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RESIST PRINTING UNDER REACTIVE DYE WITH ALKALI HYDROXY METHANE SULFONATE OR AMINO AND AMIDO METHANE SULFONATE

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No Drawing. Continuation-in-part of abandoned application Ser. No. 607,146, Jan. 4, 1967. This application June 29, 1970, Ser. No. 50,917
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U.S. Cl. 8—65 12 Claims

ABSTRACT OF THE DISCLOSURE

A resist process for dyeing fibers by printing on a fiber a resisting agent such as an alkali hydroxy methane sulfonate or a substance capable of producing an alkali hydroxy methane sulfonate followed by treatment with a reactive dye and subsequent dye fixing treatment.

This application is a continuation-in-part application of the U.S. patent application Ser. No. 607,146, filed Jan. 4, 1967, now abandoned.

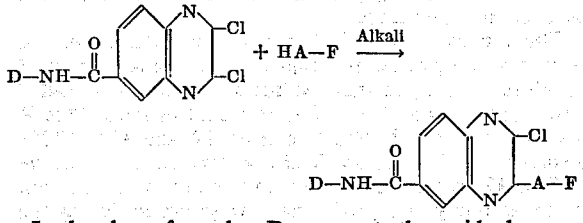
The present invention relates to a resist printing process for the reactive dyeing of fibers which are dyeable with reactive dyes, for example, natural or synthesized protein fibers such as wool and silk, polyamide type synthetic fibers, and natural, regenerated or semi-synthesized cellulose fibers such as cotton, flax, viscose rayon, cuprammonium artificial silk and cellulose acetate fibers.

The generally accepted theory of dyeing fibers with various reactive dyes marketed and generally used at present is that in case, for example, of vinyl sulfon type reactive dyes, the reactive group is decomposed by the action of alkali existing in the dyeing bath or in the printing paste to produce vinyl sulfon group and in case of 2,3 - dichloroquinoxaline - 6 - carbonamide type the reactive group is activated also by alkali to react with the groups having active hydrogen in fibers. As to the other reactive dyes, their principles are the same as above.

Reaction formulas for a vinyl sulfon type and 2,3-dichloroquinoxaline-6-carbonamide are shown below by way of example.

$$D\text{—}SO_2\text{—}CH_2CH_2\text{—}OSO_3Na \xrightarrow{\text{Alkali}} D\text{—}SO_2\text{—}CH{=}CH_2 + Na_2SO_4$$

$$D\text{—}SO_2\text{—}CH{=}CH_2 + HA\text{—}F \longrightarrow D\text{—}SO_2\text{—}CH_2CH_2\text{—}A\text{—}F$$



In the above formulas, D represents the residual group in the coloring matter; F, the residual group in the fibers; and A, an atom or atomic group combining with active hydrogen.

In the application of this kind of dyes to textile printing, addition of alkali or latent alkali, such as sodium bicarbonate, sodium trichloro-acetate or caustic soda, to printing paste is necessarily required for reaction with the hydroxyl group in cellulose by heating after dyeing. Therefore, in this case if an acidic substance is used as the resisting agent and applied in advance to fibers as by printing, the acidic substance applied region will not be acted upon by alkali, so that there will be no reaction with the particular fibers, thus making it possible to obtain desired resist printing. However, in case of alkali shock process as a method of dyeing with reactive dyes, in which fibers having been subjected to printing treatment with a dyeing paste containing such dye is immersed in a bath containing a large amount of strong alkali, it is apparent in the name of common sense that existence of a large amount of alkali will hinder the acidic substance from exerting its print resisting effect. Such being the case, no resist-printing process suitable for the fixing of reactive dyes by alkali shock process has been found as yet up to the present day.

There is another problem to be overcome with respect to resist printing process in dyeing with reactive dyes, that is, color-resist printing. As mentioned before, in order to effect the dyeing of fibers with various reactive dyes, it is essential to use alkali or latent alkali such as caustic soda, sodium carbonate, sodium bicarbonate, or sodium trichloroacetate. They may be added to dye bath or printing paste, or alternatively they may be treated in a separate process before or after dyeing. Therefore, as the conventional resisting agent in case of dyeing with reactive dyes, acidic substances such as tartaric acid and citric acid are generally used. If these are applied in advance to fibers as by printing, the alkali or alkaline substance in the applied regions necessary for color fixation will be neutralized, so that the fixation of reactive dyes can be prevented, thus making it possible to obtain desired resist printing. However, with such resist printing process, since all the reactive dyes are prevented from fixation, the effect of the so-called color-resist printing with reactive dyes alone cannot be obtained, while white resist printing would be possible. Such being the case, no such resisting agent has been found as yet. The color-resist printing by reactive dyes themselves as referred to herein is a process in which two or more kinds of reactive dyes are simultaneously printed on the same fibers and one or more kinds thereof are resist printed so as to attain coloring (the so-called effect color of printing) by another kind of reactive dyes, and a process in which a dye incapable of resist printing together with a resisting agent is applied by printing, the same being then immersed in a dye solution capable of resist printing, thereby to obtain multi-colored effect.

Accordingly, the primary object of the invention is to provide an improved resist printing process for the reactive dyeing of fibers with reactive dyes through the utilization of a new resisting agent which is capable of exerting a perfect resist printing effect even in a strong alkali bath.

Another object of the invention is to provide an improved color-resist printing process for the reactive dyeing of fibers with reactive dyes through the utilization of

a new resisting agent which is selectively reactive with certain reactive dyes.

The other objects and advantages of the invention will in part be clear and will in part appear hereinafter.

We have found a new resisting agent for coloring with reactive dyes, which can be utilized for the color-resist printing by reactive dyes. More particularly, the present invention is characterized by using as the resisting agent in fixing of reactive dyes by an alkali hydroxy methane sulfonate or a substance which will produce it by the action of heat and/or alkali during a dye fixing treatment.

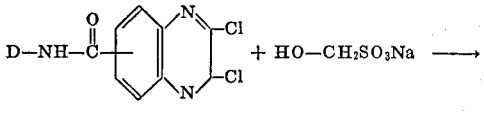
As is known alkali hydroxy methane sulfonate is a compound which can be easily obtained in the form of aqueous solution or white powder by reaction between formaldehyde and sodium bisulfite. On the other hand, as examples of the substances which will produce alkali hydroxy methane sulfonate by the action of heat and/or alkali, there may be mentioned, N-acyl-, N-alkyl- and N-alkyl acyl-amino methane sulfonate alkali. Particularly, sodium laurylamido-methane sulfonate, sodium caprylamide methane sulfonate, p-toluene sulfonamide methane sulfonate, p-ethyl benzene sulfonamide methane sulfonate, sodium p-toluylaminomethane sulfonate and sodium dodecylaminomethane sulfonate are preferred. Poly-acrylamide sulfomethylate and poly-methacrylamide sulfomethylate are useful as well. Although these are typically obtained by reacting a corresponding acid amide or amine with formaldehyde and sodium bisulfite or sulfite or alkali hydroxy methane sulfonate, various other known methods therefor may also be utilized. It has been known for long that this series of compounds will decompose by the action of heat and/or alkali to produce alkali hydroxy methane sulfonate. The resisting agents used in the present invention have as their principal ingredient alkali hydroxy methane sulfonate or a substance which will produce it by the action of heat or of alkali, and may be used singly or in combination of two or more of them. In some cases, a solution obtained by reacting the above mentioned respective ingredients may be used as it is.

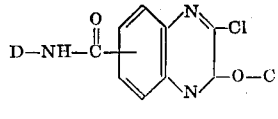
There are various ways of carrying out the resist printing process. To mention an instance thereof, cellulose type fibers which have beforehand been printed with sulfomethylate or polyacrylamide and then dried are subjected to the printing treatment with a vinyl sulfon type reactive dye according to usual practice. The fibers are then dried and passed through a concentrated alkaline solution, whereby in the regions printed with the sulfomethylate of polyacrylamide there will occur no reaction between the reactive dye and the fibers, so that the dye may be removed by the subsequent washing with water and soaping process, to provide white resist printing effect on the regions ,the remaining regions having the reactive dye fixed thereon with good fastness.

The resist printing mechanism will now be considered. When the textile, which was printed with a resisting agent and in turn with a reactive dye according to the invention, is treated with alkali, the reactive radical of the dye reacts with alkali hydroxy methane sulfonate more easily than with the fibers, with the result that the reactive group becomes a mere alkali sulfonate type. That is,

$$D\text{—}SO_2\text{—}CH_2CH_2\text{—}OSO_2Na \xrightarrow{\text{Alkali}} D\text{—}SO_2\text{—}CHCH_2$$

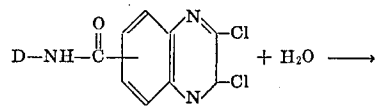
$$D\text{—}SO_2\text{—}CHCH_2 + HO\text{—}CH_2SO_3Na \longrightarrow D\text{—}SO_2\text{—}CH_2CH_2\text{—}O\text{—}CH_2\text{—}SO_3Na$$

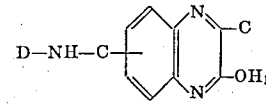




These kind of dyes, once assuming such form, will no longer react with fibers and, losing their affinity to cellulose fibers, become sufficiently water-soluble. Therefore, they can be completely sealed off by soaping process as they will not dye fibers, and resist printing is thus obtained. The principle is the same as in a process in which when a reactive dye bath is heated with concentrated alkali, the following reactive products are formed,

$$D\text{—}SO_2\text{—}CHCH_2 + H_2O \longrightarrow D\text{—}SO_2\text{—}CH_2\text{—}CH_2OH$$





each of which is water-soluble and can be completely sealed off by soaping, without combining with fibers. Another example will be mentioned with reference to a substance which will produce alkali hydroxy methane sulfonate by the action of alkali. As is commonly known, alkali laurylamide methane sulfonate will decompose by hot alkali to be converted to lauric acid amide or alkali laurate and at the same time produce alkali hydroxy methane sulfonate as shown below.

$$C_{11}H_{23}CONH\text{—}CH_2\text{—}SO_3Na \xrightarrow{NaOH} C_{11}H_{23}CONH_2 \text{ or } C_{11}H_{23}COONa + HO\text{—}CH_2SO_3Ha$$

It is believed that the sodium hydroxy methane sulfonate produced here starts reaction with reactive dyes as in the above, with resist printing effect consequently exerted. Thus, in the light of the fact that the exertion of the resist printing effect is due to the action of alkali hydroxy methane sulfonate it should be noted that the chemical composition for the resisting agents is not limited to alkali hydroxy methane sulfonate itself but includes substances which produce alkali hydroxy methane sulfonate by the action of heat and/or alkali.

The above mentioned resisting agents of the invention can also be utilized for the color-resist printing by reactive dyes. The color-resist printing process according to the invention comprises the steps of printing on fibers with a printing paste including a resisting agent and a reactive dye, said resisting agent being selected from the group consisting of alkali hydroxy methane sulfonate and a substance producing alkali hydroxy methane sulfonate during a heat treatment for fixing dyes on said fibers, said reactive dye being substantially non-reactive with alkali hydroxy methane sulfonate but reactive by a heat treatment with said fibers to be fixed thereon, printing on said fibers with another printing paste including another reactive dye which is reactive with alkali hydroxy methane sulfonate and also reactive by a heat treatment with said fibers to be fixed thereon, and subjecting said fibers printed with said two printing pastes to a heat treatment for fixing said dyes on said fibers. In the above, the resisting agent may be replaced by a substance producing alkali hydroxy methane sulfonate by the action of alkali with the additional condition that said another printing paste includes a latent alkali such as sodium bicarbonate.

The reactive dyes which are to be included in the second printing paste and capable of being resist-printed by alkali hydroxy methane sulfonate are of the so-called vinyl type, such as C.I. 61200 Remazol Brilliant Blue R also known as C.I. Reactive Blue 19 and C.I. 18852 Remazol Golden Yellow G also known as C.I. Reactive Yellow 17, having, as the reactive group, a vinyl group or an atomic group producing a vinyl group during the dye fixing treatment.

The reactive dyes other than mentioned in the above, which are substantially non-reactive with alkali hydroxy

methane sulfonate, may be used as the dye to be included together with alkali hydroxy methane sulfonate in the first printing pastes. The dye included in the first printing paste is the so-called effect color of printing.

Though not fully known, the mechanism of the color resist printing using the compounds of the present invention is assumed as follows:

The presently marketed reactive dyes are roughly divided into two types, one being the so-called vinyl type having as the reactive group a vinyl group or an atomic group which will produce a vinyl group through dyeing treatment, such vinyl group tending to start addition reaction with the gorup having active hydrogen in articles to be dyed, the other type having active chlorine included in the reactive group and tending to start combination by dehydrochlorination reaction with articles to be dyed. And this vinyl type is the most active of the reactive dyes and will sufficiently react with the compounds of the present invention and the resist printed even in case that the existence of alkali or latent alkali and water is limited to a small amount. As against this, since the other type of reactive dyes start dehydrochlorination reaction with groups having active hydrogen such as the OH group of cellulose on sodium hydroxy methane sulfonate, an excessive amount of alkali is naturally required in this case. To review the conditions of the color resist printed regions of fibers (printed surface), it will be seen that it is a mixture of the present compound and a dye for effect color of printing that are in contact with the fibers while the dye to be resist printed is not in direct contact with the fibers. If steaming is then operated, each dye will be activated, and since the vinyl type reactive dye is high in activation, it will immediately react with the compound of the present invention and will lose its ability to be fixed on the fibers before it reaches the fiber surface so that it may be resist printed, whereas because of the fact that the dye for effect color of printing is slow in reaction and is in direct contact with the fibers and that the reaction causes the amount of the compound of the present invention to be decreased, the dye for effect color of printing will react with the fibers rather than the present compound to be fixed on fibers.

While there is no particular limit to the working concentration of the resisting agents, in order to attain the full exertion of the resist printing effect it is desirable that 2% or more should be adopted as the effective component concentration in the printing paste.

Some examples will now be described, in which parts and percentage refer to parts by weight and percentage by weight, respectively, unless otherwise specified.

EXAMPLE 1

50 parts of sodium hydroxy methane sulfonate is dissolved in 450 parts of water and to this preparation is added 500 parts of 12% locust beam gum containing paste, these adding up to 1,000 parts. The thus prepared paste is printed on a cotton broad cloth, and the cloth, after being dried, is over-printed with a preparation obtained by adding 50 parts of urea to 30 parts of C.I. 61200 (Blue) followed by the addition of 410 parts of hot water to completely dissolve the same, to which are then added 500 parts of 6% sodium alginate containing paste and 10 parts of sodium meta-nitrobenzene sulfonate, these adding up to 1,000 parts, and the cloth is then dried. Subsequently, the cloth is immersed for 15–20 seconds in a bath at 90–95° C. prepared by dissolving in water 150 parts of soda ash, 50 parts of potassium carbonate, 150 parts of common salt, 50 parts of potassium carbonate, 50 parts of common salt, 50 parts of caustic soda (38° Bé) and 10 parts of sodium silicate, these adding up to 1,000 parts, the cloth being washed with water and soaped. The thus obtained colored cloth is such that the regions printed with the aforesaid sodium hydroxy methane sulfonate are resist-printed white while the regions not printed with sodium hydroxy methane sulfonate react with the fibers so that the color inherent to the coloring matter is fixed thereon with good fastness.

EXAMPLE 2

On cotton broadcloth printed with polyacrylamide sulfomethylate (20% concentration, 3000 cps, viscosity) and dried are printed with a printing paste prepared by dissolving 30 parts of C.I. 18852 (Yellow) in 460 parts of hot water, to which is added 500 parts of 6% sodium alginate containing paste, followed by the addition of 10 parts of sodium meta-nitrobenzene sulfonate with stirring, these adding up to 1,000 parts, and the fibers are then dried. Thereafter, an alkali fix treatment similar to that described in Example 1 is operated. The printed regions will be resist printed white for the sulfomethylated acrylamide polymer decomposes to produce hydroxy methane sulfonic acid.

EXAMPLE 3

80 parts of sodium laurylamide methane sulfonate or sodium caprylamide methane sulfonate is dissolved in 240 parts of hot water, to which is added 450 parts of 6% sodium alginate containing paste, these components being uniformly mixed. On the other hand, to 30 parts of C.I. 24890 (Direct, Yellow) are added 30 parts of thiodiethylene glycol, the mixture being then dissolved in 170 parts of warm water, the resulting solution being then uniformly mixed with the aforesaid paste to add up to 1,000 parts, thereby providing a paste. The paste is printed on a cotton broadcloth, and the cloth, after being dried, is over-printed with another paste prepared by adding 50 parts of urea to 30 parts of C.I. 61200 (Blue) followed by the addition of 410 parts of hot water to completely dissolve the same, to which are then added 500 parts of 6% sodium alginate containing paste and 10 parts of sodium meta-nitrobenzene sulfonate, these adding up to 1,000 parts. The cloth is then dried again. The fabric is then heated for 15–20 minutes with steam at 100° C. and subjected to an alkali fix treatment similar to that described in Example 1, followed by washing with water and soaping, whereby beautiful yellow colored resist printing against a blue background is obtained.

EXAMPLE 4

First, 200 parts of sulfomethylated acrylamide polymer (10% concentration, 1000 cps. viscosity) is added to a preparation obtained by dissolving 10 parts of polyethylene glycol oleoylether and 80 parts of p-toluene sulfonamide methane sulfonate or p-ethyl benzene sulfonamide methane sulfonate in 200 parts of water. To this is added 510 parts of mineral turpentine with stirring by a homogenizer, to prepare an emulsion paste, 1,000 parts in total amount 700 parts of this paste is uniformly mixed with 50 parts of C.I. 11710 (Yellow), 200 parts of emulsion polymer (with 45% of solid content) of methyl acrylate and 50 parts of trimethylol melamine (with 80% of solid content), to prepare a paste. This paste is printed on cellulose type fibers and then dried. Further, a paste prepared by dissolving 30 parts of C.I. 61200 (Blue) in 460 parts of hot water and uniformly mixing the same with 500 parts of 6% sodium alginate containing paste and 10 parts of sodium meta-nitrobenzene sulfonate is printed on the aforesaid printed cloth, which, after being dried, is heat treated at 140° C. for 4 minutes. Thereafter, washing with water and soaping are operated, followed by an alkali fix treatment similar to that described in Example 1, and thus two-colored effect with yellow against a blue background is obtained.

EXAMPLE 5

30 parts of C.I. 18105 Cibacron Brilliant Red 3B also known as C.I. Reactive Red 4 (Red) together with 50 parts of urea is uniformly dissolved in 200 parts of hot water, which is then uniformly mixed with 500 parts of 5% sodium alginate containing paste, and then the prep-

aration has cooled down. 30 parts of sodium metanitrobenzene sulfonate and 12 parts of sodium bicarbonate are added thereto to provide a uniform mixture, to which is added a solution prepared by dissolving 50 parts of sodium p-toluylaminomethane sulfonate in 128 parts of water, thereby providing a uniform printing paste (A), 1,000 parts in total amount. Next, a second uniform printing paste (B), 1,000 parts in total amount, is prepared in much the same way by dissolving 30 parts of C.I. 61200 (Blue) in a solution consisting of 50 parts of urea dissolved in 300 parts of hot water, followed by addition of 500 parts of 5% sodium alginate containing paste, with which, upon cooling, are uniformly mixed 10 parts of sodium metanitrobenezne sulfonate, 12 parts of sodium bicarbonate and 98 parts of water. First, the printing paste (A) is printed on silk satin and then, without drying the same, the printing paste (B) is printed thereon in such a manner as to locally overlap. After drying, steaming is operated at 100° C. for 10 minutes. The thus obtained printed fabric is subjected to successive washing with water, soaping and washing with water, whereupon a colored fabric is obtained in which the regions printed with the printing paste (A) including those overlapped by the printing paste (B) have been colored red having a beautiful hue and the printing paste (B) overlapping the printing paste (A) has perfectly been resist printed.

EXAMPLE 6

320 parts of a solution containing 30 parts of C.I. 17910 (Red) and 100 parts of urea is mixed with 500 parts of 5% sodium alginate containing paste, to which are added 20 parts of sodium metanitrobenzene sulfonate and 60 parts of 25% solution of sodium carbonate and after the mixture is made uniform, 100 parts of sulfomethylated polymethacryl amide (20% concentration, 2,000 cps. viscosity) is added thereto, to provide a paste, 1,000 parts in total amount. The paste is printed on cotton broadcloth. Next, a printing paste, 1,000 parts in total amount, is prepared by dissolving C.I. 18852 (Yellow) and 50 parts of urea in 300 parts of hot water, which is mixed with 500 parts of sodium alginate, followed by addition of 10 parts of sodium metanitrobenzene sulfonate, 12 parts of sodium bicarbonate and 98 parts of water, the mixture being made uniform. This paste is printed on said previously printed cotton cloth over the entire surface thereof to overlap the printed regions. After being dried, the cloth is steamed at 100° C. for 10 minutes, washed with water and soaped, whereby the overlap-printed regions are colored to have a beautiful red color and hence colored resist printed broadcloth with effect color of printing of red against a yellow background is obtained.

EXAMPLE 7

230 parts of a solution containing 30 parts of C.I. 61210 (Blue) and 50 parts of urea is uniformly mixed with 450 parts of 5% sodium alginate containing paste, to which are added 30 parts of sodium metanitrobenzene sulfonate, 12 parts of sodium bicarbonate and 200 parts of 25% solution of sodium dodecylamino methane sulfonate, followed by further addition of 35 parts of paraffin and 15 parts of polyethylene glycol lauryl ether, and finally 28 parts of water is added to complete a printing paste, 1,000 parts in total amount. The printing paste is printed on cotton broadcloth and dried. Besides this paste, 1,000 parts of a solution is prepared which contains 30 parts of C.I. 18852 (Yellow), 100 parts of urea, 2 parts of sodium alginate, 10 parts of sodium metanitrobenzene sulfonate and 15 parts of sodium bicarbonate. The above mentioned printed cloth is padded in this solution, followed by successive washing with water, soaping and washing with water. The thus obtained cloth has attained multi-colored effect having a beautiful blue pattern against a yellow background.

What we claim is:

1. A resist printing process for the reactive dyeing of fibers dyeable with reactive dyes, which comprises the steps of:
   printing on said fibers with a resisting agent selected from the group consisting of alkali hydroxy methane sulfonate, alkali N-acyl-amino methane sulfonate, alkali N-alkyl-amino methane sulfonate, alkali N-alkylaryl-amino methane sulfonate, poly-acrylamide sulfomethylate and poly-methacrylamide sulfomethylate.
   printing on said fibers with a reactive dye, and subjecting said fibers printed both with said resisting agent and with said reactive dye to a dye fixing treatment.

2. A resist printing process for the reactive dyeing of fibers dyeable with reactive dyes, which comprises the steps of:
   printing on said fibers with a resisting agent selected from the group consisting of alkali hydroxy methane sulfonate, sodium laurylamido-methane sulfonate, sodium caprylamide methane sulfonate, p-toluene sulfonamide methane sulfonate, p-ethyl benzene sulfonamide methane sulfonate, sodium o-toluylaminomethane sulfonate, sodium dodecylaminomethane sulfonate, poly-acrylamide sulfomethylate and poly-methacrylamide sulfomethylate,
   printing on said fibers with a reactive dye, and subjecting said fibers printed both with said resisting agent and with said reactive dye to a dye fixing treatment.

3. A resist printing process as defined in claim 2, in which said dye fixing treatment is carried out by dipping said printed fibers in an alkali solution bath.

4. A resist printing process as defined in claim 3, in which said resisting agent is a substance producing alkali hydroxy methane sulfonate by the action of alkali.

5. A resist printing process as defined in claim 2, in which said dye fixing treatment is carried out by dipping said printed fibers in a hot alkali solution bath.

6. A resist printing process as defined in claim 5, in which said resisting agent is a substance producing alkali hydroxy methane sulfonate by the action of heat.

7. A resist printing process as defined in claim 5, in which said resisting agent is a substance producing alkali hydroxy methane sulfonate by the action of heat and alkali.

8. A resist printing process for the reactive dyeing of dyeable with reactive dyes, which comprises the steps of: printing on said fibers with a printing paste including a resisting agent and a reactive dye, said resisting agent being selected from the group consisting of alkali hydroxy methane sulfonate and a substance producing alkali hydroxy methane sulfonate during a heat treatment for fixing dyes on said fibers, said substance being further selected from the group consisting of sodium laurylamidomethane sulfonate, sodium caprylamide methane sulfonate, p-toluen sulfonamide methane sulfonate, p-ethyl benzene sulfonamide methane sulfonate, sodium p-toluylaminomethane sulfonate, sodium dodecylaminomethane sulfonate, poly-acrylamide sulfomethylate and poly-methacrylamide sulfomethylate, said amino methane sulfonates and sulfomethylates, said reactive dye being substantially non-reactive with alkali hydroxy methane sulfonate but reactive by a heat treatment with said fibers to be fixed thereon, printing on said fibers with another printing paste including another reactive dye which is reactive with alkali hydroxy methane sulfonate and also reactive by a heat treatment with said fibers to be fixed thereon, and subjecting said fibers printed with said two printing pastes to a heat treatment for fixing said dyes on said fibers.

9. A resist printing process as defined in claim 8, in which said another reactive dye which is reactive with alkali hydroxy methane sulfonate is a vinyl type reactive dye.

10. A resisting printing process for the reactive dyeing of fibers dyeable with reactive dyes, which comprises the steps of: printing on said fibers with a printing paste including a resisting agent and a reactive dye, said resisting agent being a substance which produces alkali hydroxy methane sulfonate by the action of alkali, said reactive dye being substantially non-reactive with alkali hydroxy methane sulfonate but reactive by a heat treatment with said fibers to be fixed thereon, printing on said fibers with another printing paste including another reactive dye and a latent alkali, said another reactive dye being capable of reacting with alkali hydroxy methane sulfonate and also reactive by a heat treatment with said fibers to be fixed thereon, and subjecting said fibers printed with said two printing pastes to a heat treatment for fixing said dyes on fibers.

11. A resist printing process as defined in claim 8, in which said another reactive dye which is reactive with alkali hydroxy methane sulfonate is a vinyl type reactive dye.

12. A resist printing process as defined in claim 8, in which said latent alkali is sodium bicarbonate.

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DONALD LEVY, Primary Examiner

U.S. Cl. X.R.

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