

UNITED STATES PATENT OFFICE

2,090,890

TEXTILE PRINTING

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No Drawing. Application February 11, 1935,
Serial No. 6,131. In Great Britain Febru-
ary 19, 1934

9 Claims. (Cl. 8—5)

This invention relates to textile printing. More particularly, this invention deals with the printing of textile material, such as cotton fabric, with vat dyestuffs. By the term printing hereinafter we mean to embrace all processes, such as printing, padding, spraying, stencilling or otherwise applying color to fabric in areas of special design.

It is an object of this invention to provide a novel process and reagents for producing resist styles, that is areas where the fabric opposes the adsorption of color. Other and further important objects of this invention will appear as the description proceeds.

We have found that cotton fabric or other textile materials having an affinity for leuco-esters of vat dyestuffs will develop local resistance toward such dyestuffs if printed first with a composition comprising a salt of an organic compound as more fully defined below. This pre-printing step is in general the same as the process known as resist printing, and the composition mentioned may be of the usual type used in such cases, comprising a gum adapted to cause adherence, water and the special assistants or resisting agents above referred to.

The novel effect of this invention is that the resisting effect of the organic salts employed by us is greater than by the assistants generally used heretofore, the resist-areas developing into a substantially clear white, exposing the original uncolored material. Also, our novel assistants are successful in many cases where resist-effects have heretofore been impossible or difficult to obtain. This effect is particularly brought out in the case of the sulfuric acid esters of leuco-vat dyestuffs of the anthraquinone series, known generically as the "Soledons". These esters have great affinity for cotton fabric and are on this account difficult to resist to a clear white.

The novel assistants above referred to, and useful for this invention, are water-soluble salts of organic bases, or quaternary ammonium, phosphonium or sulfonium compounds, containing in their structure a saturated or unsaturated long-chain aliphatic radical or an aromatic radical which does not carry any salt forming anionic groups, such as sulfo or carboxy. This group of compounds may be defined generically as organic salts of inorganic acids, in which the organic radical contains at least 6 carbon atoms and forms the cation part of the salt. The absence of anionic groups on the long-chain organic radical insures that it will have the characteristics of a cation when in aqueous solution. In

this respect, this group of assistants contrasts with ordinary soaps, such as sodium stearate, palmitate or oleate, in which the organic radical is the anion, while the cation is inorganic.

More specifically, the assistants useful for our invention may be salts of primary, secondary or tertiary amines, quaternary ammonium compounds, salts of heterocyclic organic bases, or quaternary phosphonium or sulfonium compounds. The organic radical may contain an open chain of at least 8 carbon atoms, or it may contain the benzyl or other aralkyl groups.

The following table and examples will further illustrate the types of compounds which we have found applicable for our purpose, but it should be understood that our invention is by no means limited to these specific illustrations. In the examples which follow, the parts mentioned are by weight:

Derivatives of ammonia:

Aniline hydrochloride	
Dimethyl-aniline-hydrochloride	
Dimethyl-benzyl-phenyl-ammonium chloride	25
Tetramethyl-diamino-diphenyl-ketonimine - hydrochloride	
Cetyl-trimethylammonium bromide	
Dicetyl-dimethyl-ammonium bromide	
Octadecyl-trimethylammonium methyl-sulfate	30
Trimethylammonium - methyl - sulfate of mono-stearyl-ethylene-diamine	

Derivatives of heterocyclic bases:

Benzyl-pyridinium chloride	
Octadecyl-pyridinium bromide	
Cetyl pyridinium chloride	
Cetyl pyridinium bromide	40
Oleic acid ester of N-hydroxyethyl-pyridinium chloride	
Cetyl ether of N-hydroxymethyl-pyridinium chloride	

Derivatives of sulfur:

Cetyl-dimethyl-sulfonium methyl-sulfate	
Benzyl-cetyl-methyl-sulfonium methyl-sulfate	50
Dodecyl-dimethyl-sulfonium bromide	
Benzyl-methyl-dodecyl-sulfonium chloride	
Benzyl-ethyl-decyl-sulfonium chloride	
Benzyl-methyl-dodecyl-sulfonium methyl-sulfate	55

Derivatives of phosphorus:

Cetyl-trimethyl-phosphonium bromide
Dodecyl-trimethyl-phosphonium bromide

Some of the above are novel compounds, and are described more fully and claimed in copending applications Serial Nos. 611,236, 28,013 and 47,470. Their general schemes of synthesis, however, may be illustrated briefly by the following examples.

Dimethyl-dicetyl-ammonium bromide may be prepared by reacting one equivalent of dimethylamine and two equivalents of cetyl bromide. Dimethylcetyl-sulphonium methyl-sulfate may be prepared by treating cetyl bromide with sodium hydrosulfide in alcohol, subjecting the mercaptan thus formed to an alkylation treatment with dimethyl-sulfate and caustic soda, and thereafter obtaining the salt by treatment with dimethyl-sulfate alone. Benzylmethyldodecyl-sulphonium methyl-sulfate is obtained by treating the mercaptan derived from dodecyl bromide with a mixture of sodium ethoxide and benzyl chloride and finally treating the resulting product with dimethyl-sulfate.

Benzylcetylmethylsulphonium methyl-sulfate is made by treating cetyl mercaptan with sodium in methanol and then heating with benzyl chloride; the resulting cetyl benzyl mercaptan is then heated with dimethyl sulfide. Dodecylmethylsulphonium bromide is made by heating dodecylmethyl sulfide with methyl bromide until a completely water-soluble product is obtained; dodecyl methyl sulfide is itself made by interacting equivalent quantities of dodecyl mercaptan and dimethyl sulfate in aqueous alkaline medium. Benzylmethyldodecylsulphonium chloride is made by heating dodecyl methyl-sulfide with benzyl chloride until a completely water-soluble compound is produced.

Cetyl-trimethyl-phosphonium bromide may be prepared by interacting trimethylphosphine and cetyl bromide; and dodecyltrimethylphosphonium bromide may similarly be made from dodecyl bromide and trimethylphosphine.

Example I

Cotton cloth is printed with the following paste:

	Parts
British gum (40% solution)-----	65
Water-----	30
Benzylpyridinium chloride-----	5
	100

The printed material is dried and then overprinted with the following paste:

	Parts
Soledon jade green (sulfuric ester of leuco-dimethoxy-dibenzanthrone; Color Index No. 1101) 500 paste-----	2.5
Water-----	25
Neutral starch tragacanth thickening-----	70
Sodium nitrite (30% solution)-----	2.5
	100

The overprinted material is dried and developed by passing at 60° C. through a bath containing 20 parts of sulfuric acid (168° Tw.) per 1000 parts water, washed and soaped for 5 to 10 minutes at the boil. A sharply defined white resist on a green ground is obtained.

Example II

Cotton cloth is printed with the following paste:

	Parts
British gum (40% solution)-----	60
Water-----	30
Dimethylbenzylphenylammonium chloride--	10
	100

The printed material is dried and overprinted with a paste consisting of:

	Parts
Soledon Brilliant Purple 2R (leuco ester of dichloro-isodibenzanthrone; Color Index No. 1104) 200 paste-----	5
Water-----	12
Diethylene glycol-----	8
Neutral starch tragacanth thickening-----	60
Ammonium sulfocyanide (50% solution)---	6
Sodium chlorate (10% solution)-----	8
Ammonium vanadate (1% solution)-----	1
	100

The overprinted material is dried, steamed for 5 to 10 minutes, washed and soaped for 5 to 10 minutes at the boil.

Example III

Tetramethyldiaminodiphenylketonimine hydrochloride, dimethylaniline hydrochloride or aniline hydrochloride may be used instead of dimethyl benzylphenylammonium chloride in Example II.

Example IV

Cotton cloth is printed with the following paste:

	Parts
British gum (40% solution)-----	65
Water-----	30
Benzylpyridinium chloride-----	5
	100

The printed material is dried and padded in a solution containing:

	Parts
Soledon orange 4RS (leuco ester of dibromopyranthrone; Color Index No. 1098) paste-----	50
Water-----	1000
Sodium nitrite (30% solution)-----	25
	50

The padded material is dried and developed by passing at 60° C. through a bath containing 20 parts of sulfuric acid (168° Tw.) per 1000 parts of water, washed and soaped for 5 to 10 minutes at the boil.

Example V

Cotton cloth is printed with the following paste:

	Parts
British gum (40% solution)-----	60
Water-----	35
Cetyltrimethylammonium bromide-----	5
	100

The cloth is dried and overprinted with the following paste:

	Parts
Soledon jade green (6% solution)-----	5
Sodium nitrite-----	5
Neutral starch tragacanth thickening-----	60
Water-----	30
	100

The neutral starch tragacanth thickening is made by dissolving 225 parts of wheat starch in 1500 parts of boiling water and mixing the paste with 1000 parts of 8% gum tragacanth.

The cloth is then steamed for 5 minutes, passed through a 2% solution of sulfuric acid (168° Tw.) at 60° C., rinsed in water, boiled in a 1% soap solution for 10 minutes, rinsed in water and dried. A clean white resist on a green ground is obtained.

Example VI

Cotton cloth is printed with a paste containing:

	Parts
British gum (40% solution)-----	60
Water-----	32
Dimethylphenylbenzylammonium chloride----	8
	100

The cloth is dried and padded for 5 seconds at 60° C., in a solution containing 7 parts of a 10% aqueous paste of the sulfuric ester of Caledon yellow G (Color Index No. 1118), 5 parts of sodium nitrite, and 1000 parts of water.

The cloth is squeezed, passed through a 2% solution of sulfuric acid (168° Tw.) for 2 minutes at 60° C., rinsed, boiled in a 1% soap solution for 10 minutes, rinsed and dried.

Example VII

Cotton cloth is printed with the following paste:

	Parts
British gum (40% solution)-----	60
Water-----	25
Dimethylcetylsulfonium methyl-sulfate-----	15
	100

The printed material is dried, and then overprinted with the following paste:

	Parts
Soledon jade green XS paste-----	2.5
Water-----	25
Neutral starch tragacanth thickening-----	70
Sodium nitrite (30% solution)-----	2.5
	100

The overprinted material is dried and developed by passing at 60° C. through a bath containing 20 parts of sulfuric acid (168° Tw.) per 1000 parts of water, washed and soaped for 5 minutes at the boil. A white resist is obtained on a green ground.

Example VIII

Cotton cloth printed with the resist paste, as in Example VII, is dried and padded in the following solution:

	Parts
Soledon yellow GS (leuco ester of flavanthrone; Color Index No. 1118) paste-----	3
Sodium nitrite-----	5
Water-----	1000

The cloth is squeezed, then developed and finished as in Example VII. A white resist is obtained on a yellow ground.

Example IX

Cotton is printed with the following paste:—

	Parts
British gum-----	60
Water-----	35
Dodecyltriethylphosphonium bromide-----	5

The printed material is dried and padded in the following solution:—

	Parts
Soledon jade green XS paste-----	20
Glycerine-----	20
Water-----	1000
Gum tragacanth-----	50
Sodium nitrite (30% solution)-----	20

dried and treated as in Example VII.

Dodecyl triethylphosphonium bromide may be prepared by reacting triethylphosphine with dodecyl bromide in ethereal solution at 80° C. for 14 hours.

It will be understood that our invention is susceptible of wide variation in practice without departing from the spirit of this invention.

It will be further understood that we selected for the purpose of illustration leuco-esters of vat dyes merely because these have great affinity for cotton fabric and are therefore particularly difficult to resist to a clear white. The effects of our novel assistants are therefore best brought out by the use of this type of dyestuff. It is obvious, therefore, that good resist effects may be obtained also where the dyestuff does not have any superior affinity for the fabric, for instance, in coloring cotton with a mixture of a vat dyestuff in ordinary quinone form and the usual reducing agents such as hydrosulfite, rongalite, formopon, etc.

We claim:

1. The process of resisting cotton against coloration by leuco-esters of vat dyestuffs which have great affinity for cotton, which comprises applying to the same locally a printing gum comprising a water-soluble organic salt of an inorganic acid chosen from the group consisting of organic ammonium compounds, organic phosphonium compounds and organic sulfonium compounds, each of which contains an organic radicle of at least 6 carbon atoms but no ionizable substituents which would impart to said radicle an anionic character.

2. The process of producing colored designs upon cotton fabric which comprises printing said fabric locally with a printing paste comprising a salt of an organic nitrogenous base and inorganic acid, the organic portion of said nitrogenous base being characterized by possessing at least 6 carbon atoms and being free of anionic substituents then applying to said fabric a sulfuric acid ester of a leuco-anthraquinone vat color, and then developing the color and resist patterns.

3. The process of producing colored designs upon cotton fabric which comprises printing said fabric locally with a printing paste comprising a salt of an inorganic acid and a quaternary organic heterocyclic nitrogenous base free from anion-forming ionizable substituents, then applying to said fabric a sulfuric acid ester of a leuco-anthraquinone vat dyestuff, developing the color pattern by hydrolysis and oxidation, and washing out the resist pattern.

4. The process of producing colored designs upon cotton fabric which comprises printing said fabric locally with a printing paste comprising a salt of an inorganic acid and tertiary organic sulfonium compound, then applying to said fabric a sulfuric acid ester of a leuco-anthraquinone vat dyestuff, developing the color pattern by hydrolysis and oxidation, and washing out the resist pattern.

5. The process of producing colored designs upon cotton fabric which comprises printing said

5 fabric locally with a printing paste comprising a salt of an inorganic acid and a quaternary organic phosphonium compound, then applying to said fabric a sulfuric acid ester of a leuco-anthraquinone vat dyestuff, developing the color pattern by hydrolysis and oxidation, and washing out the resist pattern.

10 6. The process of producing white resists on cellulosic fabric under sulfuric esters of leuco vat dyestuffs which have a strong affinity for cotton, which comprises printing said fabric with a resist paste containing a salt of an organic amine which contains at least 6 carbon atoms but no water solubilizing substituents, then applying a sulfuric ester of a leuco vat dyestuff, and developing the color.

15 7. The process of producing white resists on cellulosic fabric under sulfuric esters of leuco vat dyestuffs which have strong affinity for cotton, 20 which comprises printing said fabric with a resist paste containing a quaternary ammonium halide

containing no sulfo or carboxy radicals, then applying to the fabric a sulfuric ester of a leuco vat dyestuff, and developing the color.

8. The process of producing upon cotton fabric white resists against such leuco-esters of vat dyestuffs of the anthraquinone series which are difficult to resist by ordinary methods, which comprises printing said fabric with a resist paste containing dimethyl - phenyl - benzyl - ammonium chloride, then applying to the fabric a leuco-ester of a vat dyestuff, and developing the color. 5 10

9. The process of producing upon cotton fabric white resists against the sulfuric acid ester of leuco-dimethoxy-dibenzanthrone, which comprises printing said fabric with a resist paste containing dimethyl-phenyl-benzyl-ammonium chloride, then applying said color and developing the same upon the fiber. 15

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