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PRINTING WITH ONIUM DYESTUFFS AND BUFFER MIXTURES

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This invention relates to new colouring processes and more particularly to processes for local colouration of textile materials and paper with dyestuffs which contain quaternary or ternary salt groups.

In British specifications Nos. 576,234, 576,270 and 587,636 processes are described for the manufacture of certain dyestuffs useful for the dyeing of textile materials which contain quaternary ammonium, ternary sulphonium or isothiouronium salt groups attached through methylene linkages to aromatic nuclei. Also in the specification of co-pending U. S. application S. N. 758,468, filed July 1, 1947 now issued as U. S. Patent No. 2,544,825 of March 13, 1951, a process is described for making dyestuffs of the anthraquinone series and related polycyclic ketone types, for example, dyestuffs of the acedianthranone, dibenzanthrone, isodibenzanthrone, indanthrone and perylene - tetracarboxy - di-(phenylimide) series which contain similar salt groups attached through methylene linkages to aromatic nuclei.

We have now found that dyestuffs of the above kind which we call "onium" dyestuffs are of exceptional value for application to fibrous materials, particularly textile materials and paper, by printing and other local colouration processes.

We have also found that such dyestuffs can be applied by padding processes and that when textile material or paper which has previously been printed with resists, is padded with a solution of "onium" dyestuff, the dyestuff is applied to the unresisted portions of the material or paper and valuable local colouration effects are obtained.

According to our invention therefore we provide a process for the production of coloured patterned effects on textile materials or paper which comprises applying locally to the textile material or paper dyestuffs containing quaternary ammonium, ternary sulphonium or isothiouronium salt groups.

The "onium" dyestuffs may be applied locally by spraying, or painting but the most important method of application is by printing by the hand block, screen or roller techniques.

The "onium" dyestuffs can be printed alongside other types of dyestuffs used for printing and this forms a further feature of our invention.

The "onium" dyestuffs may be applied in aqueous solution or in a printing paste in the presence of a weakly acidic substance and then the textile material or paper treated with an alkaline substance before, during or after the application of the dyestuff.

The "onium" dyestuffs are however preferably

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applied in the form of an aqueous solution or printing paste in the presence of a mixture of a weak acid or acid salt and an alkaline salt of a weak acid which on steaming or heating changes from a weakly acid to a weakly alkaline state, which change facilitates the fixation of the dyestuffs on the textile or paper.

As suitable weak acids there may be mentioned for example, formic, acetic, mono-, di- and trichloroacetic, diglycollic, citric, lactic, tartaric, maleic and oxalic acids, and as a suitable acid salt there may be mentioned sodium dihydrogen phosphate.

As suitable alkaline salts of weak acids there may be mentioned sodium salts of acetic, boric and trichloroacetic acids, trisodium phosphate and disodium hydrogen phosphate.

The choice of particular acids or salts will be determined by the conditions to be used in the printing processes. Thus for example when the "onium" dyestuff is to be printed alongside a vat dyestuff it is preferred to use a non-volatile acid, for example lactic acid, in order to avoid reducing the printing strength of the vat dyestuff.

The "onium" dyestuffs are exceptionally valuable for use in printing processes since by their use it is possible to obtain the high fastness properties of the vat and azoic dyestuffs with much simpler methods of operation than those required for printing with vat and azoic dyestuffs. Furthermore it is possible by the use of the "onium" dyestuffs to supplement existing ranges of printing dyestuffs and to fill in the fastness and shade gaps in the existing ranges of dyestuffs used for printing, notably the vat and azoic ranges. The blue and green shades obtainable from "onium" dyestuffs derived from phthalocyanines are of particular interest for these purposes.

The "onium" dyestuffs may be mixed with one another in the same solution or printing paste and they may be mixed with suitable dyestuffs of other types. For example, attractive green shades can be obtained by mixing a blue "onium" dyestuff with a yellow dyestuff of a different range, for example a yellow water soluble, or dispersed, cellulose acetate silk dyestuff.

The "onium" dyestuffs in the form of printing pastes may be printed alongside one or more printing pastes containing a vat dyestuff, a mixture of aniline and an oxidising agent suitable for yielding aniline black, a mixture of an arylamide of 2:3-hydroxynaphthoic acid and a stabilised form of a diazo compound, or a leuco sulphuric ester derivative of a vat dyestuff.

Also the "onium" dyestuff may be printed in admixture with and/or alongside a diazo compound or a stabilised form of a diazo compound on textile material which has previously been padded in an alkaline solution of an arylamide of 2:3-hydroxynaphthoic acid.

Among the other many combinations by which novel and useful effects can be obtained there may be mentioned:

(1) Padding with an alkaline solution of a 2:3-hydroxynaphthoic arylamide, printing in succession with (*a*) an "onium" dyestuff, (*b*) an acidic paste containing a stabilised diazo compound, (*c*) an acidic white resist and subsequently padding with a solution of a stabilised form of a second diazo compound, which diazo compound does not couple under acidic conditions for example Brentamine Fast Blue VB salt.

(2) Printing in succession with (*a*) an "onium" dyestuff, (*b*) a stabilised azoic combination and (*c*) a zinc oxide white resist, acid steaming, and then padding with an aniline black mixture and developing.

(3) Printing in succession with (*a*) an "onium" dyestuff, (*b*) a zinc oxide while resist, (*c*) a vat dyestuff and zinc oxide and then padding with a solution of a leuco sulphuric ester derivative of a vat dyestuff and developing.

(4) Printing with a white resist and then with one or more pastes containing a stabilised diazo compound and a wax thickening mixture, on a textile material which has previously been padded with an alkaline solution of a 2:3-hydroxynaphthoic arylamide and dried, drying and padding with an "onium" dyestuff solution.

(5) Printing with a paste containing a stabilised azoic combination and a paraffin wax emulsion, acid steaming, drying, and then padding with a solution of an "onium" dyestuff.

(6) Printing with a paste containing a vat dyestuff, a wax resist, an alkali and a reducing agent, drying and then padding with a solution of an "onium" dyestuff.

The textile materials which may be coloured locally by the process of our invention include cotton, viscose rayon, cuprammonium rayon, natural silk, acetate rayon, nylon, chlorinated wool, linen and jute.

The invention is illustrated but not limited by the following examples in which the parts are by weight.

Example 1

The printing paste is prepared as follows: A solution of

- 0.5 part of the dyestuff obtained by reacting copper tri-(chloromethyl) phthalocyanine with tetramethylthiourea and
- 5.0 parts of glacial acetic acid in
- 17.0 parts of water is added with stirring to
- 65.0 parts of a starch tragacanth thickening (made by boiling together 8.5 parts of maize starch and 3.4 parts of gum tragacanth in 88.1 parts of water).
- 12.5 parts of a solution of sodium acetate (made by dissolving 5 parts of hydrated sodium acetate in 7.5 parts of water) is then added to the thickened dyestuff paste.

100

The above printing paste is printed on cotton material. The print is dried and developed by steaming for 5 minutes at 100° C. and is then finished by rinsing in cold water, soaping at the boil for 20 minutes with 0.2% soap solution, rinsing in cold water and drying.

The print so obtained is a bright greenish-blue shade of good fastness properties.

In place of the dyestuff used in the above example there may be used any of the dyestuffs containing isothiouronium or sulphonium groups described in British specifications Nos. 576,234, 576,270 and 587,636 and in U. S. application S. N. 758,468, filed July 1, 1947, now U. S. Patent No. 2,544,825.

Example 2

A printing paste is prepared as follows: A solution of

- 0.75 part of the dyestuff obtained by reacting bis - (chloromethyl) acedianthrone with pyridine and
- 5.0 parts of glacial acetic acid in
- 12.0 parts of water, is added with stirring to
- 65.0 parts of tragacanth thickening (made by boiling together 8 parts of gum tragacanth in 92 parts of water)
- 12.5 parts of a solution of sodium acetate (made by dissolving 5 parts of hydrated sodium acetate in 7.5 parts of water) is then added to the thickened dyestuff paste.
- 4.75 parts of a solution of sodium *m*-nitrobenzene sulphonate (made by dissolving 0.1 part of sodium *m*-nitrobenzene sulphonate in 4.65 part of water) is added.

100

The above printing paste is printed on viscose rayon material. The print is dried and developed by steaming for 20 minutes at 100° C. and then finished by rinsing in cold water, soaping at 50° C. for 10 minutes with 0.2% soap solution, rinsing in cold water and drying.

The print obtained is a reddish-brown shade of good fastness properties.

Example 3

A printing paste is prepared as follows: A solution of

- 2.0 parts of the dyestuff obtained by reacting di-(chloromethyl)-4:4' - di-(6 - methylbenzthiazyl-2) azobenzene with pyridine, and
- 5.0 parts of glacial acetic acid in
- 10.5 parts of water is added with stirring to
- 65.0 parts of gum tragacanth dispersion (made by boiling 8 parts of gum tragacanth with 92 parts of water)
- 12.5 parts of a solution of sodium acetate (made by dissolving 5 parts of hydrated sodium acetate in 7.5 parts of water) is then added to the thickened dyestuff paste.
- 5.0 parts of a solution of sodium chromate solution (made by dissolving 0.2 part of hydrated sodium chromate in 4.8 parts of water) is added.

100

The above printing paste is printed on cuprammonium rayon material. The print is dried and developed by steaming for 40 minutes at 100° C. and then finished off by rinsing in water and soaping at 50° C. for 10 minutes. It is then rinsed and dried.

The print obtained is a bright yellow shade of good fastness properties.

Example 4

A printing paste is prepared as follows: A solution of

0.75 part of the dyestuff obtained by reacting copper tri-(chloromethyl) phthalocyanine with tetramethyl thiourea, and
5.0 parts of glacial acetic acid in
16.75 parts of water is added with stirring to
65.0 parts of gum tragacanth thickening (made by boiling together 8 parts of gum tragacanth with 92 parts of water)
12.5 parts of a solution of sodium acetate (made by dissolving 5 parts of hydrated sodium acetate in 7.5 parts of water) is then added to the thickened dyestuff paste.

100

The above printing paste is printed on acetate rayon material. The print is dried and developed by steaming for 20 minutes at 100° C. It is finished off by rinsing in cold water, soaping for 5 minutes at 40° C. in 0.2% soap solution and finally rinsing and drying.

The print so obtained is a bright greenish blue shade of good fastness properties.

Example 5

A printing paste (A) is prepared as follows: A solution of

1.5 parts of Solacet Fast Yellow GS in
33.5 parts of water is added with stirring to
65.0 parts of gum tragacanth thickening (made by boiling together 8 parts of gum tragacanth and 92 parts of water)

100

A printing paste (B) is prepared exactly as described in Example 4.

A printing paste is now prepared by mixing equal parts of A and B and this paste is printed on nylon textile material. The print is dried and developed by steaming for 30 minutes at 100° C. The print is then finished off by rinsing in cold water, soaping for 5 minutes at 40° C. rinsing and drying.

The print so obtained is a bright green shade of good fastness properties.

Example 6

A printing paste (A) is prepared according to the directions given in Example 1, except that the 5 parts of glacial acetic acid are replaced by 1 part of 80% lactic acid, 1 part of sodium dihydrogen phosphate and 3 parts of water.

Printing pastes B and C are prepared as follows:

	B (parts)	C (parts)
Caledon Purple 4RP 150 Paste Fine	8	
Caledon Grey 3BPS Paste		1
Thin British Gum thickening	12	19
Vat Colour thickening	80	80
Total	100	100

The thin British gum thickening is prepared by boiling 4 parts of British gum with 7.5 parts of water.

The vat colour thickening is prepared as follows:

	Parts
British gum	35.0
Water	34.4
are boiled together. The resulting thickening is cooled to 50° C. and	
Anhydrous sodium carbonate	10.0
Glycerol	7.5
Sodium formaldehyde sulphoxylate	13.1
are added and the mixture is then stirred.	
	100.0

The printing pastes A, B and C are printed successively on cotton material, dried, developed by steaming for five minutes at 100° C. oxidised in a cold solution of 0.25% potassium dichromate and 0.5% acetic acid, rinsed, soaped for 10 minutes at 100° C. in 0.2% soap solution, rinsed and finally dried.

The resulting print is a three colour patterned effect of purple, grey and bright turquoise blue shades of good fastness properties.

Example 7

A printing paste (A) is prepared according to the directions given for paste A in Example 6.

A printing paste (B) is prepared from the vat dyestuff Caledon Printing Blue RNS paste as follows:

	Parts
Caledon Printing Blue RNS paste	10
Thin British gum thickening (made as described in Example 6)	10
Vat colour thickening (made as described in Example 6)	80
	100

A printing paste (C) is prepared as follows: A dispersion of

	Parts
Brentogen Scarlet RS	6.0
In ethyl alcohol	1.5
And water	12.5
is added to	
Starch tragacanth thickening (prepared as described in Example 1)	32.5
To this thickened dispersion a mixture comprising	
β-diethylaminoethanol	12.0
Thiodiglycol	2.8
Diethyl tartrate	0.2
is added and the resulting mixture is stirred until the dyestuff dispersion is dissolved. Finally	
Starch tragacanth	32.5
is added.	
	100.0

The printing pastes A, B and C are printed successively on cotton material. The material is dried, developed by steaming for 5 minutes at 100° C. oxidised in a cold solution of 0.25% potassium dichromate and 0.5% acetic acid, rinsed, soaped for 10 minutes at 100° C. in 0.2% soap solution, rinsed and dried.

The resulting print is a three colour patterned effect of scarlet, royal blue and bright turquoise blue shades of good fastness properties.

We claim:

1. A process for the production of colored patterned effects on absorptive fibrous materials by local application of a dyestuff containing a water-solubilizing group selected from the class consisting of quaternary ammonium, tertiary

sulfonium and isothiouronium salt groups, which comprises applying said dyestuff locally to said material in the presence of a buffered composition comprising a mixture of a member selected from the group consisting of weak acids and acid salts and an alkaline salt of a weak acid, which composition on heating changes from a weakly acid to a weakly alkaline state, and thereafter heating said material to convert said composition to its alkaline state and fix said dyestuff.

2. The process of claim 1, wherein said buffered composition comprises a mixture of acetic acid and sodium acetate.

3. The process of claim 1, wherein the fibrous material is a textile material and the dyestuff is applied by printing.

4. The process of claim 1, wherein the water-solubilizing group of said dyestuff is an isothiouronium salt group.

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