ABSTRACT

A process for printing synthetic nitrogenous fibers with dyestuff that are soluble or dispersible in water is disclosed. The fibers to be printed are pretreated with an aqueous preparation consisting substantially of at least one fiber, substantive water-soluble, anionic resist for synthetic polyamide fibers selected from the group consisting of polycondensates of diaryl sulfones containing at least one phenolic hydroxyl group with formaldehyde. The fibers so pretreated are then dried and then printed with the printing paste containing the dyestuff.

10 Claims, No Drawings
The present invention provides a process for printing nitro-
genous fibers with dyestuffs that are soluble or only dispersible
in water. According to the present process the fibrous material
is pre-treated with an aqueous preparation containing at least
one fiber-substantive resist for synthetic polyamide fibers. The
impregnated material is then dried and printed in the usual
manner.

Nitrogenous fibers suitable for printing by the present
process are above all those of synthetic origin. Particularly
good results are obtained on synthetic polyamides, such as
condensation products from adipic acid and hex-
amethylene diamine, polycondensates of ε-caprolactam or of
ω-aminoundecanoic acid. The fibers may be in any desired
stage of their processing, that is to say they may in the form
of fillaments, staple fibers, textured fibers, comings, fabrics or
hosiery.

The dyestuffs must be soluble or at least dispersible in
water. Particularly valuable are the water-soluble dyestuffs,
for example substantive dyestuffs, L-1-methyl complex
dyestuffs, and especially metal-free acid wool dyes and 1:2-
metal complex dyestuffs. As dyestuffs that are only dispersible
in water there are suitable, above all, the so-called dispersible
dyestuffs, for example those of the type of the 1:2-metal com-
plex dyestuffs. The term dispersible dyestuffs refers to those
organic, coloured compounds of which at most traces are soluble
in water so that they must be applied in the form of fine
dispersions.

The printing pastes used for the application of the dyestuffs
defined above contain the conventional additives, such, for
example, as thickeners, hydrotrropic agents, solution
promoters and the like. As a rule, the dyestuffs are fixed by
steaming.

Fiber-affinic resists for synthetic polyamide fibers are com-
ounds that prevent the fibers being stained by the dyestuff,
either during dyeing or during washing. Such compounds are
as a rule water-soluble, anionic and as such known. They
should have no color of their own, or at least they should not
change the color of the fibrous material under treatment.
Thus, for example, a list of such compounds will be found in “
Vorbehandlung und Färben von synthetischen Fasern” by
H.U. Schmidlin, 1958, but this list of course does not claim to
be complete, and the present invention is not limited to the
use of the compounds listed.

Of special value are water-soluble anionic polycondensates
of formaldehyde with diarylsulfones that contain at least one
phenolic hydroxyl group. As aromatic components there are
suitable diyclic and especially monocylic compounds contain-
ing at least one phenolic hydroxyl group. However, in addi-
tion to the hydroxyl group other substituents may be
present, such as sulphonate groups, halogen atoms or alkyl
radicals, especially alkyls containing one to four carbon
atoms. Particularly suitable are compounds of the type of the
phenol, of the mono-alkylphenols or dialkylphenols, for exam-
ple of the cresols or xylanols, of the mono- or
dihalogenophenols, for example of the chlorophenols or
dichlorophenols, or resorcinol or of pyrogallol.

The sulphones are prepared from the phenolic compounds
referred to above by known methods, for example by reaction
with sulphuric acid at an elevated temperature. In this connec-
tion it is also possible to use mixtures of the aromatic com-
ponents defined above.

These sulphones are subjected to polycondensation with
formaldehyde in known manner, for example in an acidic or
alkaline medium at an elevated temperature. However, it is
not necessary to perform the condensation exclusively with
sulphones and it may be performed also with mixtures of
sulphones and sulphonlic acids or dye-phenolic compounds
described above. If this is the case, the polycondensate should
contain at least 30, preferably at least 40, mol percent of
sulphone. When, on the other hand, exclusively sulphones are
subjected to the polycondensation, the sulphones are
sulphonated either before the condensation or after it in the
form of the polycondensates. In this reaction it is possible to
introduce sulphonlic acid groups either before or after the con-
densation with formaldehyde. The polycondensates of
sulphones, whose aromatic hydroxy compounds are phenol,
cresols or xylanols, are specially preferred because of their ac-
cessibility and their potency.

These resists are applied during the pretreatment according
to the padding or preferably the exhaustion method, using
temperatures from 10° to 130° C., preferably from 80° to 100°
C. The fibrous material thus treated is then dried. The pH
values of the aqueous preparations may be in the acid, neutral
or alkaline region, but preferably they are acid, in fact in the
pH region from 3 to 5, or neutral. The acid pH value is
produced by adding inorganic, or preferably organic, acids of
low molecular weight.

The amount of resist to be used varies within wide limits and
is in the padding process 0.1 to 10 percent referred to the
padding liquor, or 0.1 to 10 percent, preferably 0.5 to 3
percent, referred to the fibrous material when working by the
exhaustion method.

Apart from the resist the preparation may also contain opti-
cal brighteners, bleaches, for example reducing agents, or
other usual additives.

The advantage of the present process is that owing to the
pretreatment a smaller quantity of resist is needed than when
the resist is added to the washing liquor. As a result of this ad-
dition the white ground of the fibers is not stained by unfixed
dyestuff during the washing operation.

Parts in the following Examples are by weight.

EXAMPLE 1

Textured hosiery from an adipic acid/hex-
amethylene diamine condensate is treated. The treatment
takes 30 minutes. The liquor has a goods-to-lGuo ratio of 1 : 
40, a temperature of 80° C., a pH value of 3.5 (adjusted with
acetic acid) and contains 2 percent, referred to the weight of
the fibers, of the polycondensate, described below, of a
phenol/sulphuric acid reaction product with formaldehyde.
The material is then rinsed for a short time and dried.

The goods thus pretreated are then printed with a printing
paste consisting of:

30 parts of the dyestuff c.l. Acid Orange 47 of the formula

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H₂C₂
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50 parts of thiourea
50 parts of thiodiethyleneglycol
510 parts of water
300 parts of a 12 percent aqueous solution of a commercial,
modified locust bean gum
60 parts of ammonium tartrate solution of 15° Be.

The printed material is dried and steamed for 20 minutes in a
conventional ager at 102° C., then rinsed in cold water,
washed in a bath heated at 50° C., containing in 1,000 parts of
water 2 parts of any desired synthetic detergent, and once
more rinsed for a short time in cold water. A brilliant orange
print is obtained. The unprinted areas remain white, whereas
when a print that has not been pretreated is washed, the white
areas display a distinct, undesirable coloration.

PREPARATION OF THE RESIST

50 Grams of concentrated sulphuric acid are stirred drop-
wise at room temperature into a suspension of 100 g. of 4,4-
dihydroxystilbene sulphone in 50 g. of acetic anhydride. The
temperature is then raised to about 100° C., and after 6 hours
300 ml of water are added portionwise, while at the same time 311 ml of liquid are distilled off under reduced pressure. The residual reaction mixture is mixed with a reaction mixture obtained in the manufacture of ortho-cresol-4-sulphonic acid from 64.9 g of ortho-cresol in 75 g of acetic anhydride with 75 g of concentrated sulphuric acid. Then 80 g of 50 percent aqueous formaldehyde solution are added to the mixture of these two reaction mixtures. The whole is heated for 5 hours at 100° to 105° C. and then allowed to cool. The thickly liquid condensation product, 40 mol percent of which consist of 4,4'-dihydroxydiphenylsulphone-3-sulphonic acid and 60 mol percent of ortho-cresol-4-sulphonic acid, is then treated with 30 percent sodium hydroxide solution until a pH value of 7 has been reached. The resulting product can be diluted with water in any desired proportion.

A product having similar, good properties is obtained with a suspension of 200 g of 4,4'-dihydroxydiphenylsulphone in 100 g of acetic anhydride is sulphonated with 100 g of concentrated sulphuric acid, 300 ml of water are added and 283 ml of liquid are distilled off. When this reaction mixture is mixed with the reaction mixture obtained in the manufacture of ortho-cresol-4-sulphonic acid from 21.6 g of ortho-cresol in 25 g of acetic anhydride with 25 g of concentrated sulphuric acid, and the two components are condensed with 80 g of 30 percent aqueous formaldehyde solution, a product is obtained in which 50 mol percent consist of sulphone.

EXAMPLE 2

Textured hosiery from polyamide 6.6 is impregnated on a padded to a weight increase after squeezing of about 5 percent with a preparation containing in 1000 parts of water 20 parts of the resist described below, and the material is then dried at 80° C.

The material thus pretreated and dried is then printed with a printing paste consisting of 30 parts of the 1:2-chromium complex of the dyestuff, prepared according to U. S. Pat. No. 2,565,895, and of the formula

\[
\text{OH} \quad \text{OH} \quad \text{OH} \\
\text{N-N-C-N} \quad \text{N-C-N} \\
\text{H-C} 
\]

50 parts of thiourea 50 parts of thiodiethyleneglycol 50 parts of water 300 parts of a 12 percent aqueous solution of a commercial, modified locust bean gum

The printed hosiery is dried and steamed for 20 minutes at 102° C. in a conventional ager, then rinsed cold, washed at 60° C. in a bath containing in 1,000 parts of water 2 parts of any desired synthetic detergent, and once more rinsed in cold water. A scarlet print is obtained and the unprinted areas remain white, whereas a print that has not been pretreated displays distinctly coloured white areas after washing.

MANUFACTURE OF THE RESIST

Thirty-five grams of concentrated sulphuric acid are stirred at room temperature dropwise into a suspension of 70 g of 4,4'-dihydroxydiphenylsulphone in 35 g of acetic anhydride. The temperature is then raised to 98° to 100° C. and maintained at this value for 6 hours. 75 ml of water are then added portion wise under a pressure of 30 to 50 mm. Hg. and at the same time 88 ml of liquid are distilled out of the reaction mixture. The residual reaction mixture is diluted with another 20 ml of water, mixed with 20 g of 30 percent aqueous formaldehyde solution and the whole is heated for 5 hours at 100° to 105° C., then allowed to cool, and 30 percent sodium hydroxide solution is added to the thickly liquid condensation product until a pH value of 7 has been reached. The resulting product can be diluted with water in any desired proportion. A product having similar properties is obtained when the reaction mixture is adjusted to a pH value from 8 to 8.5 by means of 30 percent sodium hydroxide solution before the formaldehyde is added.

EXAMPLE 3

Warps hosiery from polyamide 6 is pretreated as described in Example 1.

Similar, advantageous results are obtained by printing with a printing paste prepared as described in Example 1 but containing instead of the dyestuff mentioned there:

30 parts of the 1:1-chromium complex of the dyestuff of the formula

\[
\text{OH} \quad \text{OH} \\
\text{C-N} \\
\text{H-C} \\
\text{H-NBO}_{3} \\
\text{C.1. Acid Blue 170} 
\]

We claim:

1. A process for printing synthetic nitrogenous fibers with dyestuffs which are more than one sulfonate group, which dyestuffs are soluble or dispersible in water which comprises pretreating the fibers to be printed with an aqueous preparation consisting substantially of at least one fiber-substantive, water-soluble, anionic resist for synthetic polyamide fibers selected from the group consisting of polycondensates of diarylsulphones containing at least one phenolic hydroxy group with formaldehyde, whereupon the fibers so treated are dried and then printed under textile printing conditions with the printing paste containing the dyestuff.

2. A process according to claim 1, wherein synthetic polyamide fibers are printed.

3. A process according to claim 1, wherein the fibers are pretreated by the exhaustion method in an acid bath having a temperature of 80° to 100° C.

4. A process according to claim 3, wherein the pH-value is 3 to 5.

5. Process according to claim 1, wherein the diarylsulphone is made from monomeric hydroxaryl compounds.

6. Process according to claim 5, wherein the diarylsulphone is a dihydroxydiphenylsulphone.

7. Process according to claim 1, wherein the polycondensates consist of dihydroxydiphenylsulphones and hydroxybenzenesulfonic acid the content of sulphone being at least 30 mol percent.

8. Process according to claim 1, wherein the polycondensates consist of sulfonic acids of dihydroxydiphenylsulphones.

9. Process according to claim 1, wherein the dyestuffs are acid, metal-free wool dyes.

10. Process according to claim 1, wherein the dyestuffs are water-soluble 1:2-metal complex dyestuffs.

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Cover page, under "[73]", after "Assignee:"
delete "CIBA LIMITED" and substitute --- CIBA-GEIGY AG ---

Signed and sealed this 2nd day of April 1974.

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

G. MARSHALL DANN
Commissioner of Patents