

PATENT SPECIFICATION

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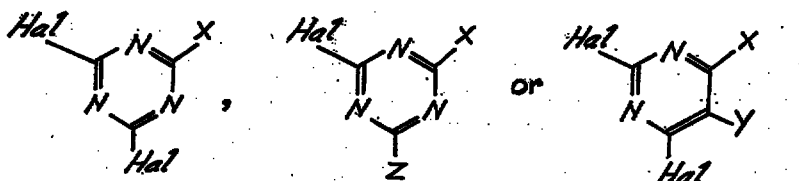
(54) PROCESS FOR RESERVING TEXTILES OF NATURAL POLYAMIDE FIBRES AND OF SYNTHETIC FIBRES DYEABLE WITH ACID DYES

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, 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:

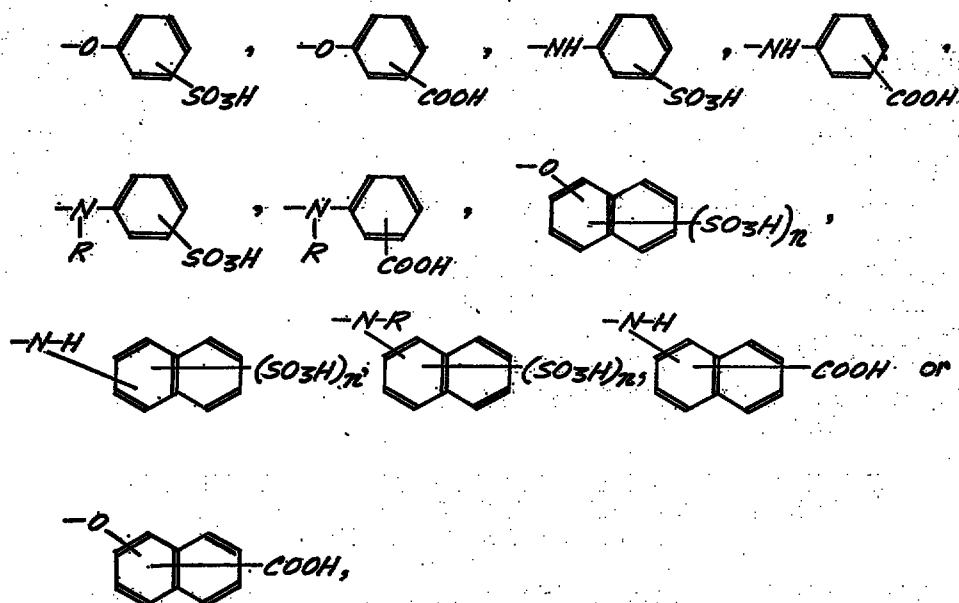
This invention relates to a process for the local reservation against anionic dyes of selected areas of textiles made of natural polyamide fibres and of textiles made of synthetic fibres dyeable with acid dyes, which process consists in impregnation of selected areas of the textiles with colourless fibre-reactive compounds and fixation of the impregnation.

It has been found that textiles made of natural polyamide fibres and of synthetic fibres dyeable with acid dyes (c.f. Colour Index, Second Edition, 1956, Volume 1, pages 1001—1404) can be locally reserved against anionic (acid) dyes by impregnating the areas intended for reservation with a liquor or a paste containing one or more colourless fibre-reactive compounds (as hereinafter defined) and then fixing the impregnation.

The term "textiles made of natural polyamide fibres" refers in particular to filaments, yarns, woven fabrics or knitted goods of wool or silk. Under "textiles made of synthetic fibres dyeable with acid dyes" are understood the aforementioned textile forms of synthetic polyamide fibres, e.g. nylon 6, 7, 11, 66, 76, 226, 610 and 6/66, of basic modified polypropylene and of basic modified polyacrylonitrile and acrylonitrile copolymer fibres. The colourless fibre-reactive compounds employed for impregnation are of formulae



where Hal stands for F, Cl or Br, X for a group of formula



Y for H, F or Cl, Z for an unsubstituted amino group, an amino group substituted by one or two alkyl groups having 1 to 4 carbon atoms, or an alkoxy group having 1 to 4 carbon atoms, n for 1, 2 or 3 and R for an alkyl group having 1 to 4 carbon atoms, and where the $-SO_3H$ and $-COOH$ groups are attached to the aromatic nucleus at positions other than those ortho to the oxygen or imino bridge member and the aromatic nuclei may be substituted by, for example, halogen atoms or nitro, cyano or alkyl groups having 1 to 4 carbon atoms.

Compounds with a pyrimidine nucleus are very stable to hydrolysis in neutral and alkaline medium. Cyanuric acid derivatives react extremely rapidly, while trifluoropyrimidyl derivatives are particularly suitable for the reservation of natural polyamide fibres. In selecting suitable colourless fibre-reactive compounds the textile colourist will be guided by these known criteria.

The areas of the textile substrate treated with these colourless fibre-reactive compounds, besides being reserved against anionic dyes, generally exhibit increased dyeability with basic dyes.

If the compounds are applied by a printing process, the known method of print paste preparation for dyes is employed. For this purpose they are preferably ground to an average particle size of 0.1 to 10 microns or more particularly 0.1 to 5 microns, if necessary in the presence of dispersing agents or fillers. For example, the dry compounds can be ground with a dispersing agent and if required fillers, or alternatively it can be kneaded in paste form with a dispersing agent and subsequently vacuum or jet dried.

It is advisable to add an acid-binding agent such as sodium or potassium carbonate or bicarbonate to preparations of compounds containing reactive halogen, so that the hydrogen halide liberated in fixation is immediately neutralized. One of the commonly used thickening agents is normally included in the padding liquor or printing paste, for example modified or unmodified natural products such as sodium alginate, British gum, gum Arabic, crystal gum, locust bean gum, gum tragacanth, starch, carboxymethyl-cellulose or hydroxyethyl-cellulose, or synthetic products such as polyacrylamides or polyvinyl alcohols.

The padding liquor or printing paste may contain the colourless fibre-reactive compounds in amounts of up to about 150 parts per 1000 parts. Fixation is effected preferably in a moist atmosphere at room temperature for periods of up to about 20 hours, or between 25° and 95° C for 2 hours, or between 95° and 130° C for about 15 minutes.

Polyamide materials treated with the colourless fibre-reactive compounds can be dyed with anionic dyes; the areas of the material treated with the compounds then remain undyed or are dyed to lighter depth than the remaining material, depending on the degree of reservation imparted by the treatment. The best reserve effects are

obtained against anionic dyes bearing two or more sulphonic acid groups; in fact 100% reservation of synthetic polyamide fibres can be obtained against this type of dye. A step by step decrease in the degree of reservation is obtained with dyes bearing only one sulphonic acid group and with premetallized dyes. This process of reservation has no effect on disperse dyes which give the normal effects obtained with this class whereas basic dyes dye the reserved areas of polyamide material to greater depth than the unreserved substrate. If the desired, the material can be subsequently dyed with anionic dyes and then with basic dyes to produce two-colour effects, since the latter class dye preferentially the areas reserved against anionic dyes. The reverse procedure is of course practicable, with the basic dyes being applied first to dye the reserved areas, followed by anionic dyes to fill in the remaining material. Dyes of these two classes can be applied from the same bath if desired.

In the following Examples the parts and percentages are by weight and the temperatures in degrees centigrade.

EXAMPLE 1

A printing paste is prepared with the following additions and vigorously stirred until homogeneous:

- 10 parts sodium alginate thickening
- 30 parts anhydrous disodium phosphate
- 2 parts anhydrous monosodium phosphate
- 921 parts water
- 24 parts octylphenyl-pentaglycol ether
- 6 parts modified sodium alkylsulphate
- 7 parts sodium 2,4-dichloro-6-phenylamino-1,3,5-triazine-4'-sulphonate.

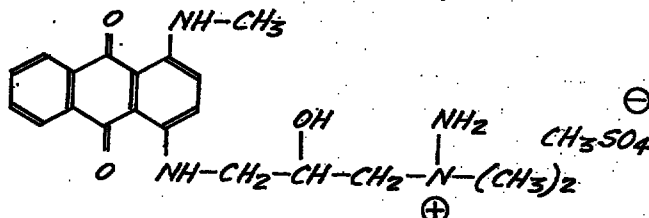
The paste is printed on a nylon 6 fabric by the Vigoureux process at a coverage of 25% and a pressure giving a 100% increase over the dry weight on the printed areas. The fabric is stored for 24 hours at room temperature (20—25°) and rinsed with cold water. It is then exhaustion dyed with C.I. Acid Red 37, which results in a pale red dyeing on the treated and a dark red dyeing on the untreated areas.

EXAMPLE 2

Textured nylon 6 yarn in package form is locally impregnated with a homogeneously stirred liquor of the following composition at a 100% increase over the dry weight on the printed areas:

- 1 part sodium alginate thickening
- 30 parts anhydrous disodium phosphate
- 2 parts anhydrous monosodium phosphate
- 949 parts water
- 8 parts octylphenyl-pentaglycol ether
- 2 parts modified sodium alkylsulphate
- 7 parts sodium 2,4-dichloro-6-phenylamino-1,3,5-triazine-4'-sulphonate.

The yarn is stored for 2 hours at 40°, rinsed with warm and cold water, and exhaustion dyed with C.I. Acid Red 37 and the basic dye of formula

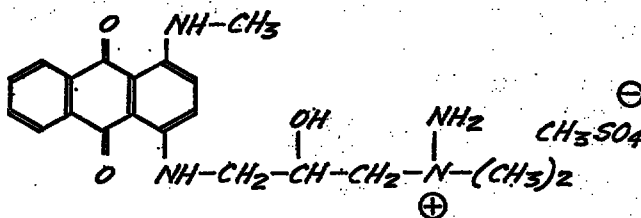


EXAMPLE 3

A paste is prepared with

- 5 parts sodium alginate thickening
 30 parts anhydrous disodium phosphate
 2 parts anhydrous monosodium phosphate
 944 parts water
 8 parts octylphenyl-pentaglycol ether
 2 parts modified sodium alkylsulphate
 7 parts sodium 2,4-dichloro-6-phenylamino-1,3,5-triazine-4'-sulphonate.

The paste is vigorously stirred until homogeneous and printed on nylon 6 yarn at a 100% increase over the dry weight on the printed areas. The yarn is treated for 4 minutes at 102° and rinsed with cold water. It is woven into fabric which is exhaustion dyed with a basic blue of formula



to give a tone-in-tone dyeing of varying strength.

EXAMPLE 4

A printing paste is made up with

- 5 parts sodium alginate thickening
 35 parts anhydrous phosphate buffer mixture giving a pH value of 8
 885 parts water
 24 parts octylphenylpentaglycol ether
 6 parts modified sodium alkylsulphate
 45 parts sodium-2,4-dichloro-6-phenylamino-1,3,5-triazine-4'-sulphonate.

It is vigorously stirred until homogeneous and printed on wool yarn at a 100% weight increase on the printed areas. The yarn is stored for 1 hours at 60°, rinsed with warm and cold water, and exhaustion dyed with a mixture of C.I. Acid Blue 23 and C.I. Acid Yellow 25. A two-colour dyeing with clear depth differentiation is obtained.

EXAMPLE 5

Unweighted silk yarn is printed as described in Example 4, treated for 10 minutes at 100° in a wet steam atmosphere, and exhaustion dyed with C.I. Acid Red 145. The impregnated fibre sites are dyed to considerably less depth than the remainder of the yarn.

EXAMPLE 6

A paste of the following composition is prepared and homogenized by powerful stirring:

- 5 parts sodium alginate thickening
 30 parts anhydrous disodium phosphate
 5 parts anhydrous trisodium phosphate
 24 parts octylphenyl-pentaglycol ether
 6 parts modified sodium alkylsulphate
 900 parts water
 30 parts sodium 2,4-dichloro-6-phenylamino-1,3,5-triazine-4'-sulphonate.

The paste is locally printed on a polypropylene yarn rendered acid dyeable by chemical modification. The yarn is steamed in wet steam for 15 minutes at 100°, rinsed with warm and cold water, and exhaustion dyed with C.I. Acid Orange 43. The treated areas are dyed to pale depth, the untreated to heavy depth.

EXAMPLE 7

A paste is prepared with

5	5 parts sodium alginate thickening	
	30 parts disodium phosphate (anhydrous)	
	2 parts monosodium phosphate (anhydrous)	5
	917 parts water	
	8 parts octylphenyl-pentaglycol ether	
	2 parts modified sodium alkylsulphate	
	9 parts 2,4-dichloro-6-3'-carboxyphenylamino-1,3,5-triazine, dispersed with	
10	27 parts sodium dinaphthylmethanedisulphonate and homogenized by vigorous stirring. It is printed on carpet yarn of texturized nylon 6 fibre at a 100% increase over the dry weight on the printed areas, stored for one day at room temperature (20—25°) and then rinsed with warm and cold water. The treated yarn is tufted on a jute backing fabric and exhaustion dyed with a mixture of C.I. Disperse Yellow 3 and C.I. Acid Blue 23. A two-colour dyeing with sharp colour differentiation is obtained.	10
15		15

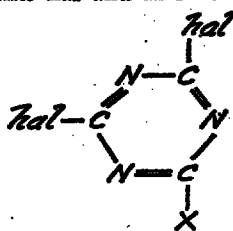
EXAMPLE 8

A paste of the following composition

20	5 parts sodium alginate thickening	
	30 parts anhydrous disodium phosphate	20
	5 parts anhydrous monosodium phosphate	
	24 parts octylphenyl-pentaglycol ether	
	6 parts modified sodium alkylsulphate	
25	400 parts of water and	
	30 parts sodium 2,4-dichloro-6-phenylamino-1,3,5-triazine-4'-sulphonate	25

is homogenized by thorough stirring and printed on yarn of modified acrylic fibre. The yarn is steamed for 15 minutes at 110° in saturated steam and then dyed with C.I. Acid Orange 43. The treated areas are dyed to considerably lighter depth than the untreated.

30	The following Table contains further Examples of dyeings with partial reservation on natural or synthetic polyamide fibres, on basic modified polypropylene fibres or on basic modified acrylonitrile polymer fibres. These dyeing are carried out according to the details of Examples 1 to 8 and are characterized in the Table by the textile material employed, the substituents hal and X in the reserving agent of the formula	30
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and by the procedure used.

TABLE

Example No.	Textile material (I)	hal (II)	substituent X (III)	Procedure according to Example (IV)
9	wool yarn	Br	4-sulphophenylamino	4
10	nylon 6	Cl	3-sulphophenylamino	2
11	nylon 6	Cl	4-carboxyphenoxy	2
12	nylon 11	Cl	3-sulphophenylamino	1
13	nylon 66	Cl	4-sulphonaphthyl-1-amino	2
14	nylon 66	Cl	6-sulpho-naphthoxy-2	2
15	nylon 66	Cl	6,8-disulphonaphthoxy-2	2
16	nylon 66	Cl	4-sulphophenoxy	2
17	wool yarn	Cl	4-carboxyphenylamino	4
18	nylon 6	Cl	4-sulphonaphthoxy-1	2
19	nylon 6	Cl	4-6-disulphonaphthoxy-1	2
20	nylon 6	Cl	7-sulphonaphthyl-1-amino	1
21	nylon 6	Cl	4,8-disulphonaphthyl-2-amino	1
22	nylon 6	Cl	5,7-disulphonaphthyl-1-amino	1
23	nylon 6/66	Cl	6-sulphonaphthyl-2-amino	1

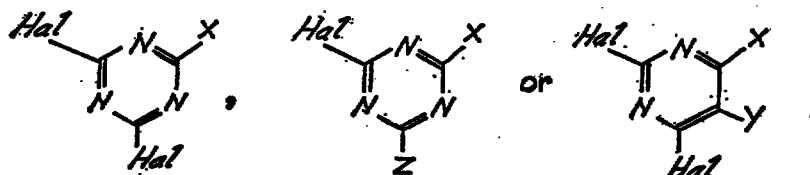
Example No.	(I)	(II)	(III)	(IV)
24	nylon 6	Cl	N-methyl-N-(6-sulphonaphthyl-2)-amino	3
25	nylon 66	Cl	N-methyl-N-(4-sulphophenyl)-amino	3
26	nylon 6	Br	4-sulphophenylamino	2
27	nylon 6	F	4-sulphophenylamino	2
28	nylon 6	Cl	4,6,8-trisulphonaphthyl-2-amino	1
29	nylon 6	Cl	3,6,8-trisulphonaphthyl-1-amino	1
30	nylon 6	Cl	3,6,8-trisulphonaphthoxy-1	1
31	PP*	Cl	4-sulphonaphthyl-1-amino	6
32	PAN*	Cl	3-sulphophenylamino	8
33	nylon 66	Cl	3,5-disulphophenylamino	2

PP* = basic modified polypropylene yarn

PAN* = basic modified polyacrylonitrile yarn

WHAT WE CLAIM IS:

1. A process for the reservation against anionic dyes of selected areas of textiles made of natural polyamide fibres or of acid dyeable synthetic fibres, which comprises the application to the areas of the material that are to be reserved of a solution of one or more colourless, fibre-reactive compounds of the formula



where Hal stands for F, Cl or Br, X for a group of formula

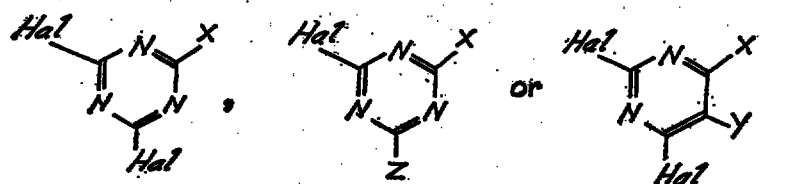
Example No.	(I)	(II)	(III)	(IV)
24	nylon 6	Cl	N-methyl-N-(6-sulphonaphthyl-2)-amino	3
25	nylon 66	Cl	N-methyl-N-(4-sulphophenyl)-amino	3
26	nylon 6	Br	4-sulphophenylamino	2
27	nylon 6	F	4-sulphophenylamino	2
28	nylon 6	Cl	4,6,8-trisulphonaphthyl-2-amino	1
29	nylon 6	Cl	3,6,8-trisulphonaphthyl-1-amino	1
30	nylon 6	Cl	3,6,8-trisulphonaphthoxy-1	1
31	PP*	Cl	4-sulphonaphthyl-1-amino	6
32	PAN*	Cl	3-sulphophenylamino	8
33	nylon 66	Cl	3,5-disulphophenylamino	2

PP* = basic modified polypropylene yarn

PAN* = basic modified polyacrylonitrile yarn

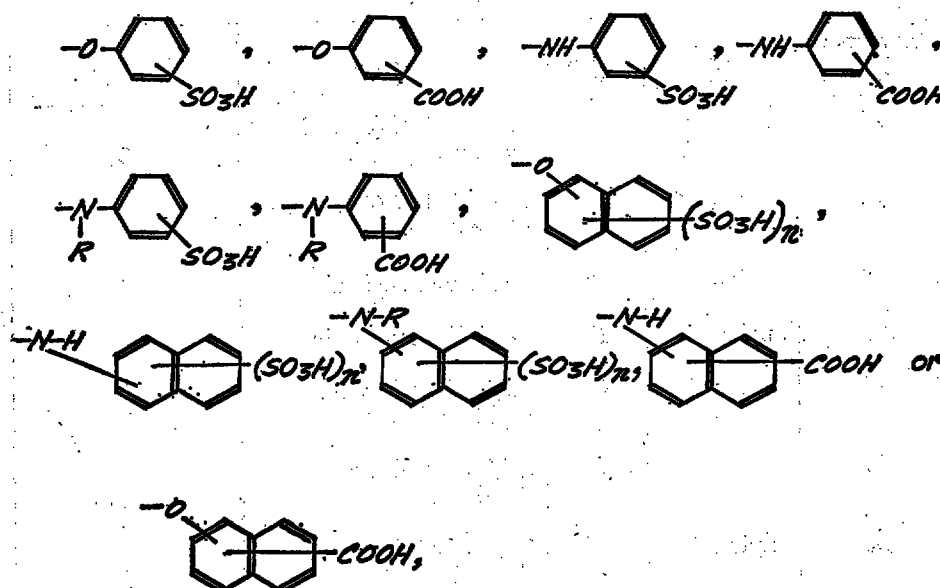
WHAT WE CLAIM IS:

1. A process for the reservation against anionic dyes of selected areas of textiles made of natural polyamide fibres or of acid dyeable synthetic fibres, which comprises the application to the areas of the material that are to be reserved of a solution of one or more colourless, fibre-reactive compounds of the formula



where Hal stands for F, Cl or Br, X for a group of formula





Y for H, F or Cl, Z for an unsubstituted amino group, an amino group substituted by one or two alkyl groups having 1 to 4 carbon atoms, or an alkoxy group having 1 to 4 carbon atoms, n for 1, 2 or 3 and R for an alkyl group having 1 to 4 carbon atoms, and where the $-SO_3H$ and $-COOH$ groups are attached to the aromatic nucleus at positions other than those ortho to the oxygen or imino bridge member and the aromatic nuclei may be substituted, followed by fixation of the compound or compounds prior to coloration of the material.

2. A process according to Claim 1, in which organic compounds containing a halogen-substituted triazinyl group in the molecule are employed as colourless fibre-reactive compounds.

3. A dyeing process for natural polyamide fibres or acid dyeable synthetic fibres, in which the fibres are reserved by a process according to Claim 1 or Claim 2 and then dyed with an anionic and/or cationic dye.

4. A process according to Claim 1 substantially as herein described and exemplified.

5. A process according to Claim 3 substantially as herein described and exemplified.

6. The product of a process according to any one of Claims 1 to 5.

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