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2,256,809

PRODUCTION OF RESIST EFFECTS

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No Drawing. Application November 28, 1938, Serial No. 242,745

13 Claims. (Cl. 8—67)

The present invention relates to the production of white and colored resist or reserve styles on ground shades obtained with oxidation colors, and, in particular, it relates to the production of colored resist styles on ground shades obtained with oxidation colors, where the resist color is obtained with vat dyes. It also relates to new resist printing pastes for the production of resist effects on oxidation colors.

The oxidation colors comprise an important class of dyestuffs which may be employed for the dyeing and printing of textile materials, such as natural and artificial cellulosic fibers, and natural silk. These colors upon oxidation in the presence of the fiber are converted to complex insoluble coloring matters. They include aromatic amino compounds, such as aniline and amino diphenylamine, which are oxidizable to form black dyeings, and para phenylene diamine, meta amino cresol, dianisidine, etc., which are oxidizable to form fast brown colorations on textile materials. The oxidation colors also include the soluble leuco ester salts of vat dyes which upon oxidation in the presence of the fiber are productive of dyeings of various shades. All of these colors are developed (oxidized) on the fiber under acid conditions. Accordingly, the term "oxidation colors," as used herein, denotes and includes colors which are applied directly to the material and then developed by oxidation under acid conditions. A conventional method of applying oxidation colors to a textile material involves padding the textile material with a solution of the desired oxidation color, drying the thus padded material, and then developing the color by a procedure including aging and steaming, and, if desired or necessary, passing the material through an acid bath containing an oxidizing agent.

It is known that white effects on oxidation colors may be obtained by applying locally to a textile material which is impregnated with a solution of an oxidation color, a paste containing an alkaline substance which is effective in inhibiting the development of the oxidation color. In a similar fashion, it is possible to obtain colored effects on grounds which are prepared with oxidation colors by applying over the said ground color printing pastes which contain appropriate dyestuffs, such as the vat dyes, and substances which exert a strong reducing action in the presence of caustic alkalies or alkali carbonates. It has also been proposed to employ alkylol-monoamines in white and vat printing pastes for the production of effects on oxidation colors. These procedures have several disadvantages. For example, the use of colored printing pastes which are composed of vat dyes and the conventional alkaline reacting substances is characterized by a number of draw-backs which are due to the extremely hygroscopic properties of these alkaline substances: for, during the development process the said hygroscopic substances cause the colored paste after it is applied by printing to the textile material to flush and to form an irregular white outline around the print and thereby to spoil the desired effect. Instead of the conventional alkaline substances, alkylol-monoamines have been used, but they are not entirely satisfactory because they are relatively weakly alkaline and to obtain sufficient alkalinity they must be used in large proportions. Further, these compounds are liquids which have a tendency to spread, and the prints obtained with pastes containing them tend to be sticky and to mark-off.

The effects produced by practicing the above procedures may be termed either "reserve effects" or "resist effects." However, inasmuch as the action of the pastes applied to selected areas of the materials is to resist the development of the ground colors, for simplicity in terminology, effects of this type are referred to herein as "resist effects." Also, the pastes used in the production of the effects are termed "resist pastes."

It is a principal object of the present invention to provide a process for the production of superior white and colored resist styles on oxidation colors.

A further object of the invention is to provide a process for the production of colored resist styles on oxidation colors, the said styles being obtained with the use of resist printing pastes containing vat dyes.

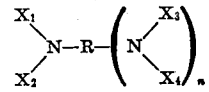
A further object of the invention is to provide novel white and colored resist printing pastes which are adapted for use in the production of resist styles with oxidation colors.

Other objects of the invention in part will be obvious and in part will appear hereinafter.

It has been found in accordance with the present invention that by incorporating in white and colored resist printing pastes certain hydroxylated aliphatic polyamines, described more fully hereinafter, resist printing pastes are produced which, when employed in place of the conventional resist printing pastes in the production of white and colored resist effects on ground colorations obtained with oxidation colors, are productive of effects which are clearly outlined and are substantially free from undesirable flushing.

In accordance with a more specific aspect of the present invention it has been found that colored resist effects on oxidation colors may be obtained with particularly satisfactory results by employing resist printing pastes containing a vat dye and a hydroxylated aliphatic polyamine of the type described below. Such colored resist pastes have been found to produce effects which are well penetrated into the material and are characterized by exceptional brilliance.

The hydroxylated aliphatic polyamines employed in the resist printing pastes of the invention are aliphatic polyamines in which the amino groups may be unsubstituted, but at least one amino group preferably contains as a substituent at least one alkyl or aralkyl radical. (In referring to an alkyl radical herein, it will be understood that cyclic alkyl as well as chain alkyl radicals are intended.) The central radical of these compounds is an aliphatic radical which may consist of a single alkyl radical or a plurality of alkyl radicals linked together by a non-carbon atom or group, such as, for example, O, S, and NX_5, wherein X_5 represents hydrogen, alkyl, aralkyl, or hydroxyalkyl. Throughout this specification and claims the term "non-carbon linkages" denotes O, S and NX_5 as herein defined. The compounds contain at least one hydroxyl group which may be in the central aliphatic radical, or in an N-alkyl radical, or both. Thus, the hydroxylated aliphatic polyamines may be represented by the following general formula:



wherein R represents an alkyl radical or a radical consisting of a plurality of alkyl radicals linked together by non-carbon atoms or groups such as O, S, and NX_5, (wherein X_5 has the above meaning); X_1, X_2, X_3, and X_4 each represents hydrogen, an alkyl radical, an aralkyl radical, a hydroxyalkyl radical, or two of the X's of X_1, X_2, X_3, X_4 joined to different nitrogen atoms conjointly represent a bivalent alkyl radical; and n represents a small whole number. In cases where the radical represented by R is free from hydroxyl groups, at least one of X_1, X_2, X_3, and X_4 represents a hydroxyalkyl radical. It is preferred to employ compounds in which the amino groups are substituted by at least one and prefererably by two or more hydroxyalkyl radicals, regardless of whether the radical represented by R contains hydroxyl groups.

As above indicated, the radical represented by R may contain hydroxyl groups as substituents. It will also be understood that this radical may contain other substituents which do not alter the essential characteristics of the compounds, such as, for example, alkoxy or aralkyloxy radicals. Further, it will be understood that the alkyl and aralkyl radicals attached to the amino groups of the compounds may contain substituents, especially hydroxyl groups. In this connection it should be noted that where an N-aralkyl radical contains two or more carbon atoms in the alkyl radical thereof and this alkyl radical contains hydroxyl groups as substituents, it is regarded as a hydroxyalkyl radical for the purposes of this invention.

Among the compounds of the above class, those which are generally preferred for use in the resist pastes of the invention are hydroxylated aliphatic diamines in which the central aliphatic radical contains 1 to 3 ethylene groups which, in cases where this radical contains more than one ethylene group, are linked together by O, S, or NX_5, X_5 having the above meaning. Further, the preferred compounds contain at least one, and preferably two or more, hydroxyethyl radicals as substituents in the amino groups.

The lower carbon chain compounds of the above type have low melting points, and are viscous liquids at ordinary temperatures; the viscosity of the compounds increasing with increase in their molecular weight. The high molecular chain compounds, on the other hand, are crystalline or amorphous solids which melt above 50° C. All of the compounds of the above type are of low volatility and possess high solubility in water, alcohol, and in most organic solvents.

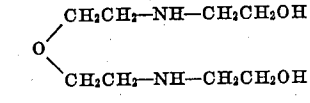
The hydroxylated aliphatic polyamines of the above type are further characterized by an exceedingly strong alkaline character. The superior prints obtainable by the process of the present invention are probably due in great measure to the fact that because of the exceedingly high basic character of the hydroxylated aliphatic polyamines the amount of alkaline reacting substances used in the preparation of resist printing pastes may be lowered to a relatively small quantity which by virtue of its paucity avoids the flushing and spreading of the printed surface while at the same time it efficiently inhibits the development of the oxidation color employed as the ground shade. Further, when used in resist pastes containing vat dyes, the hydroxylated aliphatic polyamines exert solubilizing action on the leuco vat dyes which assists in causing them to penetrate the fiber, thereby producing superior prints. The compounds of the above class which are solids are valuable because printed areas containing them, on being dried out, are free from stickiness.

It will be understood that any one or a mixture of a wide variety of hydroxylated aliphatic polyamines which contain at least one N-alkyl group containing at least two carbon atoms and at least one hydroxyl group may be employed in the preparation of the resist printing pastes of the present invention. Among such polyamines may be mentioned the following compounds:

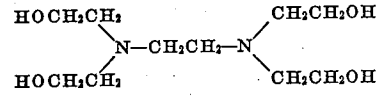
1,2-di-(2'-ethanolamino-)ethane

$HOCH_2CH_2—NH—CH_2CH_2—NH—CH_2CH_2OH$

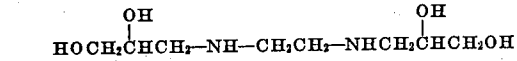
di-(2'-ethanol-2-amino-ethyl-)ether



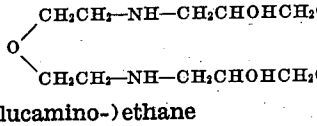
1,2-bis-(di-2'-ethanolamino-)ethane



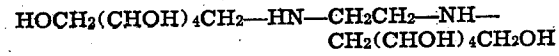
1,2-di-(2',3'-propandiol-amino-)ethane



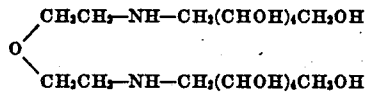
di-(2',3'-propandiol-2-amino-ethyl-)ether



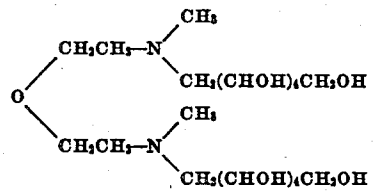
1,2-di-(glucamino-)ethane



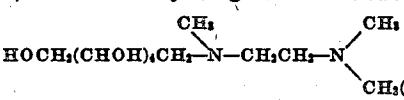
di-(gluco-2-amino-ethyl-)ether



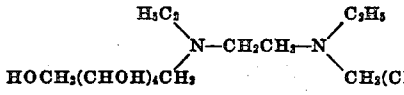
di-(N-methyl-N-gluco-2-amino-ethyl-)ether



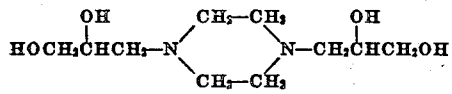
1,2-di-(N-methyl-N-glucamino-)ethane



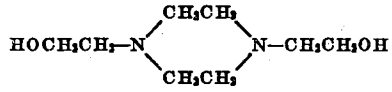
1,2-di-(N-ethyl-N-glucamino-)ethane



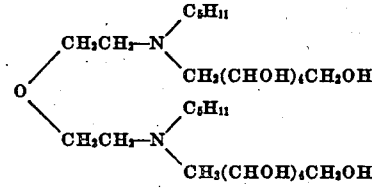
N,N'-di-(propandiol-2,3)-diethylene-diamine, otherwise known as 1,4-di-(propandiol-2,3)piperazine



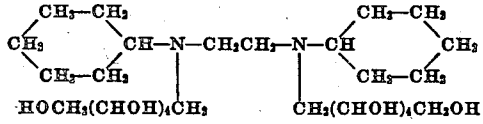
N,N'-di-ethanol-diethylenediamine, otherwise known as 1,4-diethanolpiperazine



di-(N-amyl-N-gluco-2-amino-ethyl-)ether



1,2-di-(N-cyclohexyl-N-glucamino-)ethane



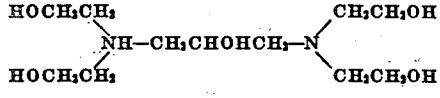
1,3-di-(glucamino-)propane

$$HOCH_2(CHOH)_4CH_2—NH—CH_2CH_2CH_2—NH—CH_2(CHOH)_4CH_2OH$$

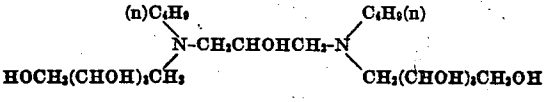
1,3-di-(2'-ethanolamino-)-2-propanol

$$HOCH_2CH_2NH—CH_2CHOHCH_2—NHCH_2CH_2OH$$

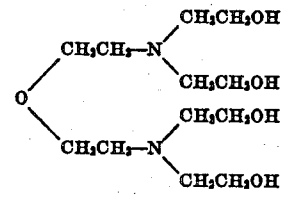
1,3-bis-(di-2'-ethanolamino-)-2-propanol



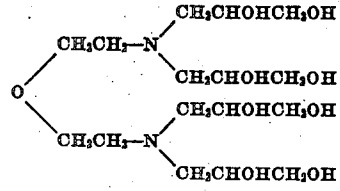
1,3-di-(N-n-butyl-N-xylamino-)-2-propanol



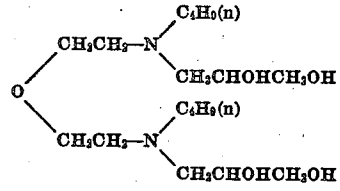
bis-(di-N-2'-ethanol-2-amino-ethyl-)ether



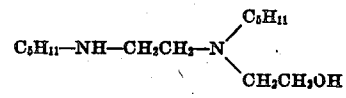
bis-(di-2',3'-propandiol-2-amino-ethyl-)ether



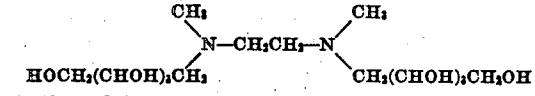
di-(N-n-butyl-N-2',3'-propandiol-2-amino-ethyl-)ether



1-(mono-amylamino)-2-(N-amyl-N-2'-ethanol-amino-)ethane



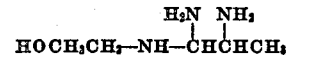
1,2-di-(N-methyl-N-xylamino-)ethane



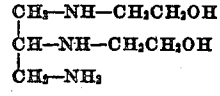
diethanol-triethylene-tetramine

$$HOCH_2CH_2—NH—CH_2CH_2—NH—CH_2CH_2—NH—CH_2CH_2—NH—CH_2CH_2OH$$

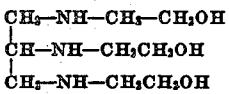
N-(1',2'-diamino-propyl)-amino-2-ethanol



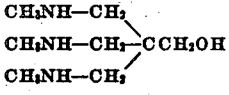
1,2-di-(ethanolamino-)3-amino-propane



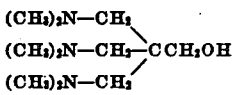
1,2,3-tri-(ethanolamino-)propane



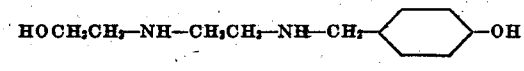
tri-(monomethylamino-methyl-)ethanol



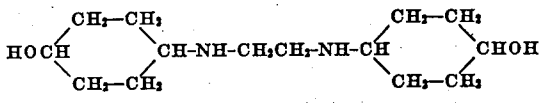
tri-(dimethylamino-methyl-)ethanol



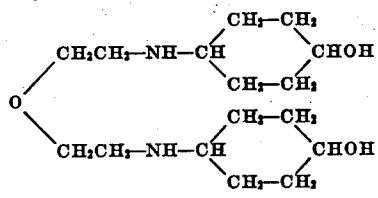
1-parahydroxy-benzylamino-2-hydroxyethyl-amino-ethane



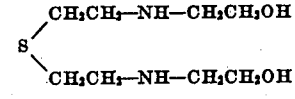
1,2-di-(4'-cyclohexanol-amino-)ethane



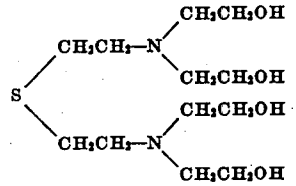
di-(N-4'-cyclohexanol-2-amino-ethyl-)ether



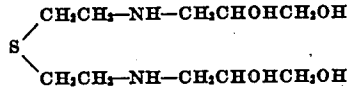
di-(ethanolamino-ethyl-)sulfide



bis-(di-2'-ethanol-2-amino-ethyl-)sulfide



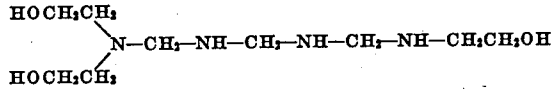
di-(2',3'-propandiol-2-amino-ethyl-)sulfide



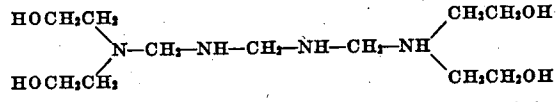
N^1N^4-diethanol-trimethylene-tetramine

$$HOCH_2CH_2—NH—CH_2—NH—CH_2—NH—CH_2—NH—CH_2CH_2OH$$

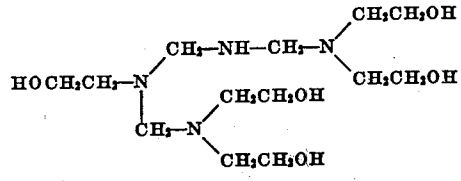
N^1N^4-triethanol-trimethylene-tetramine



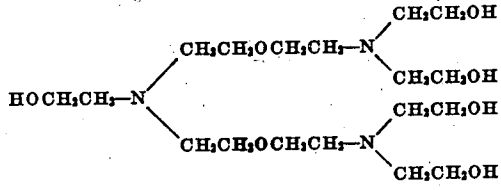
N^1N^4-tetraethanol-trimethylene tetramine



N^1N^4-bis-diethanol-N^2-ethanol-trimethylene tetramine



N-bis-(diethanol-amino-ethoxy-ethyl-)-N-ethanolamine



The resist printing pastes of the present invention may be prepared in a simple manner. For example, to prepare resist printing pastes for the production of white resist effects on oxidation colors, there may be added to the usual thickening ingredients of such pastes one or a mixture of the hydroxylated aliphatic polyamines of the above type. White resist effects on oxidation colors may be obtained in accordance with the present invention by applying this resist printing paste in the conventional manner to a fabric which has been prepared with a composition containing the oxidation color desired for the ground shade. Thereafter, the textile material is subjected to a conventional developing treatment whereupon a white resist effect is obtained on the developed ground. This development treatment may include merely a steaming and aging procedure where that is sufficient to oxidize the ground color (which has been applied to the material in a solution containing an oxidizing agent). It may include, however, an acid aging or, after the usual steaming and aging, a passage of the material through an oxidizing bath containing an oxidizing agent and an acid.

In order for the invention to be more fully understood, reference should be had to the following examples in which are described resist printing pastes and processes by which white resist effects may be obtained on oxidation colors. It will be understood, however, that the invention is in no way limited to the specific proportions and procedures described in the examples. The parts are by weight.

Example 1.—White cotton material is prepared in the usual manner with the following solution for aniline black:

48 parts sodium chlorate
115 parts sodium ferrocyanide
144 parts aniline hydrochloride dissolved in 2000 parts water.

The cloth is padded therewith, then dried and printed with the following white resist printing paste:

400 parts British gum (powder)
500 parts water, to which
100 parts 1,2-bis-(di-2'-ethanol-amino-)ethane are added.

After printing, the material is steamed for about 2½ minutes at 102° C., in a rapid ager, then passed into an oxidation bath composed of ½ per cent sodium bichromate and 1 per cent of a 28 per cent solution of acetic acid. The printed material is then rinsed, soaped, rinsed, and dried. A white resist print is thus obtained on the aniline black ground.

Example 2.—A white resist printing effect on a fast brown ground may be obtained as follows:

A white cotton and rayon mixed fabric is prepared with a padding liquor which is made by mixing the following three solutions:

(1) 20 parts Fuscamine G (meta amino phenol)
20 parts hydrochloric acid 20° Bé. are dissolved in
400 parts water by applying heat.
(2) 25 parts sodium chlorate
100 parts hot water
(3) 5 parts sodium ferrocyanide
100 parts water.

These solutions are mixed cold and standardized to 1000 parts total.

After padding, the fabric is dried, preferably in hot air and then printed with the resist paste described in Example 1. After printing, the material is passed through a rapid ager for about 5 to 10 minutes at 105° C. The fabric may then be

subjected to ammonia vapors or may be rinsed immediately after steaming in luke warm water, soaped, rinsed and dried.

Example 3.—A natural silk fabric is padded with the following padding liquor:

From 15 to 20 parts Ortamine D (ortho dianisidine) are dissolved in

from 15 to 20 parts acetine and
from 3.75 to 5 parts hydrochloric acid 20° Bé., and
from 8 to 12 parts formic acid 90%, to which solution
from 15 to 20 parts sodium chlorate and
from 5 to 8 parts sodium ferrocyanide are added.

The whole is standardized to 1000 parts total.

The silk material is then printed with a white resist paste composed of:

775 parts gum Senegal, 1:1
100 parts sodium acetate
50 parts potassium sulfite solution 45° Bé.
75 parts glyceryl diethanol-ethylene diamine.

After printing, the material is steamed for about 5 minutes whereby the brown ground shade is developed and the fabric is passed into tepid water, rinsed thoroughly, soaped, rinsed and dried. Thus, a white resist effect is obtained on a brown bottom shade.

Colored resist effects on oxidation colors may be obtained in accordance with the present invention with the use of printing pastes containing dyes of various types, it being only necessary that such dyes be applicable to a textile material in an alkaline paste. For example, colored resist effects may be obtained with the use of resist printing pastes containing dyes, such as vat dyes, sulfur dyes, and azoic printing compositions (e. g., nitrosamine and diazo-amino compositions). The present invention, however, is particularly directed to the production of resist printing pastes containing vat dyes and the above-described hydroxylated aliphatic polyamines. Such resist printing pastes have been found to yield excellent results particularly when employed on materials composed of cellulosic or natural silk fibers. Vat dye resist printing pastes may be prepared in accordance with the present invention by incorporating with the usual components of a vat dye printing paste (which ordinarily include a vat dye in the unreduced form, thickening ingredients, a reducing agent, such as sodium formaldehyde sulfoxylate, an alkali carbonate or caustic alkali, and dispersing agents, and other suitable additions) a hydroxylated aliphatic polyamine of the type already described. The total amount of alkaline material ordinarily employed in such printing pastes, however, may be reduced in most cases to a minimum because of the strongly basic character of the hydroxylated aliphatic polyamine.

Colored resist effects may be obtained on oxidation color ground dyeings in accordance with the present invention by locally applying a vat dye resist printing paste of the above type to a textile material which has been previously prepared with a grounding liquor containing an oxidation color, and then subjecting the material to a development treatment. The following examples are illustrative of procedures carried out in accordance with the present invention wherein colored resist effects are obtained with vat dyes on ground shades of oxidation colors. The parts are by weight:

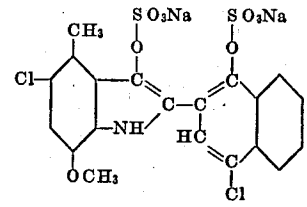
Example 4.—Cotton material is prepared with the aniline black padding solution described in Example 1, and is then printed with the following vat dye composition:

	Parts
British gum (powder)	250
Water	275
Vat Brilliant Indigo 4Br paste (tetra-brom-indigo)	90
Bis - (di-2',3'-propan-diol- 2 -amino-ethyl) ether	100
Potassium carbonate	60
and Sodium formaldehyde sulfoxylate	225
	1000

The printed material is then passed through a rapid ager for about 4 minutes and oxidized in the usual way, washed and dried; thus, a blue resist effect is obtained on a black ground.

Example 5.—Cotton material is padded with the following solution and then dried.

30 parts of the disodium salt of the sulfuric leuco ester represented by the following formula:



	Parts
Diethylene glycol	30
Water	865
Sodium nitrite	15
Ammonia solution 25%	10
Gum tragacanth 25%	50

made up to 1000 parts by volume.

Printing color

200 parts National Vat Orange R (Color Index 1217) are mixed intimately into:

720 parts of a thickening composed of:
520 parts of corn starch British gum thickening
150 parts of potassium carbonate
120 parts of sodium formaldehyde sulfoxylate
50 parts of glycerine
160 parts water

and 80 parts of di(N-butyl-N-ethanol-amino-) ethane or 1,2-di-glucamino-ethane.

After printing and drying, the material is passed through a vat dye ager for about 4 to 5 minutes, whereby the printed Vat Orange R is developed; thereafter, the material may be passed for about 3 to 5 minutes into an acid ager which will cause the ground shade to be developed, but not in the areas where the resist has been applied by the printing. Instead of developing the ground shade in an acid ager, it may be developed by padding the material with a solution containing per 1000 parts:

	Parts
Oxalic acid	10
Formic acid 85%	10
Glauber salt	25

and directly thereafter drying the padded material on a cylinder drying machine. The fabric is then rinsed and soaped for 10 minutes at the boil, rinsed, dried and finished in the usual way.

A very fast and brilliant orange print is thus obtained on a dyed vat blue ground shade.

The general procedure described in the above

example may be used for the preparation of white resists on ground colorations obtained with leuco ester salts of vat dyes by using in place of the vat dye resist printing paste the white resist printing pastes described in Examples 1 and 3. In this case the development is similar to that described in Example 5, being carried out by subjecting the material to an acid aging treatment or padding it with the acid padding liquor illustrated above.

While in the above examples there have been specifically illustrated procedures in which only white or colored resist effects are obtained on oxidation colors, it will be understood that by applying white and colored resist printing pastes simultaneously to a textile material, which has been impregnated with a grounding liquor of an oxidation color, combined white and multi-colored resist effects may be obtained. Also, it is to be understood that colored resist effects may be obtained with the use of dyes other than vat dyes applicable to textile materials in alkaline pastes, and that multi-colored resist effects may be obtained by applying simultaneously two or more resist printing pastes containing, respectively, dyes of different classes. For example, multi-colored resist effects may be obtained on oxidation colors in accordance with the process of the present invention by using simultaneously a resist paste containing a vat dye and a resist paste containing an azoic printing composition. My application Serial No. 242,746, filed of even date herewith, is directed to the production of resist printing pastes containing azoic dye compositions and to a process for the production of colored resist effects on ground colorations of oxidation colors obtained with the use of such resist printing pastes.

In the preparation of colored resist effects on ground colorations obtained with oxidation colors, it will be obvious that any suitable vat dye may be employed in place of the vat dyes specifically mentioned in the above Examples 4 and 5. For example, in the production of colored resist effects in accordance with the process of the present invention, there may be employed a vat dye selected from the following group:

	Color Index No.
Carbanthrene Blue GCD	1113
Carbanthrene Yellow G double powder	1118
Carbanthrene Golden Orange 2RT powder	1097
Carbanthrene Golden Orange G double powder	1096
Carbanthrene Blue Green FFB double powder	1173
Carbanthrene Violet 2R powder	1104
Carbanthrene Dark Blue DR	1099
Carbanthrene Flavine GC double powder	1095
Carbanthrene Red Violet 2RNX powder	1161
Carbanthrene Brilliant Green supra	1101
Brilliant Indigo 4G powder	1189
Brilliant Indigo 4B powder (tetrabrom indigo)	
Vat Scarlet G paste	1128
Vat Brown G paste (dinaphthyl-thioindigo)	
Vat Green G paste	1199
Vat Violet R paste	1222

It will be understood, of course, that in the preparation of resist printing pastes in accordance with the procedures described in the foregoing examples, the hydroxylated aliphatic polyamines employed therein may be replaced by any one or a mixture of other hydroxylated aliphatic polyamines of the class disclosed above; for example, one or a mixture of those specifically mentioned.

The proportions of ingredients specified for preparation of the resist printing pastes in the foregoing examples may be varied within wide limits. As noted above, by the use of the hydroxylated aliphatic polyamines in resist printing pastes the total amount of alkaline materials in the pastes may be reduced to a minimum. In some instances, as in the production of white resist effects, one or more of the hydroxylated aliphatic polyamines may be used in place of the entire amount of alkali normally used in pastes for the production of resist effects of this type. In other instances, superior results are obtained by replacing only a part of the alkali normally used with one or more of the amines. For best results, it is preferred to employ one or more of the amines in place of at least a part of the alkali normally used; i. e., they are used as alkaline agents. It will be understood that the particular proportions to be employed in any given case are dependent upon the character of the textile material employed, the type of effect desired, and the kind of development treatment. Hence, these proportions may be left largely to the discretion of the operator. The foregoing examples, however, are illustrative of typical procedures and may be referred to as a basis for comparison.

Although, as indicated in the above examples, it is preferred to produce the resist effects by applying the resist pastes to a material impregnated with a ground color, the invention is not limited to this manner of proceeding since the resist pastes may be applied to the material before impregnation with the ground color.

Since certain changes may be made in the above compositions and processes without departing from the scope of the invention, the above description should be taken as illustrative and not in a limiting sense.

I claim:

1. A resist printing paste for the production of resist effects on oxidation colors comprising a thickener and a hydroxylated aliphatic polyamine free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals.

2. A resist printing paste for the production of colored resist effects on oxidation colors comprising a dye applicable to textile materials in an alkaline paste, a thickener, and a hydroxylated aliphatic polyamine free from amino substituents other than alkyl radicals, aralkyl radicals, and hydroxyalkyl radicals.

3. A resist printing paste for the production of resist effects on oxidation colors comprising a thickener and a hydroxylated aliphatic polyamine having as a central radical a plurality of alkyl radicals linked together by non-carbon linkages, said polyamine being free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals and containing at least one hydroxyalkyl radical as an amino-substituent when the central radical is free from hydroxyl groups.

4. A resist printing paste for the production of colored resist effects on oxidation colors comprising a dye applicable to textile materials in an alkaline paste, a thickener, and a hydroxylated aliphatic polyamine having as a central radical a plurality of alkyl radicals linked together by non-carbon linkages, said polyamine being free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals

and containing at least one hydroxyalkyl radical as an amino-substituent when the central radical is free from hydroxyl groups.

5. A resist printing paste for the production of colored resist effects on oxidation colors comprising an unreduced vat dye, a reducing agent, a thickener, and a hydroxylated aliphatic polyamine having as a central radical a plurality of alkyl radicals linked together by non-carbon linkages, said polyamine being free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals and containing at least one hydroxyalkyl radical as an amino-substituent when the central radical is free from hydroxyl groups.

6. A resist printing paste for the production of resist effects on oxidation colors comprising a thickener and a hydroxyalkylated ethylenediamine which contains at least one hydroxyalkyl radical as an amino-substituent and which is free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals.

7. A resist printing paste for the production of colored resist effects on oxidation colors comprising an unreduced vat dye, a thickener, and a hydroxyalkylated ethylenediamine which contains at least one hydroxyalkyl radical as an amino-substituent and which is free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals.

8. In the process of producing colored resist effects on oxidation colors, the improvement which comprises applying to selected areas of a textile material impregnated with an undeveloped oxidation color a resist printing paste comprising a dye applicable to textile materials in an alkaline paste, a thickener, and a hydroxylated aliphatic polyamine free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals.

9. In the process of producing colored resist effects on oxidation colors involving the step of applying to a textile material in selected areas a printing paste adapted to prevent the oxidation of the oxidation color, the improvement which comprises applying to a textile material impregnated with an undeveloped oxidation color a printing paste comprising an unreduced vat dye, a reducing agent, a thickener, and a hydroxylated aliphatic polyamine having as a central radical a plurality of alkyl radicals linked together by non-carbon linkages, said polyamine being free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals and containing at least one hydroxyalkyl radical as an amino-substituent when the central radical is free from hydroxyl groups.

10. In the process of producing resist effects on oxidation colors, the improvement which comprises applying to selected areas of a textile material impregnated with an undeveloped oxidation color a resist printing paste comprising a thickener and a hydroxyalkylated ethylenediamine which contains at least one hydroxyalkyl radical as an amino-substituent and which is free from amino-substituents other than alkyl radicals, aralkyl radicals and hydroxyalkyl radicals.

11. A resist printing paste for the production of resist effects on oxidation colors comprising a thickener and 1,2-bis-(di-2'-ethanol-amino)-ethane.

12. A resist printing paste for the production of resist effects on oxidation colors comprising a thickener and bis-(di-2',3'-propan-diol-2-amino-ethyl) ether.

13. A resist printing paste for the production of resist effects on oxidation colors comprising a thickener and bis-(di-2'-ethanol-2-amino-ethyl-) sulfide.

JEAN G. KERN.