

PATENT SPECIFICATION

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(54) PROCESS FOR PRODUCING RESIST EFFECTS BY MEANS OF REACTIVE DYESTUFFS

(71) We, **FARBWERKE HOECHST AKTIENGESELLSCHAFT**, vormals Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides a process for producing resist effects by means of reactive dyestuffs under other reactive dyestuffs or obtained from mixtures of reactive dyestuffs having different fixation properties.

It is known that the application of commercial reactive dyestuffs, requires varying conditions because of the different affinity of the reactive atoms or groups present in the molecule for the hydroxy groups of the cellulose fibre. As is disclosed in Specification No. 1,045,268 however, special advantage of this difference in reactivity can be taken in order to produce multi-colour effects on textile fabrics containing cellulose, for example on mercerized cotton or viscose rayon, by producing over-lapping colour resists while applying several distinct types of reactive dyestuffs, provided that the dyestuffs used have sufficiently differing reaction speeds.

According to this process, the dyestuffs used for producing the printing resists contain a dichlorotriazine group or a quaternated chlorotriazine group as reactive component and are distinguished by their high reactive power with regard to cellulose fibres.

For preparing the ground, dyestuffs having a chloraminotriazine, dichloropyrimidine, trichloro-pyrimidine or sulphatoethyl-sulphonamide group may be used, which in comparison with the above mentioned dyestuffs have considerably less reactivity with cellulose fibres.

According to this well-known process, two methods for carrying out resist printings are available: (i) a printing paste containing the more reactive dyestuff in a neutral medium is printed on a textile fabric, the printed material, optionally after intermediate drying, is slop-padded or cover-printed using a padding liquor or second printing paste containing a dyestuff of less reactivity and an alkaline agent, and the fabric is then dried, steam-treated and finished, or (ii) the fabric is first treated with a dyestuff solution containing a dyestuff of less reactivity and an alkaline agent, dried, cover-printed with a neutral printing paste containing the more reactive dyestuff, dried, steamed and finished.

By steaming the material thus treated, the more reactive dyestuff is first fixed on the over-lapping parts whereby the alkaline agent contained in the paste or the padding liquor of the less reactive dyestuff is consumed, whereas the less reactive dyestuff cannot be fixed on said parts since it has lost its fixing agent.

It is also seen from the same specification that under certain circumstances a predetermined concentration of 1 - (2',4' - dichloro - s - triazin - 6' - yl amino) - naphthalene - 5 - sulphonic acid is added to the resist printing paste. This colourless compound is capable of reacting with the fibre with consumption of alkali, thus increasing the reactivity of the resist printing paste and blocking those parts on the substrate which are not taken by the more reactive dyestuff and keeping off the less reactive dyestuff from the fibre at said parts.

The methods for producing resist effects disclosed in the above mentioned specification however have certain disadvantages which considerably limit exact reproduction

in industrial practice. For example, the amount of alkali necessary for completely fixing the more reactive dyestuffs is kept very low in order to achieve a clean looking colour resist. The consequences are fluctuating dyestuff yields and the impossibility of fixing over-lapping reactive dyestuffs. Also, it had not been noticed in either of the above known processes that in spite of the high reaction speed of dyestuffs having an increased affinity, certain amounts of the cover dyestuff having a lower fixing speed may be fixed simultaneously with the bottom print resist, which may result in less clear resists. Further, the bottom dyeings obtained according to the second method cannot be stored for long periods, because under these conditions the less reactive dyestuff is prefixed and the cover print resists become more or less dull. For the same reason also the intermediate drying has to be carried out very carefully.

This invention is based on the observation that resist effects by means of reactive dyestuffs under other reactive dyestuffs can be produced on flat-surface textile structures made from natural or regenerated cellulose fibrous materials, by printing on the textile material in any order a printing paste containing a non-volatile organic or inorganic acid or acid salt as a reserving agent said reserving agent containing no fibre-reactive grouping and a reactive dyestuff which can be fixed by the two-phase pad-batch process or in a two-phase rapid-fixing process, and applying in over-lapping manner a further printing paste or padding liquor containing an alkali as fixing agent and another reactive dyestuff which cannot be fixed by the aforementioned fixing processes or which gives only low yields, and finally, after drying the material thus treated, fixing the dyestuffs by steam-treatment in combination with one of the aforementioned two-phase fixing processes.

The process of the invention utilizes the different fixation properties of the dyestuffs used as resists for producing resist effects, as well as for cover-printing. It is of no importance whether the resist printing paste containing the dyestuff and acid is bottom-printed and then either in a wet process or after intermediate drying a further printing paste or thickened dyestuff solution containing the less reactive dyestuff and the alkaline agent is topped or slop-padded, or whether these two steps are carried out in reverse order. Particularly fair and brilliant effects prints having sharp outlines are obtained by printing the bottom-print resist in the form of a water-in-oil emulsion and the top one in the form of an oil-in-water emulsion.

The fixing of the prints obtained according to the process of the invention is carried out after drying the material in a first step by a steaming process for 2 to 15 minutes at temperatures between 98 and 180°C depending on the textile material used. In this process, the less reactive dyestuff is fixed on those parts of the substrate where there is no over-lapping of the bottom- or cover-print by the more reactive dyestuff. At the over-lapping parts the alkali necessary for fixing the less reactive dyestuff is consumed, so that this dyestuff cannot be fixed. In the following step the more reactive dyestuff is fixed on the colour resist by means of a two-phase cold-dwelling or a two-phase rapid fixing process, for example the two-phase steaming or the flash-steaming method or also the infra-red process. No accumulation of either dyestuff takes place on the material since the less reactive dyestuff is not fixed by the above mentioned two-phase fixing processes or only in hardly perceptible amounts. The less reactive dyestuffs having fair shades may also be fixed by means of thermofixation, for example hot-air treatment.

When a white effect is wanted instead of a colour resist, a resist printing paste having no dyestuff content is used, i.e. printing is carried out only by means of the acid reserving agent.

Furthermore, according to a modification of the process of the invention, brilliant coloured resist effects can be produced by cover-printing or bottom-printing with printing pastes containing non-volatile inorganic or organic acids or acid salts in a wet process or after intermediate drying and then applying bottom-printing pastes or under cover-printing pastes which consist of mixtures of reactive dyestuffs of different fixation properties as defined above, and additionally contain an alkaline substance as fixing agent. In this process, the different fixation properties of the reactive dyestuffs are used so that at selected parts fixing of the less reactive dyestuff contained in mixtures of dyestuffs of both degrees of reactivity is prevented by bottom- or cover-printing of acid agents which may be mixed with a reactive dyestuff. The great advantage of this modified process is that in order to obtain an unlimited number of resist effects, only one printing roller is necessary and thus the operation is carried out in a single-step process. Such effects are very interesting especially for the so-called "Java-print" process which actually is still highly expensive as to costs as well as labour.

Reactive dyestuffs suitable for producing resist effects according to the invention

are for example, those of the various organic dyestuff classes which contain at least one substituent capable of reacting with the cellulose fibre, especially dyestuffs of the anthraquinone, azo and phthalocyanine series; those of the azo and phthalocyanine series may contain metal or may be free from metal. Reactive groups in those dyestuffs which can be fixed on the cellulose fibre by means of the two-phase pad-batch or a two-phase rapid-fixing process are, for example the β -sulphato-ethyl-sulphone and the N-alkyl-ethionylamino radicals. The reactive dyestuffs which cannot be fixed by one of the said two-phase fixing processes preferably consist of compounds having β -dialkylamino-ethylsulphone or β -dialkylamino-ethylsulphonyl-N-alkylamino groups as the group having affinity for the fibre. Of course, the process of the invention is also suitable for dyestuffs containing reactive systems other than the aforementioned ones, insofar as they are chosen in accordance with the corresponding requirements of a slow or fast rate of fixation. The amount of the dyestuffs to be used in the corresponding printing pastes or padding liquors depends on the tinctorial strength desired.

As non-volatile organic or inorganic acids or acid salts to be used according to the invention in the resist printing pastes, optionally together with the highly reactive dyestuff, tartaric acid, citric acid or primary alkali metal phosphates may for example be mentioned. The amount of the reserving agent in the resist printing paste depends on the engraving depth of the rollers in the roller-printing process or on the permeability of the screen gauze in the screen-printing process, as well as on the nature and amount of the alkali fixing agent in the dyestuff mixtures.

Alkaline substances to be used as fixing agents according to the invention are, for example alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, tertiary sodium phosphates as well as alkali metal silicates (water glass). The amount of alkali in the fixing baths used in the two-phase rapid-fixing or the two-phase pad-batch processes must be adjusted to the amount of acid in the resist printing paste. By varying the amount of alkali interesting bleeding effects, desired by manufacturers of special goods for Africa, can be obtained.

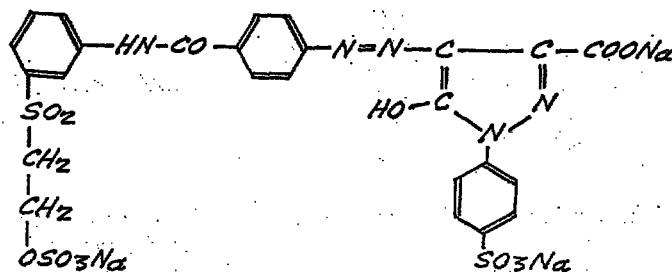
The printing pastes to be used according to the invention may be prepared in aqueous medium as oil-in-water emulsions or as water-in-oil emulsions. They may further contain the auxiliary agents normally used in the application of reactive dyestuffs, for example urea, wetting agents, weak oxidation agents, for example the sodium salt of *m*-nitrobenzene sulphonic acid, thickening agents, for example sodium alginate, the ether of locust bean flour or cellulose derivatives.

The new process for producing resist effects has the advantage of a very simple procedure and good reproducibility; a very great variety of shades as well as special multi-colour effects can also be produced. The prints obtained are distinguished by their excellent fastness properties as is usual with reactive dyestuffs. The colour yields and brightness of the resist colours are excellent.

The following Examples illustrate the invention: the parts and percentages being by weight unless otherwise stated.

EXAMPLE 1

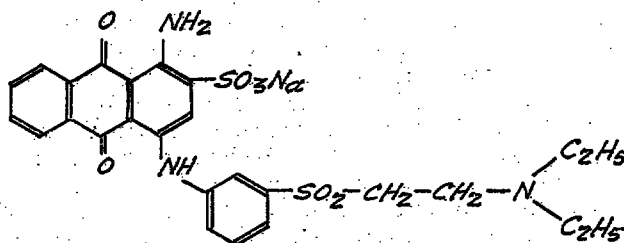
50 Parts of the reactive dyestuff of the formula



are dissolved in 250 parts of water having a temperature of 95°C and stirred into 500 parts of a 6% aqueous thickener of hydroxyethylcellulose. Subsequently, 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 100 parts of a 50% aqueous solution of tartaric acid are added, and the paste is made up to 1000 parts by adding 90 parts of water.

The resist printing paste so obtained is roller-printed on a mercerized cotton fabric by means of an engraved printing roller. In the same operation this bottom-print resist is squeezed in a wet process by means of a printing roller having no engravings, and while still wet is cover-printed by means of an engraved padding roller with a further printing paste prepared as follows:

40 Parts of a reactive dyestuff of the formula



are dissolved in a mixture of 250 parts of water and 15 parts of anhydrous sodium carbonate. This solution is stirred into 350 parts of a 10% aqueous alginate thickener having a low viscosity, and 10 parts of sodium of *m*-nitrobenzene sulphonic acid are added. The paste is made up to 1000 parts by adding 335 parts of water.

After printing and drying, the material is steamed for 5 minutes at 102°C in a rapid-steamer and subsequently padded on a two-roller pad with an alkaline fixing liquor containing electrolytes, which is prepared in the following way:

180 Parts of anhydrous sodium sulphate, 150 parts of anhydrous sodium carbonate and 50 parts of potassium carbonate are dissolved in 600 parts of water. Subsequently, 100 parts by volume of sodium hydroxide solution of 38° Bé are added. This solution is made up to 1000 parts by volume by adding water.

The material thus treated is now allowed to remain for 3 hours at room temperature in order to fix the dyestuff.

The printed material is then rinsed, as is usual in two-phase printing, first for 10 minutes with cold water (until the bath has a neutral reaction), treated for 3 minutes by means of hot water containing 3 parts per 100 parts by volume of a complex-forming agent based on a polymeric sodium phosphate, subsequently soaped for 10 minutes by means of a 1% aqueous solution of a synthetic detergent (sodium salt of the condensation product of oleic acid and N-methyltaurine), then rinsed and dried.

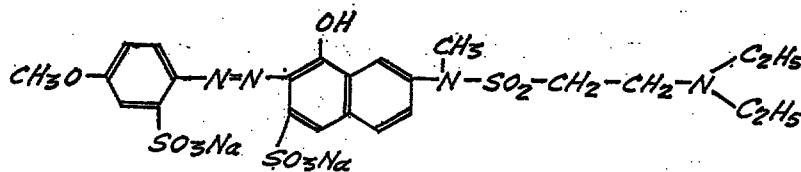
Brilliant yellow resists under a blue ground are obtained.

EXAMPLE 2

A resist printing paste as described in Example 1, paragraph 1, is printed on a spun rayon fabric.

After printing and drying, the printed material is padded on a two-roller foulard with a thickened dyestuff solution prepared as follows:

40 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 250 parts of water and 15 parts of anhydrous sodium carbonate. 100 Parts of a 10% aqueous alginate thickener having a low viscosity and 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid are added and the paste is made up to 1000 parts by adding 585 parts of water.

After drying, the material is steamed for 10 minutes at 120°C and then padded in a two-phase fixing unit with the following fixing solution:

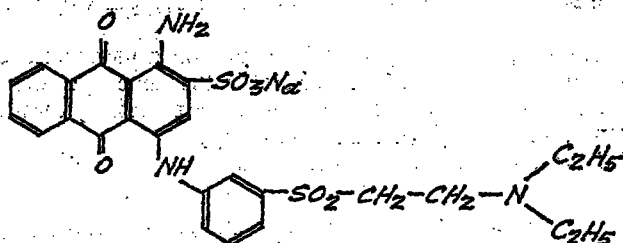
150 Parts of sodium chloride, 150 parts of anhydrous sodium carbonate and 50 parts of potassium carbonate are dissolved in 600 parts of water and after adding 40 parts by volume of sodium hydroxide solution of 38° Bé, the solution is made up to 1000 parts by volume by adding water.

Subsequently the print is steamed for 25 seconds at 110°C and then treated and finished as is usual in two-phase printing.

Brilliant yellow reserves under a red colouration are obtained.

EXAMPLE 3

30 Parts of the reactive dyestuff of the formula

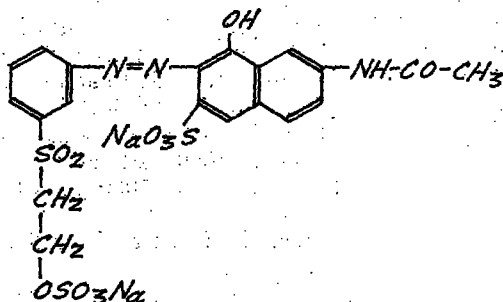


are dissolved in a mixture of 250 parts of water and 12 parts of anhydrous sodium carbonate. This solution is thickened with 100 parts of a 10% aqueous alginate thickener. Subsequently, 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid are added and the paste is made up to 1000 parts by adding 598 parts of water.

This dyestuff solution is padded onto a viscose-rayon fabric by means of a two-roller foulard and the material is dried by means of a hot-flue at 60°C.

After having been dried the fabric is printed with a resist printing paste prepared as follows:

40 Parts of the reactive dyestuff of the formula



are dissolved in 250 parts of water having a temperature of 95°C and stirred into 400 parts of a 5% aqueous thickener of hydroxyethylcellulose. 10 Parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 150 parts of a 33½% aqueous solution of primary sodium phosphate are added, and the paste is made up to 1000 parts by adding 150 parts of water.

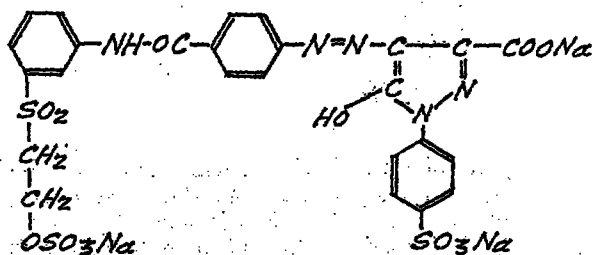
After drying, the material is steamed at 180°C, padded on a foulard with a fixing solution as described in Example 1, and allowed to remain for 5 minutes in a storehouse at room temperature. Finally, the goods thus treated are washed and finished as is usual in two-phase printing.

An orange resist effect under a blue colouration is obtained.

EXAMPLE 4

50 Parts of diglycerol-sesqui-oleate are mixed with 100 parts of heavy gasoline having a boiling range of from 160° to 200°C, and emulsified with 850 parts of a printing paste of following composition by means of a high-speed stirrer (about 1200 to 2000 rpm).

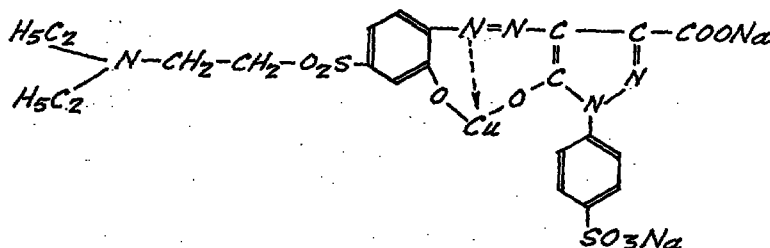
50 Parts of the reactive dyestuff of the formula



are dissolved in 250 parts of water having a temperature of 95°C and stirred into 350 parts of a 5% aqueous thickener of hydroxyethylcellulose. 100 Parts of a 50% aqueous solution of citric acid and 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid are added and the paste is made up to 850 parts by adding 90 parts of water.

The resist printing paste so obtained is printed on a mercerized cotton fabric in a roller-printing process with a patterned roller. In the same operation, a cover-printing paste is printed on this bottom-print resist in a wet process by means of a patterned roller. This cover-printing paste is prepared as follows:

40 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 250 parts of water and 15 parts of sodium bicarbonate. This solution is introduced into 500 parts of an emulsion thickener which contains per 1000 parts a composition as follows:

10 Parts of the esterified product prepared from stearic acid and polyglycol (molar weight 2000) are dissolved in 250 parts of water and stirred into 400 parts of a 10% aqueous alginate thickener. Subsequently, 300 parts of heavy gasoline (boiling range 160° to 200°C) are emulsified into this product by means of a high-speed stirrer (1200 to 2000 rpm). After adding 20 parts of the sodium salt of *m*-nitrobenzene sulphonic acid the emulsion is made up to 1000 parts by adding 20 parts of water.

The cover printing paste is then made up to 1000 parts by adding 195 parts of water.

After printing and drying, the material is steamed for 5 minutes at 102°C and treated and finished as indicated in Example 1.

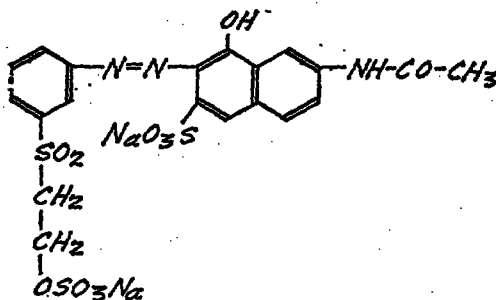
In this way, yellow resist effects having very sharp outlines are obtained under a brown cover-printing.

EXAMPLE 5

For the use of mixtures of dyestuffs derived from β -hydroxyethyl-sulphone sulphuric acid ester and from diethylaminoethylsulphone the following stock pastes are prepared:

Stock Paste 1

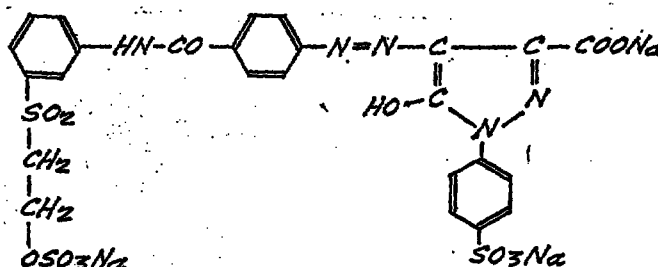
50 Parts of the reactive dyestuff of the formula



are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. Subsequently, 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 50 parts of water glass of 48° Bé are added and the paste is made up to 1000 parts by adding 90 parts of water.

Stock Paste 2

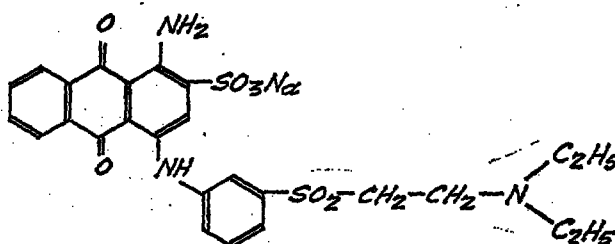
50 Parts of the reactive dyestuff of the formula



are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 50 parts of water glass of 48° Bé, the paste is made up to 1000 parts by adding 90 parts of water.

Stock Paste 3

50 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 300 parts of water and 50 parts of water glass of 48° Bé. This solution is stirred into 500 parts of a 10% aqueous alginate solution and, after adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid, the paste is made up to 1000 parts by adding 90 parts of water.

The stock pastes obtained in this way are now mixed in the proportion given below and printed successively on a mercerized cotton fabric on a screen-printing machine:

Printing Paste A: mixture of 600 parts of stock paste 1 and 400 parts of stock paste 3

Printing Paste B: mixture of 500 parts of stock paste 2 and 500 parts of stock paste 3.

In the same operation, the fabric is printed in a wet process with a cover-print resist prepared as follows:

100 Parts of a 50% aqueous solution of citric acid are stirred into 500 parts of a 6% aqueous thickener of hydroxyethylcellulose and the paste is made up to 1000 parts by adding 400 parts of water.

After printing and drying, the material is steamed for 8 minutes at 102°C and then padded on a two-roller foulard with the following fixing solution:

150 parts of anhydrous sodium carbonate, 150 parts of sodium chloride and 50 parts of potassium carbonate are dissolved in 600 parts by volume of water and then 100 parts by volume of sodium hydroxide solution of 38° Bé are added. This solution is made up to 1000 parts by adding water.

Without intermediate drying, the material is immediately steamed at 140°C and subsequently after-treated and finished as usual in two-phase printing.

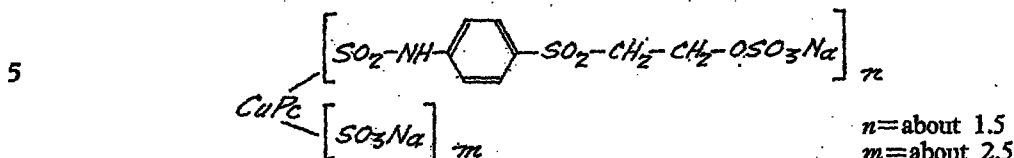
A yellow resist effect (Printing Paste B) under a green bottom-print and an orange coloured resist effect (Printing Paste A) under a brown bottom-print are obtained.

EXAMPLE 6

For the application of dyestuff mixtures the following stock pastes are prepared:

Stock Paste 1

50 Parts of the reactive dyestuff of the formula

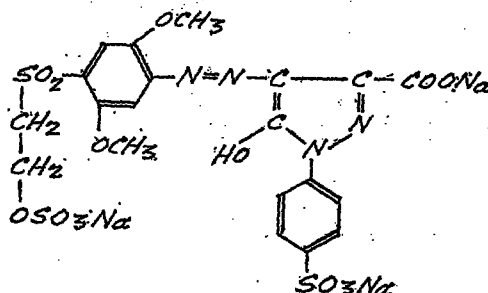


are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener, and 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid are added. After further addition of 50 parts of water glass of 48° Bé, the paste is made up to 1000 parts by adding 90 parts of water.

10

Stock Paste 2

50 Parts of the reactive dyestuff of the formula



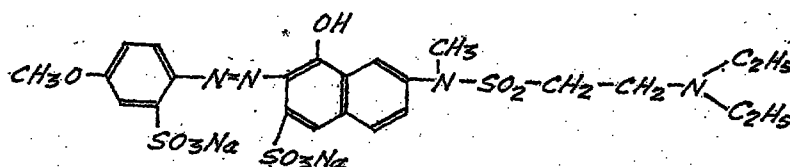
are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 50 parts of water glass of 48° Bé, the paste is made up to 1000 parts by adding 90 parts of water.

15

15

Stock Paste 3

50 Parts of the reactive dyestuff of the formula



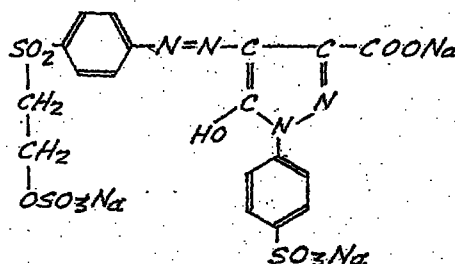
are dissolved in a mixture of 300 parts of water and 50 parts of water glass of 48° Bé. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. 10 Parts of the sodium salt of *m*-nitrobenzene sulphonic acid are added and the paste is made up to 1000 parts by adding 90 parts of water.

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20

Stock Paste 4

50 Parts of the reactive dyestuff of the formula



are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. 10 Parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 50 parts of water glass of 48° Bé are added and the paste is made up to 1000 parts by adding 90 parts of water.

5

Stock Paste 5

5

Identical with stock paste 3 of Example 5.

Stock Paste 6

Identical with stock paste 2 of Example 5.

10

The stock pastes prepared in this way are mixed in the proportion given below and then printed successively on a mercerized cotton fabric by means of a screen-printing machine:

10

Printing Paste A: mixture of 600 parts of stock paste 5 and 400 parts of stock paste 1

15

Printing Paste B: mixture of 500 parts of stock paste 3 and 500 parts of stock paste 2

15

Printing Paste C: mixture of 200 parts of stock paste 5, 300 parts of stock paste 3, 300 parts of stock paste 4 and 200 parts of stock paste 1

20

Printing Paste D: mixture of 500 parts of stock paste 5 and 500 parts of stock paste 6.

20

After printing and drying, the fabric treated in this way is cover-printed on a roller-printing machine by means of a pattern roller, using the following cover-printing paste:

25

150 Parts of a 50% aqueous solution of tartaric acid are stirred into 500 parts of a 5% aqueous thickener of hydroxyethylcellulose. The paste is made up to 1000 parts by adding 350 parts of water.

25

The fabric is steamed for 5 minutes at 102°C after having been dried, and subsequently padded on a foulard by means of a fixing solution prepared as follows:

30

180 Parts of anhydrous sodium sulphate, 150 parts of anhydrous sodium carbonate and 50 parts of potassium carbonate are dissolved in 600 parts by volume of water and 100 parts of sodium hydroxide solution of 38° Bé are added. This solution is made up to 1000 parts by volume.

30

The material is then allowed to remain for 4 hours at room temperature in order to fix the dyestuff. The prints are after-treated and finished according to the usual two-phase process to obtain a turquoise coloured resist effect (printing paste A) under a blue print, an orange coloured resist effect (printing paste B) under a red print, a green resist effect (printing paste C) under a brown print and a yellow resist effect (printing paste D) under a green print.

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EXAMPLE 7

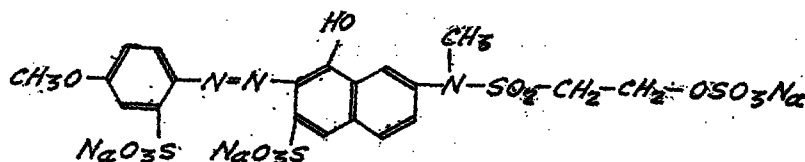
40

For the application of dyestuff mixtures the following stock pastes are prepared:

40

Stock Paste 1

30 Parts of the reactive dyestuff of the formula



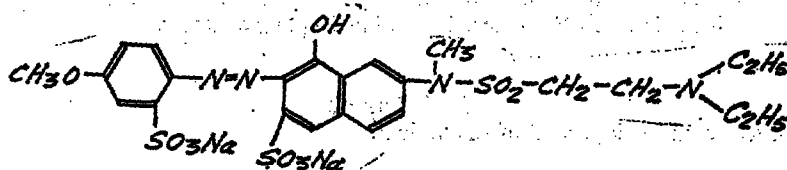
45

are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. Subsequently, 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 15 parts of sodium bicarbonate are added and the paste is made up to 1000 parts by adding 125 parts of water.

45

Stock Paste 2

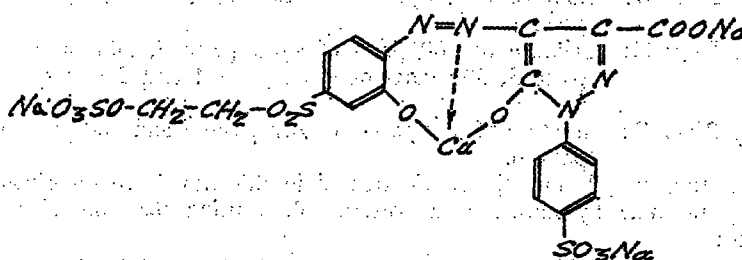
50 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 300 parts of water and 15 parts of sodium bicarbonate. This solution is stirred into a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid, the paste is made up to 1000 parts by adding 125 parts of water.

Stock Paste 3

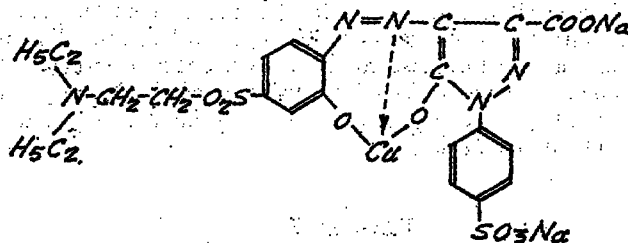
50 Parts of the reactive dyestuff of the formula



are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 15 parts of sodium bicarbonate, the paste is made up to 1000 parts by adding 125 parts of water.

Stock Paste 4

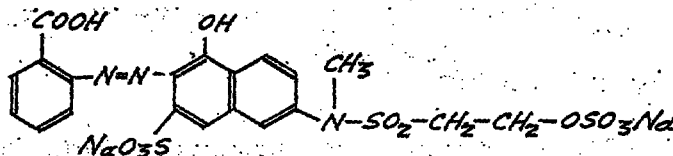
50 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 300 parts of water and 15 parts of sodium bicarbonate. The solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid, the paste is made up to 1000 parts by adding 125 parts of water.

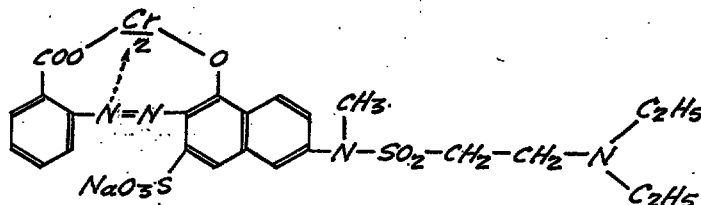
Stock Paste 5

50 Parts of the reactive dyestuff of the formula



are dissolved in 300 parts of water having a temperature of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid and 15 parts of sodium bicarbonate, the paste is made up to 1000 parts by adding 125 parts of water.

Stock Paste 6
50 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 300 parts of water and 15 parts of sodium bicarbonate. This solution is stirred into a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid, the paste is made up to 1000 parts by adding 125 parts of water.

The stock pastes prepared in this way are now mixed in the proportion given below and a four-coloured ornament is printed on a mercerized cotton fabric by means of a screen-printing process with the printing pastes as described above as well as a resist printing paste as follows:

Resist printing paste:

100 Parts of a 50% aqueous solution of citric acid are stirred into 500 parts of a 5% aqueous thickener of hydroxyethylcellulose. The paste is made up to 1000 parts by adding 400 parts of water.

The following printing pastes are cover-printed in the same printing operation in a wet process:

Printing Paste A: mixture of 750 parts of stock paste 2 and 250 parts of stock paste 1

Printing Paste B: mixture of 750 parts of stock paste 4 and 250 parts of stock paste 3

Printing Paste C: mixture of 750 parts of stock paste 6 and 250 parts of stock paste 5.

After printing and drying, the material is steamed for 15 minutes at 102°C and then padded on a foulard with a fixing solution as indicated in Example 1. Subsequently, the material treated in this way is allowed to remain for 2 hours at room temperature and then after-treated and finished as is usual in a two-phase fixing process.

In this way fair shade-in-shade effects in red (printing paste A), brown (printing paste B) and red-brown (printing paste C) under darker cover-prints are obtained.

EXAMPLE 8

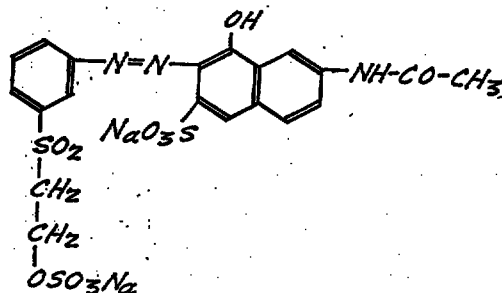
For the application of dyestuff mixtures the following stock pastes are prepared:

Stock Paste 1

Identical with stock paste 3 of Example 5.

Stock Paste 2

50 Parts of the reactive dyestuff of the formula

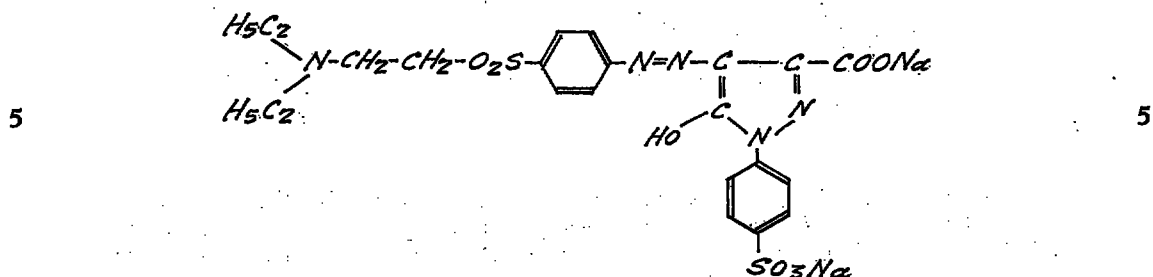


are dissolved in 250 parts of water of 95°C. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-

nitrobenzene sulphonic acid and 50 parts of water glass of 48° Bé, the paste is made up to 1000 parts by adding 140 parts of water.

Stock Paste 3

50 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 250 parts of water and 50 parts of water glass of 48° Bé. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid, the paste is made up to 1000 parts by adding 140 parts of water.

By mixing the aforementioned stock pastes in the proportion given below, printing pastes are prepared which are printed successively in a wet process and by means of a screen-printing procedure on a mercerized cotton fabric, together with the following resist printing paste:

Resist printing paste: prepared as described in Example 7.

Printing Paste A: mixture of 600 parts of stock paste 2 and 400 parts of stock paste 1

Printing Paste B: mixture of 500 parts of stock paste 3 and 500 parts of stock paste 1.

After printing and drying, the material is steamed for 5 minutes at 102°C and subsequently padded on a foulard with a fixing solution prepared as follows:

180 Parts of anhydrous sodium sulphate, 150 parts of anhydrous sodium carbonate and 50 parts of potassium carbonate are dissolved in 600 parts by volume of water. After adding 50 parts by volume of sodium hydroxide solution of 38° Bé, the whole is made up to 1000 parts by volume of adding water.

Subsequently, the material is allowed to remain for 2 hours at room temperature in order to fix the dyestuff, and then after-treated and finished as is usual in two-phase printing to obtain an orange coloured resist effect having an interesting bleeding effect (printing paste A) under a brown cover-print and a white resist (printing paste B) under a green cover-print.

WHAT WE CLAIM IS:—

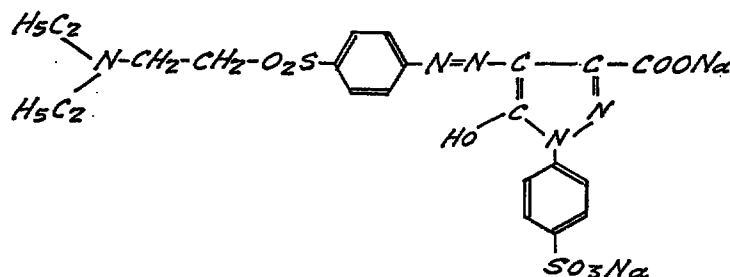
1. A process for producing resist effects by means of reactive dyestuffs under reactive dyestuffs on a flat-surface textile structure made of natural or regenerated cellulose fibre material, wherein the textile material is printed in any order with a printing paste containing a non-volatile organic or inorganic acid or acid salt as reserving agent said reserving agent containing no fibre-reactive grouping and a reactive dyestuff which can be fixed by means of the two-phase pad-batch or a two-phase rapid fixing process, and applying in over-lapping manner a further printing paste or padding liquor containing an alkali as fixing agent and another reactive dyestuff which cannot be fixed by the aforesaid fixing processes or which gives only low yields, and after drying the material thus treated, fixing the dyestuffs by steaming in combination with one of the aforesaid two-phase fixing processes.

2. A process as claimed in claim 1, wherein the steaming is carried out for 2 to 15 minutes at a temperature of from 98 to 180°C.

3. A modification of the process as claimed in claim 1 or 2, wherein the textile material is printed in any order with a printing paste containing a non-volatile organic or inorganic acid or acid salt as reserving agent said reserving agent containing no fibre-reactive grouping, and applying in over-lapping manner a further printing paste or padding liquor containing an alkali as fixing agent and a mixture of both kinds of reactive dyestuffs having different fixation characteristics, and finally fixing the dyestuffs on the material after drying.

nitrobenzene sulphonic acid and 50 parts of water glass of 48° Bé, the paste is made up to 1000 parts by adding 140 parts of water.

Stock Paste 3
50 Parts of the reactive dyestuff of the formula



are dissolved in a mixture of 250 parts of water and 50 parts of water glass of 48° Bé. This solution is stirred into 500 parts of a 10% aqueous alginate thickener. After adding 10 parts of the sodium salt of *m*-nitrobenzene sulphonic acid, the paste is made up to 1000 parts by adding 140 parts of water.

By mixing the aforementioned stock pastes in the proportion given below, printing pastes are prepared which are printed successively in a wet process and by means of a screen-printing procedure on a mercerized cotton fabric, together with the following resist printing paste:

Resist printing paste: prepared as described in Example 7.

Printing Paste A: mixture of 600 parts of stock paste 2 and 400 parts of stock paste 1

Printing Paste B: mixture of 500 parts of stock paste 3 and 500 parts of stock paste 1.

After printing and drying, the material is steamed for 5 minutes at 102°C and subsequently padded on a foulard with a fixing solution prepared as follows:

180 Parts of anhydrous sodium sulphate, 150 parts of anhydrous sodium carbonate and 50 parts of potassium carbonate are dissolved in 600 parts by volume of water. After adding 50 parts by volume of sodium hydroxide solution of 38° Bé, the whole is made up to 1000 parts by volume of adding water.

Subsequently, the material is allowed to remain for 2 hours at room temperature in order to fix the dyestuff, and then after-treated and finished as is usual in two-phase printing to obtain an orange coloured resist effect having an interesting bleeding effect (printing paste A) under a brown cover-print and a white resist (printing paste B) under a green cover-print.

WHAT WE CLAIM IS:—

1. A process for producing resist effects by means of reactive dyestuffs under reactive dyestuffs on a flat-surface textile structure made of natural or regenerated cellulose fibre material, wherein the textile material is printed in any order with a printing paste containing a non-volatile organic or inorganic acid or acid salt as reserving agent said reserving agent containing no fibre-reactive grouping and a reactive dyestuff which can be fixed by means of the two-phase pad-batch or a two-phase rapid fixing process, and applying in over-lapping manner a further printing paste or padding liquor containing an alkali as fixing agent and another reactive dyestuff which cannot be fixed by the aforesaid fixing processes or which gives only low yields, and after drying the material thus treated, fixing the dyestuffs by steaming in combination with one of the aforesaid two-phase fixing processes.

2. A process as claimed in claim 1, wherein the steaming is carried out for 2 to 15 minutes at a temperature of from 98 to 180°C.

3. A modification of the process as claimed in claim 1 or 2, wherein the textile material is printed in any order with a printing paste containing a non-volatile organic or inorganic acid or acid salt as reserving agent said reserving agent containing no fibre-reactive grouping, and applying in over-lapping manner a further printing paste or padding liquor containing an alkali as fixing agent and a mixture of both kinds of reactive dyestuffs having different fixation characteristics, and finally fixing the dyestuffs on the material after drying.



4. A process as claimed in any one of claims 1 to 3, wherein a reactive dyestuff of the azo, anthraquinone or phthalocyanine series is used.
5. A process as claimed in any one of claims 1 to 4, wherein the non-volatile acid or salt is tartaric acid, citric acid or a primary alkali metal phosphate.
- 5 6. A process as claimed in any one of claims 1 to 5, wherein the printing pastes contain urea, a wetting agent, a weak oxidizing agent and/or a thickening agent.
7. A modification of the process as claimed in claim 1, wherein the acid resist is applied without the addition of a reactive dyestuff.
- 10 8. A process as claimed in claim 1, 2 or 3 conducted substantially as described herein.
9. A process as claimed in claim 1, 2 or 3 conducted substantially as described in any one of the Examples herein.
- 10 10. Textile material made from natural or regenerated cellulose, whenever treated according to a process claimed in any one of claims 1 to 9.

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