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3,414,368

RESIST PRINTING METHOD FOR
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38/38,819; Mar. 26, 1964, 39/16,616

6 Claims. (Cl. 8—64)

ABSTRACT OF THE DISCLOSURE

A process for the resist printing of hydrophobic fibers, yarns, fabrics, etc., particularly polyesters, characterized by the employment of at least one disperse dye containing in its molecule at least 2 radicals, each with an unshared pair of electrons, the disperse dye being capable of forming a copper chelate compound, and further characterized by the employment of a resist printing paste containing a copper compound capable of forming a chelate with said disperse dye. The printing of the resist printing paste can be accomplished either before or after the dyeing of the fiber, etc., with the disperse dye, the dyed fabric being finished by a subsequent aqueous washing and drying.

The present invention relates to a resist printing method for hydrophobic fibers or preferably for fibers of a high hydrophobic nature. More particularly, the present invention relates to a resist printing method for hydrophobic fibers which, in dyeing hydrophobic fibers with at least one kind of disperse dyestuffs containing in the molecule at least two radicals each with an unshared pair of electrons and capable of forming metal chelate compounds, is characterized by using as a resist agent the resist printing paste which contains metal compounds capable of forming chelate compounds with said disperse dyestuffs. It should be noted that as used herein, the term "fiber" includes filament, yarn, tow, sliver, knit fabric, woven fabric, and non-woven fabric. Also, the term "hydrophobic fiber" is a general term for individual fibers such as acetate, nylon or synthetic fibers of polyester base or fibers containing them. Again, the term "resist printing" means a printing method whereby undyed material is printed with a resist agent to present on subsequent dyeing or developing a white pattern on a colored ground, or a pattern of contrasting color to the ground by incorporating suitable dyes in the resist printing paste.

Heretofore, where disperse dyestuffs are applied to hydrophobic fibers such as acetate, nylon, and other synthetic fibers of a polyester base, it has been considered extremely difficult to conduct resist printing. Attempts for this purpose mainly involved the joint use of physical resist agents such as starch, clay, active carbon and oil. Due to the weak resisting power of the disperse dyestuff, however, it was necessary to apply a resisting additive in substantially thick layers. In practice, many problems were encountered such as the unsuitableness of resist agents for roller printing, and the clogging of mesh openings by the resist agent in screen printing. A number of proposals have been made relating to another common technique namely, discharge printing in order to obtain the same effect of resist printing. However, since none of these suggestions are practical, it has been desired to establish a method of resist printing particularly where hydrophobic fibers are dyed with disperse dyestuffs.

Previously, when acetate fiber is dyed with disperse dyestuffs of an anthraquinone base, the fiber has been pretreated before said dyeing with metal compounds capable of forming chelate compounds with such dyestuffs. Other

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methods (United States Patent No. 2,895,967 and British Patent No. 799,708) were also proposed to improve the fastness properties of dyestuffs by treating the fiber after dyeing with said metal compounds for formation of chelate compounds.

The inventors have studied a process for resist printing of hydrophobic fibers with disperse dyestuffs, particularly one which gives high effect of resist printing and offers resist prints with sharp outlines. As a result, they have discovered the surprising fact that the chelate forming function which was previously used in improving the fastness properties of dyestuffs can be diverted to an industrially advantageous and effective process for carrying out resist printing of highly hydrophobic fiber, for example, synthetic fibers of polyester base which were formerly known to be incapable of satisfactory resist printing. No proposals have heretofore been made as to the technique of resist printing making use of the above mentioned new application of the chelate forming function.

Quite contrary to the former technical idea of improving the fastness properties of dyestuffs by means of chelation, the present invention provides an easy and very effective process for resist printing of even those hydrophobic fibers by means of said chelation which have hitherto defied good resist printing.

The inventors have further discovered that azoic dyeing may also be applicable in resist printing by the above said method of chelation and that the process of the present invention can be used in mixed fibers such as those containing cellulosic material which have no affinity to disperse dyestuffs.

The inventors have also discovered that said dyestuffs should contain in the molecule at least two radicals each with an unshared pair of electrons and should also be capable of forming chelate compounds with metals, and that resist printing has become possible with disperse dyestuffs by adding those metal compounds to resist printing paste as resist agent, which form chelate compounds with said disperse dyestuffs.

Therefore, the object of the present invention is to provide an industrially advantageous and effective process for resist printing of hydrophobic fibers including synthetic fiber of polyester base for which no satisfactory resist printing has been known to be available, and mixtures of said synthetic fibers and those which admit of only poor affinity of disperse dyestuffs or practically no affinity thereof.

Another object of the present invention is to provide a new method of azoic dyeing by the use of the process of the present invention which might be called "chelating resist printing" and also a new method of illuminated resist printing similarly by means of said process.

Further objects and advantages of the present invention will be more clearly understood from the following description.

The hydrophobic fibers used in the process of the present invention include all kinds of hydrophobic fiber that can be dyed with disperse dyestuffs, such as acetate, nylon, polyester synthetic fibers, polyacrylonitrile synthetic fibers, polyvinyl chloride synthetic fibers, and polyolefins synthetic fibers or mixtures thereof.

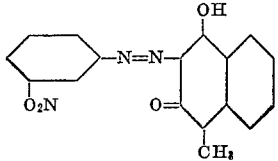
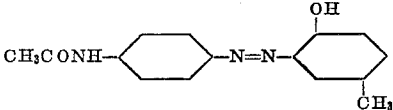
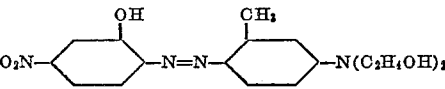
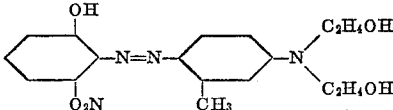
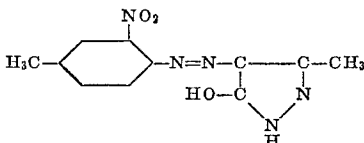
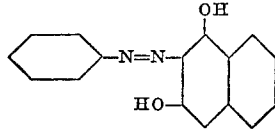
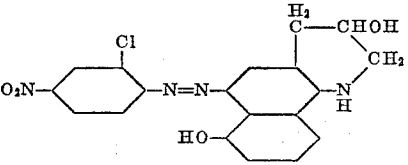
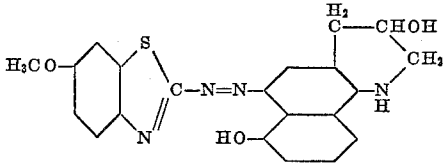
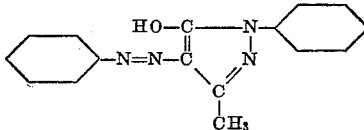
With the process of the present invention, it is also possible to obtain excellent resist printing of mixed fibers, for example, mixed yarn or mixed fabric consisting of the above individual hydrophobic fibers or combinations thereof and the natural or regenerated fibers of animal or plant source. All the foregoing fibers may be used in the form of filament, yarn, tow, sliver, knit fabric or non-woven fabric. The process of the present invention can be used particularly suitably in the resist printing of polyester synthetic fiber (for example, commercially available

Dacron and Dacron Type 64 of Dupont, U.S.A.; Terylene of I.C.I., England; Tetoron of Teijin and Toyo rayon, Japan; Tetoron T-89 of Teijin, Japan; Kodel of Eastman, U.S.A.; Vycron of Beaunit mill, U.S.A.; Glyrene of Inventa, Switzerland; K-3 of Chemstrand, U.S.A.; Trevira WA of Hoechst, Germany, and mixed yarn, mixed weaves, and mixed knittings thereof.

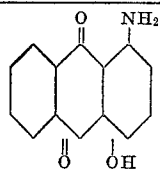
In the process of the present invention any kinds of disperse dyestuff may be applicable if they contain in the molecule at least two radical each with an unshared pair of electrons and are capable of forming chelate compounds with metals. As used herein, the "disperse dyestuffs" mean those which are insoluble or hardly soluble in water and are used in the dyeing of hydrophobic fibers from the suspension liquid in which they are dispersed.

As used herein, the radicals containing unshared pairs of electrons may include at least one kind of radical selected from the group consisting of $-\text{N}=\text{N}-$, $-\text{OH}$, $-\text{COOH}$, $\text{C}=\text{O}$ and $-\text{NH}_2$.

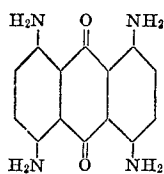
The aforesaid disperse dyestuffs may comprise those known types which are capable of forming chelates with metal compounds, namely, the known disperse dyestuffs such as azo series, anthraquinone series, diphenylamine series, triphenylmethane series, methine series, naphthoquinone series and anthrone series. Since it would be too long a list to illustrate the individual dyestuffs belonging to all these groups, the following are some representative ones. (The abbreviation C.I. used in the following illustrations denotes the Color Index numbers.)

| AZO SERIES | |
|--|---|
|  | C.I. 12790; Celliton Yellow 5G (B.A.S.F., Germany). |
|  | C.I. 11855; Celliton Fast Yellow G (B.A.S.F., Germany). |
|  | C.I. 11225; Celliton Discharge Rubine BBF (B.A.S.F., Germany). |
|  | C.I. 11135; Celliton Discharge Pink BRF (B.A.S.F., Germany). |
|  | C.I. 12690; Cibacet Yellow GN (Ciba, Switzerland). |
|  | C.I. 12770; Dispersol Yellow 3G (I.C.I., England). |
|  | C.I. 11430; Celliton Discharge Blue 3G (B.A.S.F., Germany). |
|  | C.I. 11435; Celliton Discharge Blue 5G (B.A.S.F., Germany). |
|  | C.I. 12700; C.I. Disperse Yellow 16, |

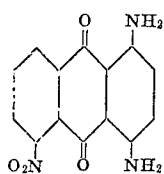
ANTHRAQUINONE SERIES



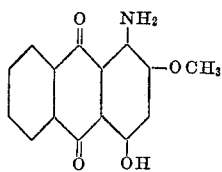
C.I. 60710, Celliton Fast Pink BN
(B.A.S.F., Germany).



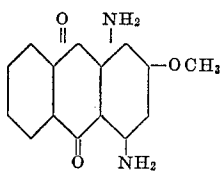
C.I. 64500, Duranol Brilliant Blue CB
(I.C.I., England).



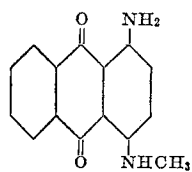
C.I. 62030, Celliton Fast Violet B
(B.A.S.F., Germany).



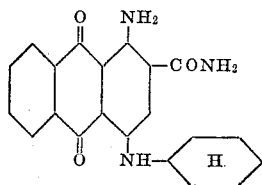
C.I. 60755, Celliton Fast Pink RF
(B.A.S.F., Germany).



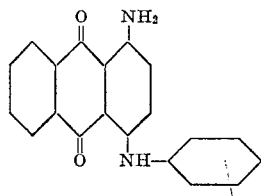
C.I. 62015, Celliton Fast Pink FF3B
(B.A.S.F., Germany).



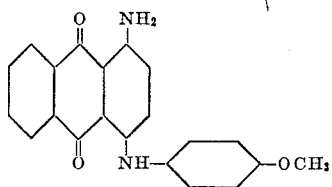
C.I. 61105, Celliton Fast Violet 6B
(B.A.S.F., Germany).



C.I. 62050, Celliton Fast Blue FFG
(B.A.S.F., Germany).

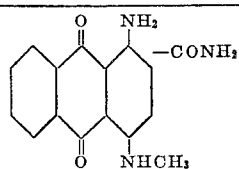


C.I. 61110, Cibacet Blue 2R (Ciba,
Switzerland).

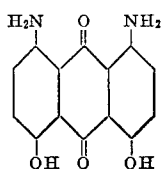


C.I. 61115, Celliton Fast Blue FR
(B.A.S.F., Germany).

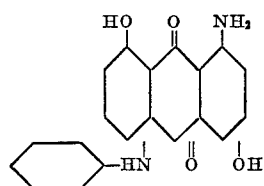
ANTHRAQUINONE SERIES



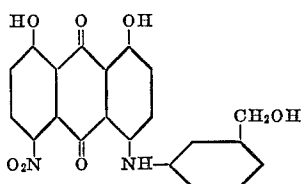
C.I. 62035, Celliton Fast Blue FFB
(B.A.S.F., Germany).



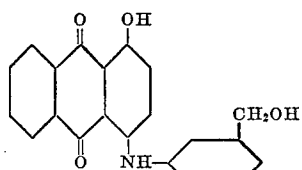
C.I. 63600.



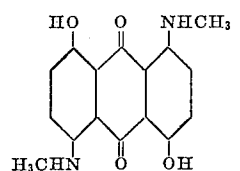
C.I. 63300.



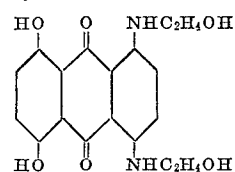
Eastman Fast Blue GLF (Eastman,
U.S.A.).



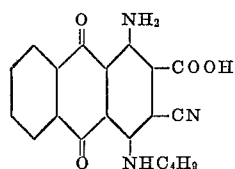
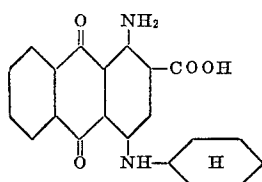
Latyl Violet B (Dupont, U.S.A.).



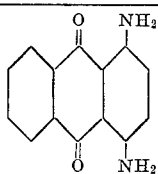
C.I. 63305, Duranol Blue G (I.C.I.,
England).



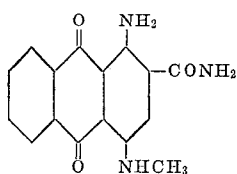
C.I. 62500, Celliton Fast Blue Green B
(B.A.S.F., Germany).



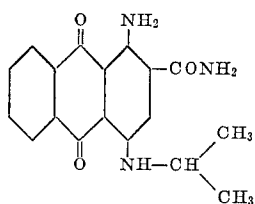
ANTHRAQUINONE SERIES



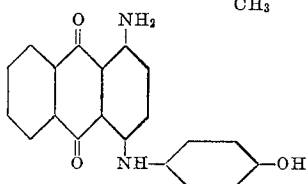
C.I. 61100, C.I. Disperse Violet 1.



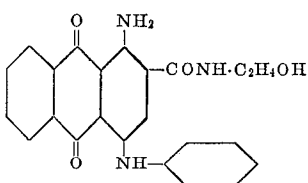
C.I. 62035, C.I. Disperse Blue 5.



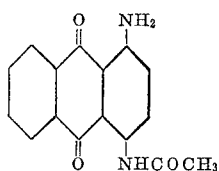
C.I. 62040.



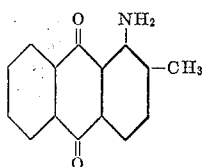
C.I. 61120.



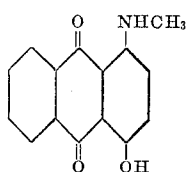
C.I. 62065, C.I. Disperse B.



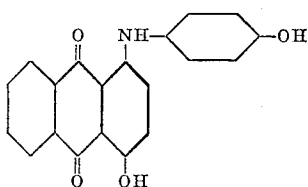
C.I. 61140, C.I. Disperse Violet. 6



C.I. 60700, C.I. Disperse Blue 22.

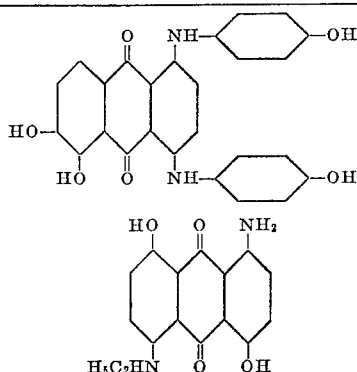


C.I. 60715, C.I. Disperse Blue 22.

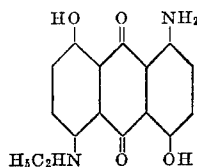


C.I. 60740, C.I. Disperse Blue.

ANTHRAQUINONE SERIES

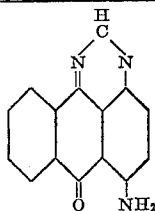


C.I. 62580.



C.I. 63295.

ARTHRONE SERIES



The metal compounds which form chelate compounds with said disperse dyestuff may preferably include at least one kind of metal compound selected from the group consisting of Cu, Cr, Co, Fe, Al, Mg, V, Vr, Ni and preferably Pb, Cu, Cr, Ni and Co are more desirable metals. These metal compounds may represent either organic or inorganic compounds.

For instance, the chromium compounds may include chromium chloride, chromium fluoride, chromium formate, chromium hydroxide, chromium acetate, chromium sulfate, chromium chloride, potassium dichromate, etc.; the copper compounds may comprise cupric formate, cupric acetate, cuprous acetate, cupric ammonium hydroxide; cupric chloride, cuprous chloride, cuprous citrate, copper hydroxide, cupric nitrate, copper oxalate, cupric sulfate, copper tartrate, cupric benzoate, cupric acetate basic, cupric aminoacetate, cupric ammonium chloride, cupric bromide, cupric butyrate, cupric chlorate, cupric citrate, cupric dichromate, cupric fluoride, cupric gluconate, cupric lactate, cupric perchlorate, cupric phenol-sulfonate, cupric phosphate, cupric salicylate, cupric selenate, cupric silicofluoride, cupric sulfate ammoniate, cupric sulfate anhydrous, cuprous bromide, cuprous iodide, cuprous nitride, cuprous potassium cyanide, etc.; the iron compounds may consist of ferric chloride, ferrous sulfate, etc.; the nickel compounds may include nickel formate, nickel oxalate, nickel acetate, nickel hydroxide, etc.; the cobalt compounds may comprise cobalt hydroxide, cobalt chloride, etc.; and the aluminum compounds may consist of aluminum chloride, aluminum sulfate. Particularly preferable for the process of the present invention are cupriferous compounds, for example, copper formate, copper acetate, copper sulfate, and copper benzoate.

According to the process of the present invention, when the fiber with affinity to disperse dyestuffs is printed using the resist printing paste containing at least one kind of

chelate formable metal compounds with the disperse dyestuff which contains in the molecule at least two radicals each with an unshared pair of electrons and is also capable of forming chelate compounds with such metal compounds, said disperse dyestuffs may be uniformly applied on the whole surface of fabric by any of the commonly used padding, color brushing, cover printing, and spray printing after printing and thereafter dyeing may be accomplished by dry or wet (steam) heating.

The conditions of heat treatment may be properly selected depending on the type of fiber used. Usually this treatment is made at a temperature of 100–130° C. for wet heating and at 150–200° C. for dry heating. In this case the disperse dyestuff which contains in the molecule at least two radicals each with an unshared pair of electrons forms chelates with metal compounds at those portions of the fiber printed with paste containing said metal compounds and considerably decreases in affinity to the fiber and does not fix on the fiber even by heat treatment. This tendency becomes more prominent, as the fiber has more compact construction. On the other hand, the non-printed portions obtain good dyeing effect by heat treatment. Thus, effective resist printing is made possible. The foregoing resist printing process may also be conducted by first applying the dyestuff to the fiber and then printing the paste containing said metal compound, followed by dry or wet heat treatment.

It is also possible to carry out illuminated resist printing by the use of resist printing paste containing no chelate dyestuffs but other types with affinity to the hydrophobic fiber, for example, fluorescent dyestuffs including Uvitex E R (Ciba, Switzerland) and vat dyestuffs including Indanthrene yellow G (B.A.S.F., Germany) and Indanthrene printing scarlet GG (Hoechst, Germany).

The disperse dyestuffs used in said illuminated resist printing may include the following which do not form chelates with metal compounds.

AZO SERIES

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|--|--|
| | Interchem Acetate Yellow M (Interchemical Co., U.S.A.). |
| | C.I. 11005, Celliton Fast Orange GR (Bayer, Germany). |
| | C.I. 11100, Celliton Fast Brown 3R (B.A.S.F., Germany). |
| | C.I. 11110, Celliton Scarlet B (B.A.S.F., Germany). |
| | C.I. 11150, Celliton Fast Rubine 3B (B.A.S.F., Germany). |
| | C.I. 10345, Dispersol Fast Yellow RR (I.C.I., England). |
| | C.I. 26090, Celliton Fast Yellow 5R (B.A.S.F., Germany). |
| | C.I. 11080, Dispersol Fast Orange A (I.C.I., England). |
| | C.I. 11115, Dispersol Fast Crimson B (I.C.I., England). |
| | C.I. 11120, Celliton Red Violet RR (B.A.S.F., Germany). |
| | C.I. 10340, C.I. Disperse Yellow 14. |
| | C.I. 10350, C.I. Disperse Orange 15. |
| | C.I. 10375, C.I. Disperse Yellow 9. |
| | C.I. 11025, C.I. Disperse Black 3. |
| | C.I. 1030. |
| | C.I. 11035, C.I. Disperse Black 7. |
| | C.I. 11040, C.I. Disperse Red 41. |
| | C.I. 11060. |

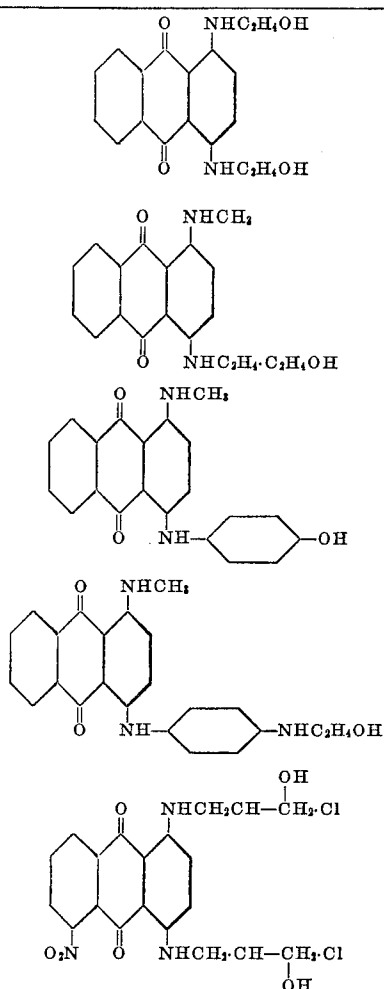
AZO SERIES

| | |
|--|--------------------------------------|
| | C.I. 11070. |
| | C.I. 11080, C.I. Disperse Orange 1. |
| | C.I. 11118, C.I. Disperse Red 2. |
| | C.I. 11130, C.I. Disperse Red 19. |
| | C.I. 11195, C.I. Disperse Violet 13. |
| | C.I. 11210, C.I. Disperse Red 17. |
| | C.I. 11215, C.I. Disperse Red 5. |
| | C.I. 11240, C.I. Disperse Orange 7. |
| | C.I. 11250, C.I. Disperse Red 31. |

ANTHRAQUINONE SERIES

| | |
|--|---|
| | C.I. 60505, Duranol Red GN (I.C.I., England). |
| | C.I. 61500, Celliton Fast Blue B (B.A.S.F., Germany). |
| | C.I. 61505, Celliton Fast Blue FFR (B.A.S.F., Germany). |
| | C.I. 61515, Duranol Blue 2G (I.C.I., England). |

ANTHRAQUINONE SERIES



C.I. 61545, Celliton Fast Blue BF (B.A.S.F., Germany).

C.I. 61510, C.I. Disperse Blue 34.

C.I. 61535.

C.I. 61540.

C.I. 62505.

As can be seen from the above examples, as well as from the previous illustrations of the disperse dyestuffs capable of forming metal chelate compounds, application of the process of the present invention involves the use of not only the disperse dyestuffs which contain in the molecule at least two radicals each with an unshared pair of electrons, but also of the materials as ground colors containing said radicals at the portions where said dyestuff can form metal chelate compounds. Normally, at least two of these radicals are preferred to be in an ortho position with each other.

The amount of the metal compounds added to the resist printing paste varies with the volumes and types of disperse dyestuffs which contain in the molecule at least two radicals each with an unshared pair of electrons and is capable of forming metal chelate compounds. For full development of the resist printing effect, however, said metal compounds should be used in sufficient amounts to obtain complete chelation of the aforesaid dyestuffs applied at least to the printed sections. To give the tone-in-tone effect, however, the amount of said metal compounds may, of course, be more or less than required in said complete chelation.

In the process of the present invention, it is also possible to add to the resist printing paste not only at least one kind of disperse dyestuffs which do not form chelates with said metal compounds, but also at least one kind of direct dyestuffs forming chelates with said metal compounds. This method may be profitably used in dyeing hydrophobic fibers without substantial affinity to the dis-

perse dyestuffs, for example, synthetic polyester fibers mixed with artificial fibers of cellulosic base.

To illustrate an example, illuminated resist printing of mixed fibers can be carried out so as to develop different colors between the resist printing sections and other sections when printing is made by the aforementioned resist printing paste containing said metal compounds and at least one kind of disperse dyestuffs not forming chelates with said metal compounds, and direct dyestuffs, preferably those capable of forming chelates with said metal compounds, and also at least one kind of a weak oxidant known as resist printing agents for vat dyestuffs, and thereafter over printing is applied with the color paste containing chelate forming disperse dyestuffs and vat dyestuffs. In this case dry or wet heat treatment and subsequent color treatment (reduction—steaming—oxidation) of the vat dyestuffs are conducted in accordance with the conventional method.

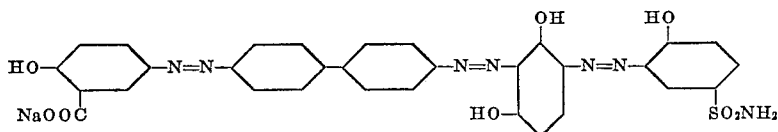
In the foregoing process the direct dyestuff forms chelates with the metal compound and is protected from being destroyed by the presence of a weak oxidant during the color development of the vat dyestuff, and is also fixed on the cellulosic fiber with greater fastness.

For said vat dyestuffs and weak oxidants may be used the known types, for example, Indanthrene golden orange G (B.A.S.F., Germany), Indanthrene printing red violet RH (Hoechst, Germany) and Indanthrene blue RSN (B.A.S.F., Germany), etc., as the former and Na salt of m-nitrobenzene sulfone acid, Na salt o- or p-nitro-

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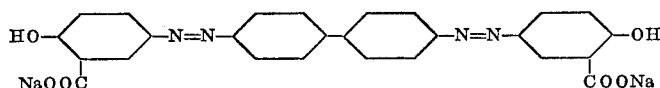
toluol sulfonic acid, Ca or Zn salt of m-nitrobenzene sulfonic acid, etc. as the latter.

Also, for improvement of fastness the aforesaid direct dyestuffs are desired to contain in the molecule at least two radicals each with an unshared pair of electrons ($-\text{N}=\text{N}$, $-\text{OH}$, $-\text{COOH}$, $>\text{C}=\text{O}$, $-\text{NH}_2$) ortho positioned in or the relation to each others and capable of forming chelates with metal compounds. Following are some examples of these direct dyestuffs.



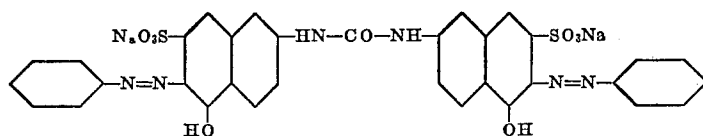
C.I. 30150

Coprantine Brown 5RLL (Ciba, Switzerland)



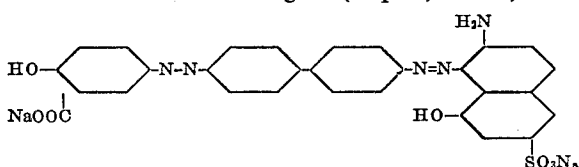
C.I. 22250

Chrysamine G (Ciba, Switzerland)



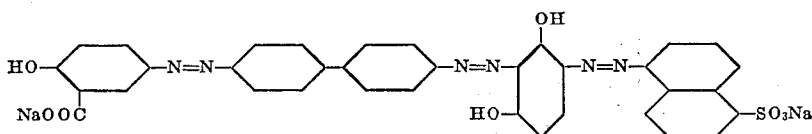
C.I. 29150

Pontamine Fast Orange S (Dupont, U.S.A.)



C.I. 22310

Diphenyl Fast Red B conc. (Geigy, Switzerland)



C. I. 30155

Pontamine Brown CR conc. 150% (Dupont, U.S.A.)

The above examples are just for illustration. Furthermore, according to the process of the present invention, the direct dyestuffs and vat colors may be replaced by other known dyestuffs suitable for the dyeing of fibers of animal or plant source in accordance with the kinds of natural fibers of said source and/or artificial fibers when they are spun into mixed fibers.

The process of the present invention also permits azoic dyeing. In this case the disperse dyestuff which contains at least one $-\text{NH}_2$ radical and is capable of forming

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metal chelate compounds is used as a diazo component. This azoic dyeing comprises printing the paste containing one or more kinds of chelate forming metal compounds on fabric consisting of hydrophobic fibers and carrying out uniform application of azoic dyestuffs (consisting of diazo component and coupling component) by padding, color brushing, cover printing or spray printing in accordance with the conventional method. For this purpose the diazo component should be capable of forming chelates

with metal compounds. After application, said dyestuff undergoes dry or wet heating, and diazotization at ele-

30 vated temperatures to combine the diazotized products with the coupling component.

In this case the coupling component may also be of such type as forming metal chelate compounds. The aforesaid dry or wet heating may be carried out after the dyestuff has been applied on the fiber and the aforementioned resist printing paste has been printed thereon. Diazotization and coupling are conducted at temperatures of about 70-120° C. using acids and nitrites pursuant to the conventional practice so as to obtain formation of insoluble azoic pigments within the fibers.

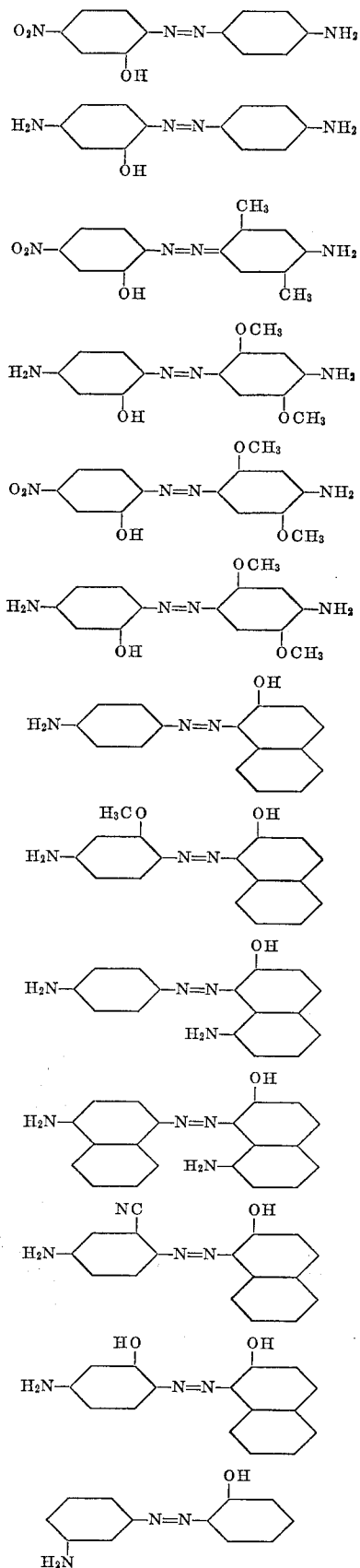
In the portions of the fiber where the paste containing metal compounds has been printed, the diazo component

65 capable of forming chelates with metal compounds or said component and the coupling component considerably decrease in affinity to the fiber due to chelation and do not fix to the object of dyeing even by heat treatment. This tendency becomes more prominent, as the fiber has more compact construction.

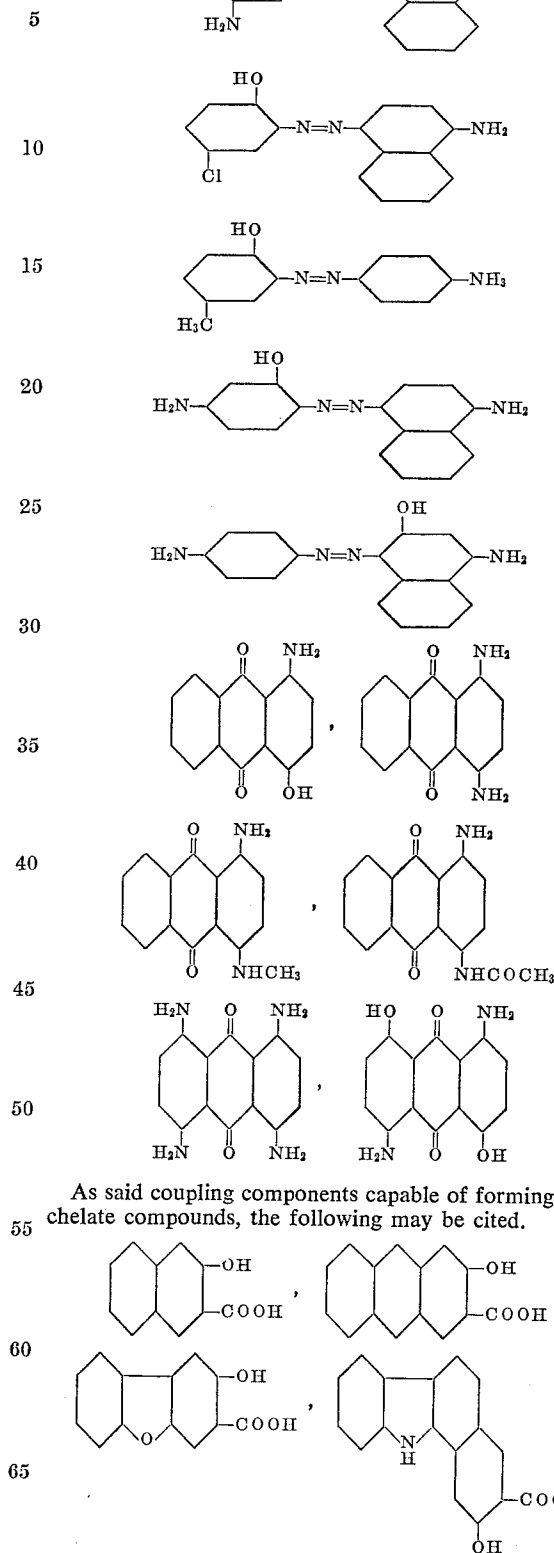
On the other hand, the non-printing sections present good color development due to heat treatment and diazotization. Thus the effect of resist printing is obtained with different color between the portions printed with the paste and those not printed therewith.

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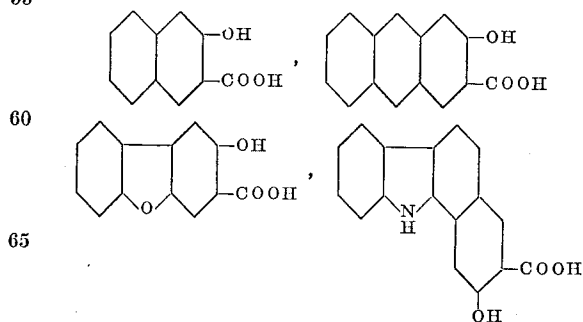
The dyestuffs which contain at least one —NH_2 radical and are capable of forming chelates with metal compounds are all suitable for use as diazo component. For reference, some examples are shown below.



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As said coupling components capable of forming metal chelate compounds, the following may be cited.



Obviously, the process of the present invention permits for the purpose of accelerating reaction between metals and dyestuffs the use of alkaline or acid compounds or materials developing the physical effect of resist printing, for example, water repellents such as paraffin emulsion, active carbon, clay, oil etc.

Where the hydrophobic fibers are spun or woven with other types of fiber, concurrent use of resist printing agents for such other types will bring about more effective resist printing.

Any kind of paste material may be available for use in the process of the present invention if it is inactive to the metal compounds involved. For instance, it is advisable to avoid pastes such as sodium alginate, and C.M.C., C.M.S. containing the radicals of $-\text{COOH}$ and $-\text{COONa}$. However, if the alginate is converted into an alkyl ester, for example, with propylene glycol it may serve the purpose well.

The pastes used in the process of the present invention may include starches such as wheat flour, rice flour, corn flour, and rice bran; natural rubber material such as gum tragacanth, gum arabic, gum Senegal and gum locust bean; roasted starch such as dextrin and British gum; processed natural rubbers such as nafka crystal rubber, and industry rubber; and other synthetic thickening agents such as polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, urethane rubber, and butadiene rubber.

As above described, the process of the present invention develops the effect of resist printing, because dyestuffs form chelates with metal compounds. Due to high reactivity and consequent high resisting power, it has become possible to obtain a printed fabric with sharp outlines.

The process of the present invention does not primarily rely on the physical resist printing method and makes it completely unnecessary to use such resist printing paste in thick layers. Consequently the process of the present invention is also applicable on the roller printing machine. Again where said process is used, in the screen printing, it does not cause any such trouble as the clogging of the mesh opening.

Formation of chelates occurs so selectively that the metal compounds exercise no effect on the non-chelate forming dyestuffs, whereas said compounds react very vigorously with the chelate forming dyestuffs. Consequently it has become possible to perform white resist printing and illuminated resist printing quite freely if proper dyestuffs are selected.

The stability of products of chelation between the dyestuff and metal compound is considerably affected by the pH. When the pH is reduced the bonding of the metal ion with the dyestuff is disturbed by increased concentration of the hydrogen ion, thus resulting in dissociation of the chelate combination. It is therefore inadvisable to practise the resist printing of the present invention in too low pH conditions; it is generally preferable to use a pH level of about 5 or more. It has also been discovered that utilization of this fact enables washing after color development to be carried out effectively. In other words, it has been disclosed that if washing is made while the pH still remains at a low level after color development it will promote dissociation of insoluble chelate compounds where the paste of metal salt is printed and make said compounds readily removable.

Utilization of the foregoing fact also permits the use of the following resist printing method; it comprises applying metal salts, dyestuffs and acids to the fabric, and, upon drying, printing alkaline paste materials, and thereafter conducting color developing treatment. As a result, color development at the paste printed sections is weakened due to formation of chelate compounds, while in the portions bearing only said metal salts, dyestuffs and acids, formations of chelate compounds is interrupted by said acids. Thus effective resist printing has been made possible.

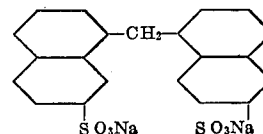
The same effect of the foregoing process may be attained by first printing the alkaline paste and then treating with the dyeing liquid containing the aforementioned acids and metal salts. Any kinds and volumes of acids and alkalis may be used satisfactorily if they have no harmful effect on the fabric. It will be sufficient to reduce the pH of acids only to the extent that formation of the che-

late compounds is interrupted. It will also be sufficient to use alkalis in amounts required only to contract the harmful effect of reductions in the pH value caused by said acids. Of course, the amounts of acids and alkalis vary with the types of their combinations. The acids may include weak acids such as the organic acids of acetic acid (including glacial acetic acid) and formic acid, etc. The alkalis may include, for example, caustic soda, caustic potash, sodium carbonate and sodium bicarbonate.

The process of the present invention will be more clearly understood with reference to the examples which follow. It should be noted, however, that these examples are intended just for illustration. The process of the present invention can be modified without departure from the primary objective of the claims contained hereinafter. As used in the example, the term "parts" represents parts by weight.

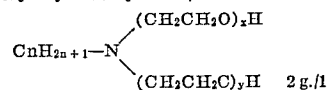
Example 1

A resist printing paste consisting of 5 parts of cupric acetate and 95 parts of Yuzen thickening agent (consisting of 20 parts of glutinous rice flour, 20 parts of non glutinous rice flour, 5 parts of sodium chloride and 75 parts of water) and water was printed on a piece of fabric of polyester synthetic fiber. When the printed fabric was dried, dispersion liquid was uniformly padded which consisted of 4% of 1,4-dihydroxyethylamino-5,8-dihydroxyanthraquinone and 0.5% of dispersant Disper TL, sodium dinaphthyl methane disulfonic acid type of



(Meisei Chemical Industry Co., Japan). Upon drying, the mass was steam heated in the star steamer at a temperature of about 120°C . for 30 min. Thereafter, washing was conducted in an aqueous solution containing 1% of acetic acid at a temperature of 80°C . for 20 min. Then the treatment of reduction washing was conducted in a solution of the following composition at a temperature of 80°C . for 20 min.

| | |
|---|--------|
| Hydrosulfite | 2 g./l |
| NaOH (35%) | 2 g./l |
| Amirajin (Daiichi Kogyo Seiyaku Co., Japan) (polyoxyethylene alkylamine) | |



Bath ratio 1:100

Afterwards, water washing and drying were conducted for finishing. As a result a white resist print with sharp outlines was obtained on a blue ground. When 5 parts of 4'-nitro-4-N-ethyl-N-hydroxyethylamino-1,1'-azobenzene were dispersed into the aforesaid resist printing paste a red pattern of illuminated resist print was obtained on a blue ground. Also when the cupric acetate contained in said resist printing paste was replaced by copper formate, copper sulfate and copper benzoate a white resist print and an illuminated resist print were similarly obtained.

Example 2

The following metal salts were added to the resist printing paste as resist agent. Resist printing was carried out by exactly the same process of Example 1. As a result, the following effects of resist printing were obtained depending on the kinds of metal salts used.

Metal Salt:

| | Effect of resist printing |
|-------------------------|---------------------------|
| Cupric acetate ----- | Excellent. |
| Cuprous chloride ----- | Very good. |
| Cupric chloride ----- | Rather good. |
| Chromium chloride ----- | Good. |
| Nickel formate ----- | Do. |
| Cobalt chloride ----- | Do. |
| Aluminium sulfate ----- | Do. |

All the metal salts tested were shown to have resist printing effect. Copper salts in particular were found to be excellent.

Example 3

A dispersion liquid consisting of 4% of 1-amino-2-methoxy-4-hydroxy-anthraquinone and 0.5% of the dispersant Disper TL (Meisei Chemical Industry Co., Japan) was uniformly padded on a fabric of polyester synthetic fiber. Upon drying, a resist printing paste of the following composition was printed thereon.

| | Parts |
|--|-------|
| Cupric formate ----- | 5 |
| Wheat starch, gum tragacanth and water ----- | 95 |

Again upon drying, the mass was steam heated in the star steamer at a temperature of about 120° C. for about 30 min. Washing was made in a solution containing 1% acetic acid at a temperature of 60° C. for 10 min. Then reduction, water washing and drying were performed for finishing in the same way as in Example 1. As a result, a good white resist print was obtained on a bright red ground.

When heat treatment was performed by the thermosol process at a temperature of 200° C. for 60 sec. instead of the aforesaid steaming method a similar print was also obtained.

When 5 parts of the fluorescent dyestuff Uvitex ER (Ciba, Switzerland) were added to the above resist printing paste the resist printed sections were far more whitened. Again when 5 parts of 1,4-dimethylamino anthraquinone were dispersed into said resist printing paste a blue pattern of illuminated resist print was obtained on a red ground.

Example 4

A resist print paste consisting of 5 parts of cupric sulfate and 95 parts of British gum and water was printed on a piece of 100% acetate fabric. Upon drying, a dispersion liquid consisting of 5% of 1,4,5,8-tetramino anthraquinone and 0.5% of the dispersant Disper TL (Meisei Chemical Industry Co., Japan) was uniformly padded. Again upon drying, the mass was steam heated in the Star Steamer at a temperature of about 100–105° C. for 30 min. Then a series of treating steps—water washing, soaping, water washing and drying—was taken for finishing. As a result, a white resist print with sharp outlines was obtained on a blue ground.

When 5 parts of 4-nitro-3'-p'-dichloro-4'-hydroxy-1,1'-azobenzene were dispersed into the aforesaid resist print paste a yellow pattern of illuminated resist print was obtained on blue ground.

Example 5

A piece of 100% nylon fabric was used as the object of dyeing. Good white and illuminated resist prints were obtained by the same process of Example 4.

Example 6

A piece of fabric consisting entirely of synthetic fiber of acrylonitrile base was used as the object of dyeing. Good white and illuminated resist prints were obtained by the same process of Example 4.

Example 7

A resist print paste consisting of 5 parts of cupric acetate, 10 parts of glycolic acid (40%) and 85 parts of

wheat starch, gum tragacanth and water was printed on a piece of broad fabric. Upon drying a dyeing liquid of the following composition was padded.

| | Parts |
|---|-------|
| 1-amino 2-methoxy-4-hydroxy anthraquinone ----- | 5 |
| Remazol Red B (Hoechst, Germany) ----- | 3 |
| Sodium alginate and water ----- | 92 |

Upon drying, the thermosol treatment was conducted by dry heating at a temperature of 200° C. for 1 min. A series of treating steps—water washing, soaping and water washing—was taken for finishing. As a result, a good white resist print was obtained on a red ground.

Example 8

A printing paste consisting of

| | Parts |
|---------------------------------------|-------|
| Cupric acetate ----- | 5 |
| m-Nitrobenzene sodium sulfonate ----- | 7 |
| Uvitex ER (Ciba, Switzerland) ----- | 5 |
| Wheat starch and gum tragacanth ----- | 60 |
| Water ----- | 23 |

was printed by the screen printing method on a piece of broad fabric consisting of 65% of polyester synthetic fiber and 35% of cotton. Then a dyeing liquid of the following composition was padded by means of a mangle. Upon drying, the mass was steam heated in the star steamer at a temperature of 120° C. for 30 min.

| | Parts |
|---|-------|
| 1-amino-4-hydroxy anthraquinone ----- | 4 |
| Indanthrene Red FBB (B.A.S.F., Germany) ----- | 3 |
| Sodium alginate and water ----- | 93 |

Then an alkaline reduction paste of the following composition was applied all over the fabric. Immediately afterwards, the mass was steam heated in the flash ager at a temperature of 100–102° C. for 30 sec. Then a series of treating steps—oxidation, soaping and water washing—was taken for finishing.

| | Parts |
|--|-------|
| Flotex (9%) (National Starch Products, U.S.A.) ----- | 35 |
| Water ----- | 45 |
| NaOH (35%) ----- | 15 |
| Hydrosulfite ----- | 5 |

As a result, a white pattern was obtained on a red ground.

Example 9

A piece of broad fabric consisting of 35% of cotton and 65% of polyester synthetic fiber was used as the object of dyeing. The cotton component alone was subjected to ground dyeing beforehand with the direct dyestuff Durazol Blue 2R (I.C.I., England). A dyeing liquid of the following composition was padded on said fabric, followed by drying.

| | Parts |
|--|-------|
| Resoline Blue FBL (Bayer, Germany) ----- | 4 |
| Sodium alginate and water ----- | 96 |

Next a resist printing paste consisting of

| | Parts |
|---------------------------------------|-------|
| Cuprous chloride ----- | 5 |
| Hydrosulfite ----- | 5 |
| Wheat starch and gum tragacanth ----- | 50 |
| Water ----- | 40 |

was roller printed. Upon drying, the mass was steam heated in the star steamer at a temperature of 120° C. for 30 min. Then a series of treating steps—water washing, soaping and water washing—was taken for finishing.

As a result, the direct dyestuff on the cotton was discharged by the action of reduction and the disperse dyestuff in the polyester synthetic fiber was resisted by chelation, thus resulting in a white patterns on a blue ground.

Example 10

A resist printing paste consisting of

| | Parts |
|---|-------|
| Cupric acetate | 5 |
| O-nitrotoluol sodium sulfonate | 10 |
| 1-methylamino-4-hydroxyethylamino anthraquinone | 5 |
| Coprantine Blue 4GLL | 5 |
| Yuzen thickening agent and water | 75 |

was printed by the screen printing method on a piece of broad fabric consisting of 65% of polyester synthetic fiber and 35% of cotton. Upon drying, a dyeing liquid of the following composition was padded by means of a mangle. Again upon drying, the mass was steam heated in the Star Steamer at a temperature of 120° C. for 30 min.

| | Parts |
|--|-------|
| 1,4-diamino-2-methoxy-anthraquinone | 4 |
| Indanthrene Brilliant Pink R (Cassella, Germany) | 3 |
| Sodium alginate and water | 93 |

Then an alkaline reduction paste of the following composition was applied all over the fabric by means of blotch roller. Immediately afterwards, two mass was steam heated in the flash ager at a temperature of 100–102° C. for 30 sec. Then a series of treating steps—oxidation, soaping and water washing—was taken for finishing.

| | Parts |
|--|-------|
| Flotex (9%) (National Starch Products, U.S.A.) | 35 |
| NaOH (35%) | 15 |
| Hydrosulfite | 5 |
| Water | 45 |

As a result, a blue pattern of illuminated resist print was obtained on a red ground.

Example 11

A resist printing paste consisting of 5 parts of cupric formate, 10 parts of Bantonite and 85 parts of Yuzen thickening agent and water was printed on a piece of plain weave consisting of 50% of polyester synthetic fiber and 50% of silk. Upon drying, a dyeing paste of the following composition was overprinted.

| | Parts |
|---|-------|
| 1-amino-2-methoxy-4-hydroxy anthraquinone | 5 |
| Wheat starch, gum tragacanth and water | 95 |

Then the mass was steam heated in the star steamer at a temperature of 120° C. for 30 min. Next a series of treating steps—water washing, soaping and water washing—was taken for finishing. As a result, a good white resist print was obtained on a red ground.

When 5 parts of 1,4-dimethylamino anthraquinone and 3 parts of Astrazon Blue B (Bayer, Germany, C.I. 42595) were added to the aforesaid resist printing paste a blue pattern of illuminated resist print was obtained on a red ground.

Example 12

A resist printing paste consisting of 5% of cupric acetate and 95% of water and British gum was printed on a piece of fabric of polyester synthetic fiber. Upon drying, a dyeing liquid of the following composition was padded.

| | Percent |
|---|---------|
| 4 - amino - 2,5 - dimethoxy - 2' - oxy - 4' - nitro-1,1'-azobenzene | 4 |
| 3-hydroxy-2-napthoortho-toluidide | 4 |
| Disper TL (Meisei Chemical Industry Co., Japan) | 0.5 |

Again upon drying the mass was steam heated in a high pressure steamer of 120° C. for 30 min. After water washing, reduction washing was conducted under the following conditions:

| | | |
|---|-----|------|
| NaOH (35%) | g/l | 1 |
| Hydrosulfite | g/l | 1 |
| Amirajin (Daiichi Kogyo Seiyaku Co., Japan) | g/l | 1 |
| Bath ratio | | 1:50 |
| Temperature | ° C | 80 |
| Time | min | 20 |

Next diazotization and coupling were performed under the following conditions:

| | | |
|----------------------------|----------------|---------|
| | | Percent |
| 10 Sodium nitrite | ----- (O.W.F.) | 8 |
| Concentrated sulfuric acid | ----- (O.W.F.) | 16 |
| Bath ratio | | 1:50 |
| Temperature | ----- ° C | 90 |
| Time | ----- min | 20 |

Then a series of treating steps—water washing, soaping, water washing and drying—was taken for finishing. As a result, a yellow pattern of illuminated resist print was obtained on black ground.

Example 13

A resist printing paste consisting of 5% of cupric formate and 95% of water and British gum was printed on a piece of fabric of polyester synthetic fiber. Upon drying, a dyeing liquid of the following composition was padded.

| | Percent |
|--|---------|
| 1,4-diamino-anthraquinone | 4 |
| 3-hydroxy-2-napthoic acid | 4 |
| Dispersant Disper TL (Meisei Chemical Industry Co., Japan) | 0.5 |

Again upon drying the mass was steam heated in a high pressure steamer at a temperature of 120° C. for 30 min. After water washing, reduction washing was carried out under the following conditions:

| | | |
|---|-----|------|
| NaOH (35%) | g/l | 2 |
| Hydrosulfite | g/l | 2 |
| Amirajin (Daiichi Kogyo Seiyaku Co., Japan) | g/l | 2 |
| Bath ratio | | 1:50 |
| Temperature | ° C | 80 |
| Time | min | 20 |

Next diazotization and coupling were performed under the following conditions:

| | | |
|----------------------------|----------|------|
| Sodium nitrite | (O.W.F.) | 80% |
| Concentrated sulfuric acid | (O.W.F.) | 16 |
| Bath ratio | | 1:50 |
| Temperature | ° C | 95 |
| Time | min | 30 |

Then a series of treating steps—water washing, soaping, water washing and drying—was taken for finishing. As a result a white resist print was obtained on a black ground.

Example 14

A dyeing liquid consisting of

| | Percent |
|-------------------------------------|---------|
| Cupric sulfate | 5 |
| Glacial acetic acid | 8 |
| 1,4-diamino-2-methoxy-anthraquinone | 5 |

was uniformly padded on a piece of fabric consisting of 100% polyester synthetic fiber. Upon drying, a dyeing paste of the following composition was printed.

| | Parts |
|------------------------|-------|
| NaOH (solid) | 3 |
| Wheat starch and water | 97 |

Then the mass was steam heated in the star steamer at a temperature of 120° C. for 20 min. Next a series of treating steps—water washing, reduction, water washing and drying—was taken for finishing. As a result, a good white pattern of resist print was obtained on a reddish violet ground.

Having described the specifications, we claim:

1. A process for resist printing a hydrophobic fiber comprising a polyester wherein said fiber is dyed with at least one disperse dye containing in its molecule at least two radicals, each with an unshared pair of electrons, said disperse dye being capable of forming a copper chelate compound, said process being characterized by (1) dyeing said fiber with said disperse dye; (2) printing on said dyed fiber a resist printing paste containing a copper compound capable of forming a chelate with said disperse dye; and (3) subsequently finishing the dyed fibers by aqueous washing and drying.

2. The method of claim 1 wherein the radicals containing the unshared pair of electrons are selected from the group consisting of $-\text{N}=\text{N}-$, $-\text{OH}$, $-\text{COOH}$, $>\text{C}=\text{O}$ and $-\text{NH}_2$.

3. The method of claim 1 wherein said resist printing paste contains in addition a dyestuff which does not react with said copper compound to form a copper chelate compound.

4. A process for resist printing a hydrophobic fiber comprising a polyester wherein said fiber is dyed with at least one disperse dye containing in its molecule at least two radicals, each with an unshared pair of electrons, said disperse dye being capable of forming a copper chelate compound, said process being characterized by (1) printing on said fiber a resist printing paste containing a copper compound capable of forming a chelate with said disperse

dye prior to the dyeing of said fiber with said disperse dye; (2) dyeing said printed fiber with said disperse dye; and (3) subsequently finishing the dyed fiber by aqueous washing and drying.

5. The method of claim 4 wherein the radicals containing the unshared pair of electrons are selected from the group consisting of $-\text{N}=\text{N}-$, $-\text{OH}$, $-\text{COOH}$, $>\text{C}=\text{O}$, and $-\text{NH}_2$.

6. The method of claim 4 wherein said resist printing paste contains in addition a dyestuff which does not react with said copper compound to form a copper chelate compound.

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