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2,315,870

ISOALKYLAMINE SALTS OF ORGANIC SULPHONIC OR CARBOXYLIC ACIDS

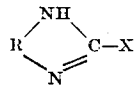
Friedrich Nadler, Cologne-Mulheim, Richard Wegler, Leverkusen-Schlebusch, and Otto Bayer, Leverkusen-I. G. Werk, Germany, assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application March 2, 1940, Serial No. 322,014. In Germany November 5, 1938

3 Claims. (Cl. 260—208)

The present invention relates to isoalkylamines salts of organic sulphonic acids or carboxylic acids which salts possess superior solubility in organic solvents.

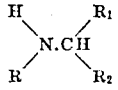
It is known that organic sulphonic acids and carboxylic acids can be rendered soluble in organic solvents such as alcohols by converting the same into their salts with certain amines. Thus, the U. S. Patent 1,860,036 to Georg Kränzlein et al, discloses salts formed from an organic dyestuff containing at least 1 acid salt forming group and from a cyclic organic base of the general formula



wherein R stands for a bivalent hydrocarbon radical of the group consisting of ethylene, phenylene and naphthylene and X stands for a substituent of the group consisting of hydrogen, methyl, amino, methylimino, phenylimino, tolylimino and cyclohexylimino.

These salts are stated to be insoluble or difficultly soluble in water but soluble in alcohol, acetone, benzyl alcohol, butanol, cyclohexanone or cyclohexanol.

The present invention is based upon the discovery that amines of the following constitution



wherein R stands for a member of the group consisting of hydrogen and alkyl and R_1 and R_2 each stand for a member of the group consisting of alkyl and cycloalkyl,

the number of the carbon atoms present in the radicals defined by R, R_1, R_2 being at least 8, of converted into salts with organic compounds containing at least one acid salt forming group, impart to the latter a much better solubility in organic solvent than could be achieved by means of previously used amines. In consequence thereof, such salts are capable of yielding relatively highly concentrated solutions in organic solvents and can be employed for other applications than the hitherto known salts of the character described. The alkyl groups defined by the symbols R, R_1 and R_2 may bear various substituents without departing from the scope of our invention. Amines of the type defined by the above formula can be prepared in various ways, for instance by causing ketones to react upon formamide or alkylated formamides. Reference is made in this connection to the co-pending application Ser. No. 299,522 to Richard Wegler, now Patent No. 2,251,245 of July 29, 1941. Another method of preparing such amines consists in causing ketones to react upon ammonia or alkyl amines in the presence of hydrogen. In preparing amines of the character described such mixtures of ketones are preferred as are obtainable in a manner known per se from mixtures of aliphatic carboxylic acids obtainable by the oxydation of paraffines. As organic compounds containing acid salt forming groups there are preferably employed sulphonic acids or carboxylic acids of various dyestuffs such as those of the azo, anthraquinone, triphenylmethane or phthalocyanine series. Moreover, there can be employed those dyestuffs of the character described containing heavy metals in complex combination such as chromium or copper. The term "organic dyestuffs" is not limited to those exerting an absorbing action within the visible part of the spectrum but includes also those absorbing for instance ultra violet rays, and also fluorescent compounds. Salts of the character described can be employed for the coloring of organic solvents and of lacquers and molded articles prepared from organic plastic materials such as cellulose esters and cellulose ethers. Salts of fluorescent compounds are employed for instance for marking lubricating oils, benzenes and alcohols. Salts of compounds absorbing within the ultra violet part of the spectrum can also be employed in lacquers, coatings and the like.

As a matter of fact, our new salts also present valuble pigment dyestuffs as they are insoluble or at least difficultly soluble in water.

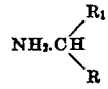
Such salts can be prepared by causing the free sulphonic or carboxylic acids to react upon the free amine in the presence of water or an organic solvent. In case of working with water the resulting salts are mostly precipitated owing to their being insoluble or difficultly soluble therein. In case of working in the presence of an organic solvent the resulting solutions can be directly employed for the preparation of lacquers, coatings and the like; furthermore, the salts can be isolated therefrom by precipitation by means of water (in case solvents miscible with water are employed), or by evaporation.

The following examples illustrate the present invention without, however, restricting it thereto, the parts being by weight:

Example 1

10 parts of the dyestuff obtainable by coupling the diazocompound of 3-chloro-2-toluidine with

the pyrazolone of the 2-toluidine-5-sulphonic acid are dissolved in 200 parts of water. The solution is rendered slightly acid by means of acetic acid. Thereupon the dyestuff is precipitated by means of the calculated quantity of an aqueous acetic acid solution of the amines



wherein the average number of the carbon atoms in $R_1+R_2=14$. The whole is stirred for some time at room temperature. Thereupon the dyestuff is sucked off. It is soluble in ether, alcohol, acetone, chloroform, benzene and nitrocellulose lacquers with a yellow coloration.

Example 2

The dyestuff obtainable from the diazocompound of the p-aminoazobenzene and β-naphthol-6.8-disulphonic acid is precipitated from its aqueous acetic acid solution by means of the amine suggested in Example 1 and in the manner more fully described in that example. After filtration and drying there is obtained a dyestuff which is easily soluble with a clear red coloration in alcohol, acetone, benzene and nitrocellulose lacquers. Contrary thereto, the corresponding dyestuff from dicyclohexylamine is only sparingly soluble in alcohol, acetone and benzene.

Example 3

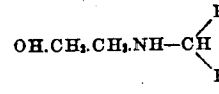
10 parts of the dyestuff obtainable from the diazocompound of the p-aminoazobenzene and β-naphthol-3.6.8-trisulphonic acid are dissolved in 200 parts of water and precipitated by means of an aqueous acetic acid solution of the amine described in Example 1. With a scarlet red solution the dry dyestuff is easily soluble in alcohol, acetone, chloroform and nitrocellulose lacquers. Contrary thereto, the corresponding dyestuff from dicyclohexylamine is difficultly soluble in acetone and nitrocellulose lacquers.

Example 4

5 parts of the dyestuff, obtainable by coupling the diazocompound of the p-aminoazobenzene with β-naphthol-6.8-disulphonic acid, are dissolved in 200 parts of water, the solution is rendered slightly acetic acid and, thereupon, the dyestuff is precipitated by means of the calculated amount of the amine of Example 1. With a clear red color the isolated dyestuff is easily soluble in alcohol, chloroform, benzene, acetone, nitrocellulose and butylacetate lacquers.

Example 5

5 parts of the dyestuff of Example 4 are dissolved in 200 parts of water and precipitated in an aqueous acetic acid solution with the amine of the following constitution



wherein the average number of the carbon atoms in $R_1+R_2=14$. With red color the dyestuff is easily soluble in acetone, alcohol, chloroform, benzene, nitrocellulose and butylacetate lacquers.

Example 6

10 parts of sodium pyrentetrasulphonic acid are dissolved in 100 parts of water and the solution is rendered slightly acetic acid. The sulphonic acid is precipitated by means of an aqueous acetic acid solution of the amine of Example 1. The resulting colorless salt solidifies on stirring. It is easily soluble in alcohol and chloroform.

Example 7

30 parts of sodium pyrene-3-sulphonate are dissolved in 1500 parts of water and rendered slightly acetic acid. To the solution there are slowly added 20 parts of the amine of Example 1 dissolved in 100 parts of an aqueous acetic acid. The salt of the pyrene sulphonic acid precipitates. It is sucked off and washed with water. After drying it represents a white powder which is easily soluble in alcohol, acetone, benzene and chloroform. It can be used in admixture with pyrene derivatives as an agent absorbing ultraviolet rays for lacquers.

Example 8

10 parts of the dyestuff obtainable by coupling the diazonium compound of the 1-amino-6-nitro-β-naphthol-4-sulphonic acid with β-naphthol and subjecting the dyestuff thus formed to an aftertreatment by means of chromium compounds are dissolved in 100 parts of water and rendered acetic acid. Thereupon there are added thereto at room temperature so much of an acetic acid solution of the amine of Example 1 that the dyestuff is completely precipitated. It is sucked off and dried by exposure to the air. The dyestuff is easily soluble in acetone, alcohol and chloroform. It represents a black dyestuff suitable for coloring nitrocellulose lacquers.

Example 9

3 parts of the sulphonated oxazine dyestuff obtainable by condensing 2 mols of 3-aminocarbazol with 1 mol of chloranil and subsequently sulphonating the condensation product, are dissolved in 100 parts of water and precipitated in a slightly acetic acid solution with 3 parts of the amine of Example 1. The dyestuff is easily soluble in alcohol and nitrocellulose lacquers with a blue-violet color.

Example 10

The copper phthalocyanine sulphonic acid chloride obtainable by heating copper phthalocyanine with the 15 fold quantity of chlorosulphonic acid to 135–150° C. is stirred at room temperature with an excess of the amine of Example 1. In the resulting product part of the sulphonic acid groups are converted into salts with the said amine, whereas the remaining part is present in form of the corresponding sulphonamides. It is easily soluble in chloroform, carbon disulphide and ether with a vivid bluish coloration.

Example 11

15 parts of tetraphenylcopperphthalocyaninesulphochloride obtainable from tetraphenylcopperphthalocyanine and chlorosulphonic acid are suspended in 100 parts of water and stirred with 7 parts of the amine of Example 1 in the presence of 3.5 parts of sodium carbonate for 12 hours. The dyestuff is sucked off, washed and dried at 100° C. The dyestuff which probably contains sulphonamide groups besides sulphonic acid groups converted into amine salts is easily soluble with a vivid greenish coloration in alcohol, acetone, chloroform, benzene and ether.

Example 12

5 parts of 1-amino-4-bromoanthraquinone-2-sulphonic acid are dissolved in 100 parts of wa-

ter. Thereupon 5.5 parts of the amine of Example 1 are added thereto. The whole is heated to boiling and then acidified by means of glacial acetic acid. After recrystallization from benzene it shows the melting point 191°. With an orange-yellow coloration it is easily soluble in alcohol, acetone, chloroform, nitrocellulose and butylacetat-lacquers.

Example 13

5 parts of the chromium complex dyestuff obtainable by coupling the diazoniumcompound of the o-anisidine-4-diethylsulphonamide with β-naphthol-3.6-disulphonic acid followed by an aftertreatment with chromium salts are dissolved in 100 parts of water and rendered slightly acetic acid. The dyestuff is precipitated with 2.5 parts of the amine of Example 1 dissolved in 10 parts of an aqueous acetic acid. The dyestuff is sucked off and dried. With red color it is easily soluble in alcohol, acetone, chloroform, nitrocellulose and butylacetat-lacquers.

Example 14

5 parts of the dyestuff obtainable from the diazoniumcompound of p-aminoazobenzene and β-naphthol 3.6.8-trisulphonic acid are dissolved in 200 parts of water, rendered slightly acetic acid and precipitated with an acetic acid solution of isotetradecenylamine, prepared from ethyldodecylketone, ammonia and hydrogen. With a scarlet red coloration the dyestuff is easily soluble in alcohol, acetone, chloroform, ether, nitrocellulose and butylacetat-lacquers.

Example 15

A moist paste of the copperphthalocyaninesulphonic acid chloride prepared from 150 parts of copper phthalocyanine as described in Example 10 are suspended in 1200 parts of water. While stirring there are slowly added 165 parts of the amine corresponding to the formula



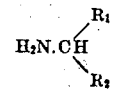
wherein the average number of carbon atoms in R_1 and R_2=10 to 11. Subsequently 52 g. of soda dissolved in 250 ccm. of water are added. After 12 hours' stirring the precipitated dyestuff is sucked off, washed with 2% acetic acid and then washed with water. After drying there is obtained a dyestuff in form of a blue powder which is easily soluble in alcohol, acetone and ethylacetat. The dyestuff molecule contains besides sulphamidgroups at least one sulphonic acid group which is converted into a salt with the said amine.

Example 16

100 parts of the azodyestuff from p-aminoazobenzene and β-naphthol-3.6.8-trisulphonic acid are suspended in 1000 parts of water and precipitated with a solution of 70 parts of the amine of Example 15 in 700 parts of water and 70 parts of glacial acetic acid, the solution of the amine being slowly added drop by drop. The precipitated dyestuff is sucked off, washed and dried. It represents a red powder which is excellently soluble in organic solvents.

Example 17

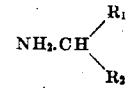
In Example 5 the amine of the formula stated therein is replaced by the tertiary amine obtainable by causing 8 mols of ethyleneoxide to react upon the amine of the formula



(number of carbon atoms in R_1 and R_2 being 14). The resulting dyestuff is equally well soluble in organic solvents as that of Example 5.

Example 18

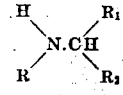
A 10 per cent acetic acid solution of an amine of the formula



(number of carbon atoms in R_1 and R_2 being about 10) is added drop by drop into an aqueous suspension of the azodyestuff from diazotized anthranilic acid and 1-phenyl-3-methyl-5-pyrazolone until the dyestuff is completely precipitated. It represents a yellowish powder being easily soluble in alcohol, acetone, benzene and esters.

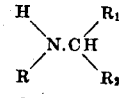
We claim:

1. Salts formed from an organic dyestuff containing at least one acid salt-forming group and from an isoalkylamine of the following constitution



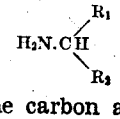
wherein R stands for a member of the group consisting of hydrogen and alkyl, and R_1 and R_2 each stand for a member of the group consisting of alkyl and cycloalkyl, the number of the carbon atoms present in the radicals defined by R, R_1 and R_2 being at least 8, said salts being insoluble or difficultly soluble in water, but soluble in organic solvents.

2. Salts formed from an organic dyestuff containing at least one acid salt-forming group and selected from the group consisting of dyestuffs of the azo, anthraquinone, triphenylmethane and phthalocyanine series, and from an isoalkylamine of the following constitution:



wherein R stands for a member of the group consisting of hydrogen and alkyl, and R_1 and R_2 each stands for a member of the group consisting of alkyl and cycloalkyl, the number of the carbon atoms present in the radicals defined by R, R_1 and R_2 being at least 8, said salts being insoluble or difficultly soluble in water, but soluble in organic solvents.

3. Salts formed from an organic dyestuff containing at least one acid salt-forming group, and from an isoalkylamine of the following constitution



the number of the carbon atoms contained in R_1 and R_2 being 14.

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