Patented Feb. 17, 1953

2,628,882

UNITED STATES PATENT OFFICE

2,628,882

LEUCO ESTER PRINTING COMPOSITIONS AND SOLUBILIZERS THEREFOR

David I. Randall and Nicholas W. Solonen, Easton, Pa., assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application August 23, 1950, Serial No. 191,718

6 Claims. (Cl. 8—70)

1

The present invention relates to the solubilization of leuco esters of vat dyestuffs to the compounds used for solubilization purposes, and to the compositions of such solubilizers and the leuco esters of a vat dyestuff.

It is conventional practice to employ vat dyes in the form of their leuco ester salts, rather than in the form of the simple leuco compounds.

This is attributable to the fact that the leuco ester salts are more soluble than the leuco compounds per se, a fact which facilitates the application of the reduced vat dyes to the fiber.

These leuco ester salts are generally utilized for the printing of textiles by dissolving the ester salts in water and a thickening agent, applying the resulting paste to the fabric, and fixing the insoluble vat dyestuff on the fabric by subsequent hydrolysis and oxidation. The oxidizing agents generally employed are sodium and ammonium salts.

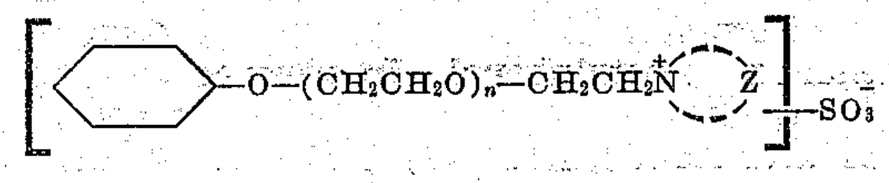
Some of the leuco ester salts are readily soluble in water but others are considerably less soluble and are easily salted-out by electrolytes, such as the salts used as the oxidizing agents in forming the printing pastes.

It has been proposed to facilitate the solubilization of such leuco ester salts by adding compounds operating to effect dispersion of the salts. A group of compounds which have found extensive use in this relationship are described in United States Letters Patent 2,431,708, and are betaines or sulfobetaines containing an aralkyl radical. A very effective compound in this category is, for instance, the sulfobetaine of dimethyl - benzyl - phenyl - ammonium - p-sulfonic acid.

We have now found that compounds which are even more effective in the solubilization of leuco ester salts of vat dyestuff than those described in the above United States patent are compounds of the quaternary Zwitter ion type, in which a phenoxy group is linked through an alkyl or alkoxy alkyl group to the nitrogen atom of a radical of the pyridine or quinoline series. Such compounds, used in the solubilization of leuco esters of vat dyestuffs and compositions containing such compounds and the leuco esters constitute the purposes and objects of the present invention.

The compounds, the use of which are contemplated herein, may be typified by the following structural formula

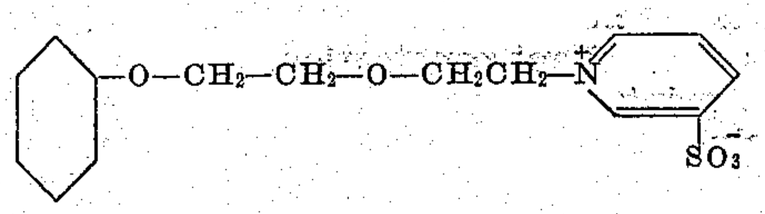
2



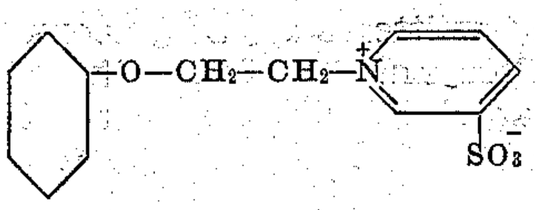
wherein n is a number ranging from zero to 4, Z represents the atoms necessary to complete a pyridine, C-alkyl pyridine or a quinoline radical, and the SO_3^- group is present either in the phenyl ring or in the heterocyclic radical.

Examples of such compounds are the following:

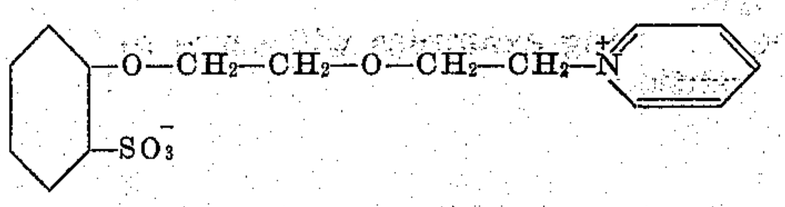
(1) Phenoxyethoxyethylpyridinium sulfonic acid of the formula



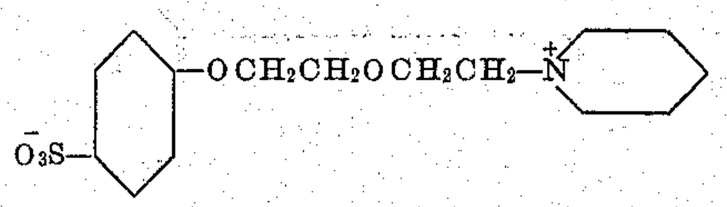
(2) Phenoxyethyl pyridinium sulfonic acid of the formula



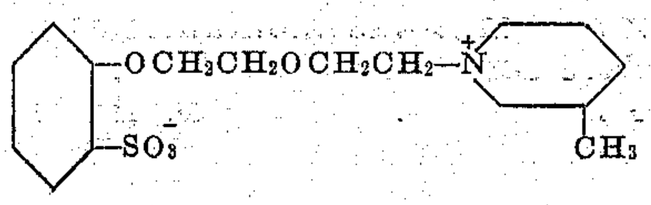
(3) o-Sulfo phenoxyethoxyethyl pyridinium derivative of the formula



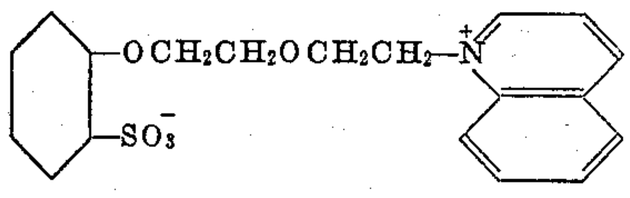
(4) p - Sulfophenoxyethoxyethyl pyridinium derivative of the formula



(5) o - Sulfophenoxyethoxyethyl picolinium derivative of the formula



(6) o - Sulfophenoxyethoxyethyl quinolinium derivative of the formula



The above compounds are prepared by the reaction of a phenoxy alkyl halide or a phenoxy alkoxy alkyl halide with the desired nitrogenous base, and subsequently sulfonating the product if desired.

The above products may be used for the solubilization of widely divergent types of leuco ester salts of vat dyestuffs. We have thus found them to be applicable in the solubilization of esters derived from indigos, thioindigos, indanthrenes, pyranthrones and the like. In all cases the solubilizing effect is permanent in that the print pastes remain stable and unprecipitated for many days.

For some reason for which we have no theory to offer, the phenoxy group in the above compounds adds appreciably to the solubilizing power of this class of compounds. It might be added that the unsubstituted phenoxy moiety contributes most to the solubilizing effect. Thus we have prepared compounds of the type contemplated herein from 2,4-dichlorophenol, 4-chlorophenol and 4-octylphenol. In every case the solubilizing effect of such compounds was poor.

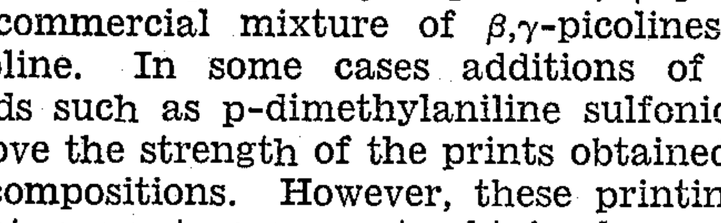
Greater leeway, however, is allowed in the selection of the heterocyclic nitrogenous radical. Thus, the good results obtained, when such radical is pyridine, are likewise obtained when the pyridine is replaced by α-picoline, β-picoline, the commercial mixture of β,γ-picolines, and quinoline. In some cases additions of compounds such as p-dimethylaniline sulfonic acid improve the strength of the prints obtained with our compositions. However, these printing assistants are not necessary to obtain clear, smooth prints of excellent penetration.

The printing compositions are made up with our solubilizers according to the usual practice, to wit, they contain the leuco ester, an agglutinant such as starch tragacanth, an oxidizing agent such as sodium chlorate, ammonium chlorate or the like, a catalyst such as ammonium vanadate, and an acid splitter such as gluconic acid, ammonium sulfocyanide and the like. In use the pastes are applied to the fabric which are dried and steamed to effect development of the dyes thereon. The quantity of the solubilizer employed may vary but will usually range from about 100 to 200% by weight of the leuco ester employed.

The following examples will serve to illustrate the invention, but it is to be understood that the invention is not restricted thereto.

EXAMPLE 1

Preparation of

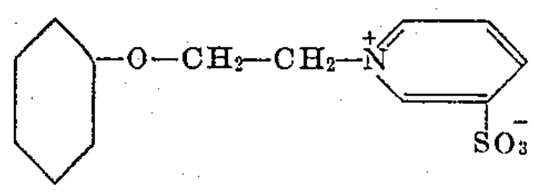


100 grams of sodium pyridine-3-sulfonate, 110.5 grams phenoxyethoxyethyl chloride (prepared by the procedure of United States Patent 2,205,393), and 111 milliliters of distilled water.

The above charge was maintained at 130° C. in an autoclave for a period of 22 hours. It was cooled to room temperature and filtered. The product was triturated with cold (5° C.) 20% methanol until all of the chloride ion had been washed out and then it was washed with absolute ethyl alcohol. (This removes an oily product from the reaction.) The crude product was then dried in a vacuum desiccator. Yield=90 g. or about 50.6%.

EXAMPLE 2

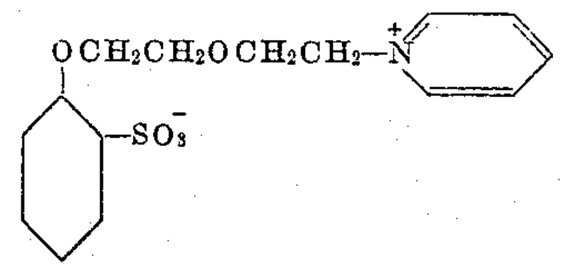
Preparation of



A mixture of 56.1 grams of phenoxyethyl bromide (Org. Syn. Coll., vol. I, p. 436), 54.4 grams of sodium pyridine-3-sulfonate and 100 cc. of water was heated at 120° C. for 20 hours in an autoclave. On cooling the sulfobetaine salt precipitated. It was filtered and washed first with 100 cc. ice water and secondly with 200 cc. acetone. The yield amounted to 63% of shiny white crystals sparingly soluble in cold water.

EXAMPLE 3

Preparation of



(a) Quaternization of pyridine with phenoxyethoxyethyl chloride

A solution of 153.6 grams of phenoxyethoxyethyl chloride and 63.2 grams of pyridine were heated at 95° C. for 48 hours. After removing excess pyridine under vacuum, the thick oil remaining was induced to crystallize by scratching and cooling 206 grams of a crystalline solid were obtained.

(b) Sulfonation

Twenty-five grams of this compound are sulfonated by heating with 30.0 grams of 100% H_2SO_4 at 80° C. for 12 hours. The soluble Zwitter ion was isolated by standard liming out and evaporation technique.

EXAMPLE 4

The procedure is the same as in Example 3, excepting that the pyridine is replaced by α-picoline.

EXAMPLE 5

The procedure is the same as in Example 3, excepting that the pyridine is replaced by quinoline.

EXAMPLE 6

A mixture is made of 3.5 grams of the assistant of Example 1, 4.0 grams of a 55% strength leuco ester of the vat dye of Example 2 of United States Letters Patent 1,095,731, 4.0 grams urea, 18.5 cc. hot water, 60 grams starch tragacanth, 4.0 cc. of sodium chlorate 1:3, 2.0 cc. ammonium vanadate 1:100, 2.0 cc. of ammonia 28%, 2.0 cc. gluconic acid 50%. A clear yellow solution is obtained which is stable on standing. This composition is printed on cotton and after drying is steamed 5 minutes. Bright full-bodied prints are obtained.

EXAMPLE 7

A mix of 3.5 grams of assistant mentioned in Example 2, 4.0 grams of a 55% leuco ester of bis-2,1-naphthathiophen indigo, 4.0 grams of urea,

17.5 cc. water, 60.0 grams of starch tragacanth, 4.0 cc. of sodium chlorate 1:3, 2.0 cc. ammonium vanadate 1:100, 4.0 cc. of ammonium sulfocyanide 1:1, 1.0 cc. of ammonia 28% is made. Part of the leuco ester is precipitated in very finely divided form. After drying and steaming, rich brown shades are obtained which possess excellent penetration in the cotton fiber.

EXAMPLE 8

4.0 grams assistant of Example 3, 4.0 grams of the leuco ester of 4,4'-dichloro-6,6'-dimethyl thioindigo, 5.0 grams of sodium benzyl sulfinilate, 13.0 cc. hot water, 6.0 grams starch tragacanth, 5.0 cc. ammonium sulfocyanide, 6.0 cc. ammonium chlorate 1:3, 2 cc. ammonium vanadate 1:100, 1 cc. ammonia 28%. A finely divided suspension of the leuco ester is obtained. After printing in the accepted manner exceedingly bright and full prints were obtained.

EXAMPLE 9

A mix of 4.0 grams of a 54% leuco ester of the vat dye described in United States Letters Patent 995,936, 4.0 grams of assistant of Example 1, 4.0 grams urea, 20.0 cc. water, 60 grams starch tragacanth, 8 cc. sodium chromate 1:5 is made. A clear reddish brown solution is obtained of the leuco ester. The prints are dried and steamed in acid fumes of formic and acetic acid five minutes. Pure strong prints are obtained.

EXAMPLE 10

A mix of 4.0 grams of assistant of Example 2, 4.0 grams of 55% of the leuco ester of the vat dye of Example 9 of United States Letters Patent 1,803,757, 10 cc. of glyecine, water, 50.0 grams of starch tragacanth, 2.0 cc. of ammonium sulfocyanide 1:1, 3.0 cc. sodium chlorate 1:3, 2.5 cc. ammonium vanadate 1:100, ½ cc. ammonia 28%. A clear brown solution is obtained which is stable to storage. Prints are developed by steaming 5 minutes in a rapid ager. Smooth and deep shades result from this procedure.

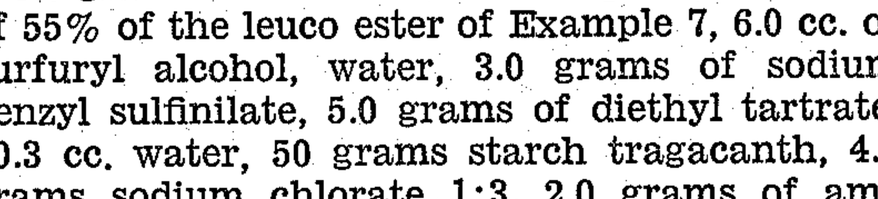
EXAMPLE 11

3.7 grams of assistant of Example 2, 4.0 grams of 55% of the leuco ester of Example 7, 6.0 cc. of furfuryl alcohol, water, 3.0 grams of sodium benzyl sulfinilate, 5.0 grams of diethyl tartrate, 20.3 cc. water, 50 grams starch tragacanth, 4.0 grams sodium chlorate 1:3, 2.0 grams of ammonium vanadate 1:100, 2 cc. ammonia 28%. Clear bright prints with excellent penetration are obtained.

EXAMPLE 12

A mixture consisting of 25 grams of phenol, 11.7 grams sodium hydroxide, 15 cc. water and 187 grams β-chloroethyl-β'-chloroethoxyethyl ether was heated at 110–115° C. for 7 hours while stirring under reflux. After removal of the water, sodium chloride and excess dichloroether, the residual product was an oil distilling at 148–151°/4 mm. (col. 2, page 2, U. S. 2,097,441). Yield 32 grams.

The product was condensed with sodium pyridine-3-sulfonate as in Example 1 to yield 15 grams of:

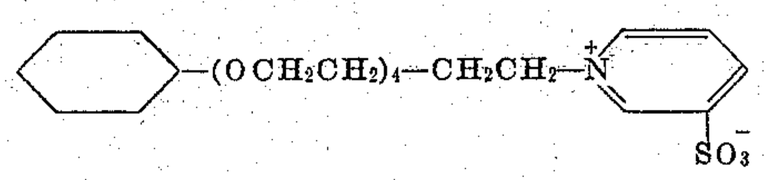


EXAMPLE 13

94 parts of phenol is mixed with 1 part sodium

ethylate and the mixture heated in an iron pressure vessel with 220 parts of ethylene oxide to 90–100° C. (as in U. S. Patent 2,213,477). To the product was slowly added 250 grams of thionyl chloride. After the initial reaction ceased, the solution was refluxed for three hours and permitted to stand overnight at room temperature. After removal of the excess thionyl chloride by distillation, the product was distilled in vacuo.

The product was condensed with sodium pyridine-3-sulfonate as in Example 1 to yield:



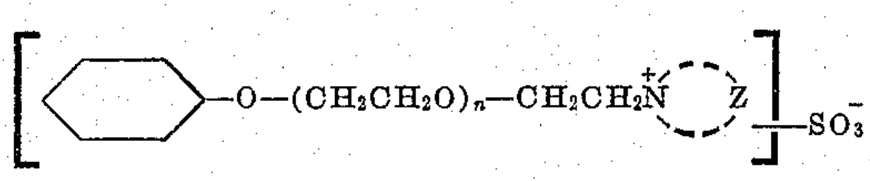
Quantitative measurements have been run with our compounds, and a compound described in United States Letters Patent 2,431,708, to wit, the dimethyl-benzyl-phenyl-ammonium-p-sulfonic acid thereof, and while using as the leuco ester the product of Example 2 above. The results of these measurements establish that our products solubilize from 15 to 25% more of such leuco ester than the prior art product. In the quality of penetration our compounds are also materially superior to said prior art compounds.

The very obvious commercial advantage of increased solubility of our preparations lies in the fact that less of the solubilizing agent is needed, and hence a greater concentration of dye may be employed.

Various modifications of the invention will occur to persons skilled in the art, and hence we do not intend to be limited in the patent granted excepting as necessitated by the prior art and the present claims.

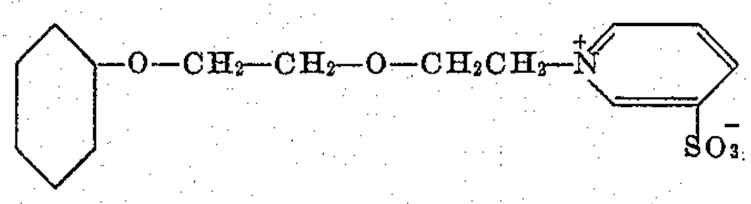
We claim:

1. Compounds of the following formula

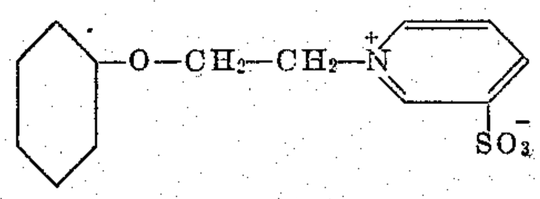


in which n is a number ranging from zero to 4, Z represents the atoms necessary to complete a radical selected from the class consisting of pyridine, C-lower alkyl pyridine and quinoline, and the group SO_3^- is positioned on a carbon atom in a radical selected from the class consisting of the phenyl and the heterocyclic radical.

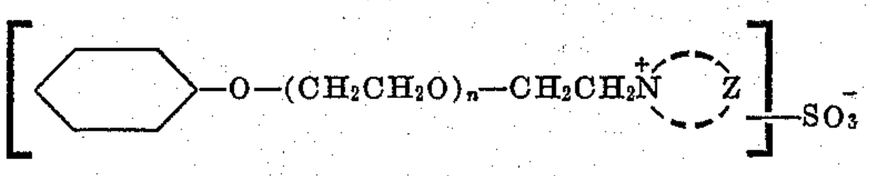
2. The compound of the following formula



3. The compound of the formula



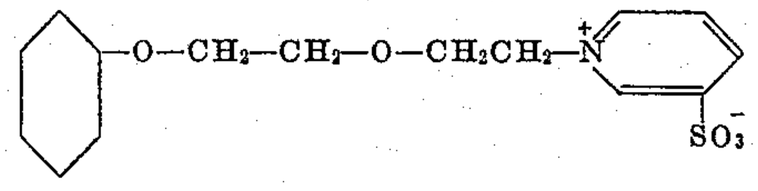
4. A dyestuff composition for printing textile fibers comprising an ester salt of a leuco vat dyestuff and a compound of the following formula



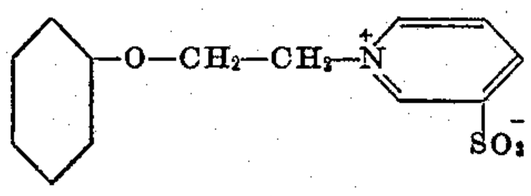
in which n is a number ranging from zero to 4, Z represents the atoms necessary to complete a radical selected from the class consisting of pyridine, C-lower alkyl pyridine and quinoline, and the group SO_3^- is positioned on a carbon

atom in a radical selected from the class consisting of the phenyl and the heterocyclic radical.

5. A dyestuff composition for printing textile fibers comprising an ester salt of a leuco vat dyestuff and the compound of the following formula



6. A dyestuff composition for printing textile fibers comprising an ester salt of a leuco vat dyestuff and the compound of the following formula



DAVID I. RANDALL.
NICHOLAS W. SOLONEN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,299,782	Allen et al.	Oct. 27, 1942
2,336,465	Buck	Dec. 14, 1943
2,388,285	Ratti et al.	Nov. 6, 1945
2,431,708	Ratti et al.	Dec. 2, 1947

FOREIGN PATENTS

Number	Country	Date
684,432	Germany	Nov. 28, 1939

OTHER REFERENCES

Fieser et al., "Organic Chemistry" (D. C. Heath and Co., Boston, 1944), page 32.