454; and volume 84, page 651) that the trithiocarbonic acid diester with glycollic acid is decomposed in the cold by alkali and ammonia to form thioglycollic acid, and that in the case of the reaction with alkali as second decomposition products carbonic acid and hydrogen sulfide and that in the case of the reaction with ammonia, thiourea and ammonium thiocyanates are formed. The reaction with amines proceeds analogously in that, in addition to thioglycollic acid, N-substituted dithiocarbamyl-S-glycollic acids are formed as intermediates, which according to the findings of Holmberg (ibid., volume 81, page 454) are easily decomposed and are thereby transformed into substituted thioureas and other products. Furthermore trithiocarbamic acid diesters having no acid groups are reacted with secondary amines (see Houben-Weyl, Methoden der organischen Chemie, 4th edition, volume IX, page 842). In this reaction N,N-disubstituted dithiocarbamyl esters are formed being, owing to their lack of sulfonic groups, liable to decomposition and not qualified for electroplating purposes. The stability of the present N.N-disubstituted dithiocarbamyl-S-alkane-sulfonic acids in the presence of alkalis is therefore totally unexpected.

The high yields of N,N-disubstituted dithiocarbamyl-S-alkane-sulfonic acids or their salts, which are achieved by the process according to the invention, may probably be explained by the fact that because of the use of secondary amines on the one hand and thiocarbonic acid esters containing sulfonic groups on the other hand, side reactions and ring closure reactions are suppressed, as well as by the fact that the N,N-disubstituted dithiocarbamyl-S-alkane-sulfonic acid salts formed thereby are surprisingly stable toward alkalis.

The following examples are illustrative of the invention. They are not to be considered as limitative, however, as other expedients known to those skilled in the art can be employed without departing from the scope of the invention.

EXAMPLE I

Sodium N,N-diethyl-dithiocarbamyl-S-propane-ω-sulfonate

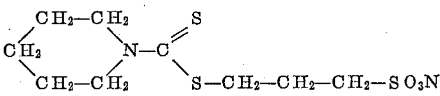


39.8 parts by weight of sodium, S,S-bis-(propane-ω-sulfonate)-trithiocarbonate (0.1 mol), which may be readily obtained from sodium trithiocarbonate and 1.3-propane sultone in aqueous solution, were dissolved or suspended in 200 parts by volume of water. After adding 7.3 parts by weight of diethylamine (0.1 mol) and 50 parts by volume of 8% sodium hydroxide (0.1 mol) the mixture was stirred at 50° C. until the solution became clear and colorless, which took about six hours. After adding three times the amount of saturated sodium chloride solution, sodium N,N-diethyldithiocarbamyl-S-propane-ω-sulfonate separated out in crystalline form with excellent yields. It was separated by vacuum filtration and was obtained in analytically pure form by recrystallization from twelve times the amount of alcohol.

In addition to the above mentioned product, an equivalent amount of sodium 3-mercaptopropane sulfonate was obtained, which was also isolated from the mother liquor.

EXAMPLE II

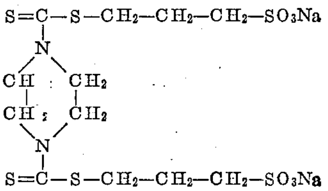
Sodium N,N-pentamethylene-dithiocarbamyl-S-propane-ω-sulfonate



By working in close analogy to the method described in Example I, but reacting 8.5 parts by weight of piperidine (0.1 mol) in place of diethylamine, and working up the reaction mixture in like manner, pure sodium N,N-pentamethylene-dithiocarbamyl-S-propane-ω-sulfonate was obtained with a yield in excess of 90%.

EXAMPLE III

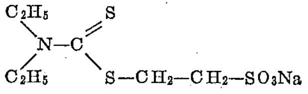
Sodium piperazine-N,N'-bis-(thiocarbonylthiopropane-ω-sulfonate)



19.4 parts by weight of piperazine hexahydrate (0.1 mol) and 100 parts by volume of 8% sodium hydroxide (0.2 mol) were added to a solution of 79.6 parts by weight of sodium S,S-bis-(propane-ω-sulfonate)-trithiocarbonate (0.2 mol) in 400 parts by volume of water. The resulting mixture was stirred for eight hours at 25° C., allowed to cool and the sodium piperazine-N,N'-bis-(thiocarbonylthiopropane-ω-sulfonate) formed thereby with excellent yield was separated by vacuum filtration, dried and recrystallized from a tenfold amount of a mixture of equal parts of isopropanol and water.

EXAMPLE IV

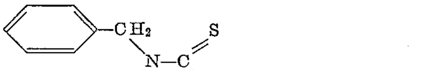
Sodium N,N-diethyl-dithiocarbamyl-S-ethane-ω-sulfonate



A solution of 37.0 parts by weight of sodium S,S-bis-(ethane-ω-sulfonate)-trithiocarbonate (0.1 mol) in 200 parts by volume of water was admixed with 7.3 parts by weight of diethylamine (0.1 mol) and 50 parts by volume of 8% sodium hydroxide (0.1 mol). The resulting mixture was stirred for six hours at 50° C. and was then worked up in the manner described in Example I, yielding a good yield of sodium N,N-diethyl-dithiocarbamyl-S-ethane-ω-sulfonate of the above formula, which was obtained analytically pure by recrystallization from alcohol.

EXAMPLE V

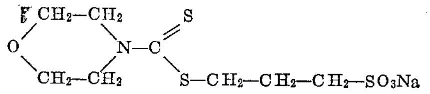
Sodium N-benzyl-N-methyl-dithiocarbamyl-S-propane-ω-sulfonate



A solution or suspension of 39.8 parts by weight of sodium S,S - bis - (propane-ω-sulfonate)-trithiocarbonate (0.1 mol) in 150 parts by volume of water was admixed with 12.1 parts by weight of N-methyl-benzylamine (0.1 mol) and 50 parts by weight of 8% sodium hydroxide (0.1 mol). The resulting mixture was stirred for six hours at 50° C., after which sodium N-benzyl-N-methyl-dithiocarbamyl-S-propane-ω-sulfonate precipitated out. The reaction mixture was allowed to cool, the precipitate was separated by vacuum filtration and dried. 31.8 parts by weight of the product were obtained, which corresponds to a yield of 93.3% of theory.

EXAMPLE VI

Sodium N,N-3-oxa-pentamethylene-dithiocarbamyl-S-propane-ω-sulfonate



Analogous to the method described in Example I, a mixture of 39.8 parts by weight of sodium S,S-bis-(propane-ω-sulfonate)-trithiocarbonate (0.1 mol) and 150 parts by volume of water was stirred for six hours at 50° C. with 8.7 parts by weight of morpholine (0.1 mol) and 50 parts by weight of 8% sodium hydroxide (0.1 mol). Thereafter, 250 parts by volume of a saturated sodium chloride solution was added, whereupon sodium N,N - 3 - oxa - pentamethylene - dithiocarbamyl - S - propane-ω-sulfonate separated out in crystalline form. After allowing the reaction mixture to cool, the precipitate was separated by vacuum filtration and dried. The salt, which was obtained with excellent yields, was recrystallized from alcohol, to which a small amount of water was added, and was obtained practically free from sodium chloride.

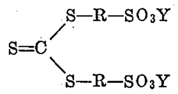
EXAMPLE VII

A solution was prepared analogous to the method described in Example I, from 39.8 parts by weight of sodium S,S - bis - (propane - ω - sulfonate) - trithiocarbonate (0.1 mol), 200 parts by volume of water, 7.3 parts by weight of diethylamine (0.1 mol) and 50 parts by weight of 8% sodium hydroxide (0.1 mol). 12.65 parts by weight of benzyl chloride (0.1 mol) were added to this solution which contain 0.1 mol of sodium N,N-diethyl-dithiocarbamyl-S-propane-ω-sulfonate and 0.1 mol of sodium 3-mercapto-propane-ω-sulfonate in the form of its sodium mercaptide by stirring for six hours at 50° C. until all of the benzyl chloride had entered into reaction and the solution had become clear. After evaporating the water a dust-dry mixture was obtained which consisted of 47.3% sodium N,N-diethyl-dithiocarbamyl-S-propane-ω-sulfonate, 43.25% of sodium benzylthiolpropane-ω-sulfonate and 9.45% sodium chloride.

The above examples disclose many of the embodiments of the invention. It is to be understood that other embodiments such as utilization of other reactants, alkali metal hydroxides, etc., known to those skilled in the art may be employed without departing from the spirit of the invention or the scope of the appended claims.

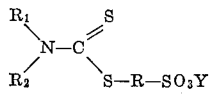
I claim:

1. A process for the production of a dithiocarbamate selected from the group consisting of N,N-di-substituted dithiocarbamic acid alkyl esters-ω-sulfo acids and alkali metal salts thereof which comprises the steps of reacting a compound of the formula

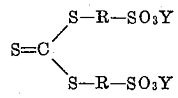


wherein R represents alkylene of 1 to 7 carbon atoms and Y is an alkali metal with a stoichiometric amount of an alkali metal hydroxide and a stoichiometric amount of a secondary amine at a temperature between about room temperature and about 100° C. and recovering said dithiocarbamate.

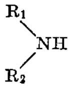
2. A process for the production of a dithiocarbamate of the formula



wherein R_1 and R_2 are radicals selected from the group consisting of alkyl having from 1 to 22 carbon atoms, alkenyl having from 3 to 22 carbon atoms, hydroxyalkyl having from 2 to 22 carbon atoms, cycloalkyl having from 5 to 6 carbon atoms, alkylcycloalkyl having from 7 to 22 carbon atoms, alkylcycloalkenyl having from 7 to 22 carbon atoms, phenylalkyl having from 7 to 22 carbon atoms, dialkylaminoalkyl having from 4 to 22 carbon atoms, and when taken together with the nitrogen atom form a heterocyclic radical selected from the group consisting of piperidino, morpholino, pyrrolidino and piperazino, R represents alkylene of 1 to 7 carbon atoms and Y is an alkali metal which comprises the steps of reacting a compound having the formula

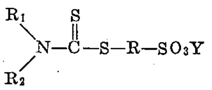


wherein R and Y have the above assigned meanings with a stoichiometric amount of a secondary amine having the formula

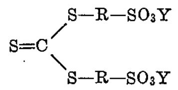


wherein R_1 and R_2 have the above assigned meanings in the presence of a stoichiometric amount of an alkali metal hydroxide in an aqueous solution at a temperature between about room temperature and about 100° C. and recovering said dithiocarbamate.

3. A process for the production of a dithiocarbamate of the formula



wherein R_1 and R_2 together with the nitrogen atom form a heterocyclic radical selected from the group consisting of piperidino, morpholino, piperazino and pyrrolidino, Y is an alkali metal and R is alkylene of 1 to 7 carbon atoms which comprises reacting a compound of the formula



wherein R and Y have the above definitions with a stoichiometric amount of an alkali metal hydroxide in aqueous solution and a stoichiometric amount of a heterocyclic amine selected from the group consisting of piperidine, morpholine, piperazine and pyrrolidine at a temperature between room temperature and 100° C. and recovering said dithiocarbamate.

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