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SIMULTANEOUS AMINOPLAST IMPREGNATION AND DIRECT DYEING BY THE PAD DWELL PROCESS FOLLOWED BY HOT CURING OF THE AMINOPLAST

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This invention relates to a process for dyeing cellulosic fibers, and more particularly relates to a process for dyeing cellulosic fibers which comprises employing an amino resin treating agent such as an aminoplast precursor as an accelerator for direct dyes to effect concurrent level dyeing and resin treatment.

The use of reactive dyes, acid dyes, basic dyes or the like has heretofore proposed in order to concurrently effect both dyeing and resin treatment. However, according to any of these techniques, it has been very difficult to obtain level dyeing since the resulting dyeings have become uneven by various causes. For example, there have been found the migration of the dyes to the surface of textile fabrics caused by the migration of water in a drying process, the unevenness at a selvage formed in a tentering process, the unevenness formed by heating, etc. As non-substantive dyes have been fixed with an amino resin for resin treatment in such techniques, the dyes as well as the resin have been released by washing, and it has been impossible to obtain a dyeing of good fastnesses.

According to the present invention, there is provided a process for dyeing cellulosic fibers which comprises padding a textile fabric with an aqueous solution of direct dyes containing amino resin treating agent and acid catalyst, and allowing the padded fabric to stand in (dwell) a wet state while suppressing the evaporation of water, without immediately drying the fabric, to sufficiently dye the fabric, and then drying and baking the treated fabric to effect concurrent dyeing and resin treatment.

When cellulosic fibers are padded with an aqueous solution of a direct dye and the padded fibers are allowed to stand at room temperature, it takes about 24 hours to approach adsorption equilibrium. However, if an amino resin treating agent is added thereto, the time required to approach adsorbtion equilibrium may be reduced to only one to two hours and a high degree dye absorption (dye up-take) can be obtained.

The reason why such an accelerating effect is obtained by the addition of the amino resin treating agent has not been sufficiently explained. The facts that the diffusion of the dye is facilitated by the improved swelling of the cellulosic fibers and that the diffusion of direct dyes is improved by the interaction of the amino resin treating agent having a very rapid diffusion rate are considered as the reason for this.

Maintaining the padded fibers in a wet state while suppressing the evaporation of water permits level dyeing at a low temperature and in a short time, which has not been achieved by any previous known technique, and perfectly obviates the disadavantage caused by the migration of dyes. According to the process of the present invention, through dyeing is accomplished prior to a heating process while preventing the migration of the dyes, and the unevenness of the resultant dyeing caused by the migration of the dyes, which has been a problem difficult to solve in the known art, can be obviated.

By subjecting the fibers thus treated to a baking process, part of direct color which has been loosely attached to the fibers may be fixed on the fibers owing to the condensation of the resin treating agent. Therefore, the up-take of the dyes reaches about 100 percent and a subsequent water washing, which has been required in any previous known technique, can be omitted.

The fibers to which the process of the present invention can be applied include viscose rayon, cuprammonium rayon, polynosic rayon, cotton, hemp and the like in the form of yarn, fabrics, knitting or the like.

Impregnation with treating liquid may be carried out by spraying, padding, a mangle or dipping. In the process of the present invention the use of direct dyes is effective, and the use of the other dyes is undesirable in that a uniform dyeing can not be obtained and the fastnesses of the resultant dyeing are also poor. Even if direct dyes are used, it is important to thoroughly proceed with dyeing of the padded fibers in a wet state as in the present process. It is very dangerous to immediately subject the padded fibers to a drying process since uneven dyeings may be given by such an operation. The other dyes have no affinity to cellulosics, and the dyeing can proceed no further. This invention is limitted to only the dyeing with direct dyes. The dyes other than direct dyes have no affinity to cellulosics. These dyes do not make proper dyeing in the treating solution of this invention.

The amino resin treating agents which may be employed in the process of the present invention include methylolurea, methylolmelamine, methylol ethylene urea, methylol hydroxyethylene urea, methylolurone and a methyl etherified product thereof or a mixture thereof. They may be employed singly or in combination in an amount necessary to give crease resistance, shrink resistance, shaping property, wash and wear property and the other effects of the resin on the fibrous material.

In order to maintain the padded fibrous material in a wet state while suppressing the evaporation of water, the material may be immediately rolled up and then wrapped in an air impermeable sheet, for example, plastic sheet produced from synthetic materials such as polyvinyl chloride, polyvinylidene chloride, polyamide, polyester, polyolefin, polyacrylic resin, etc. Alternatively, the material may be either immediately packed in a box or immediately introduced into a room of high humidity.

The time for which the padded fibrous material is maintained in a wet state may be generally about one to three hours at ordinary temperature. As the diffusion rates of direct colors within a fiber depends upon the molecular structure of the colors, time of such an effective maintenance ranges widely. It is possible to reduce the maintenance time by increasing the maintenance temperature. The maintenance time varies also according to the kind of cellulosic substance to be dyed. Thus the maintenance time may be relatively short for cuprammonium rayon, while it should be relatively long for cotton.

If a urea-formaldehyde resin treating agent or a melamineformaldehyde resin treating agent is employed, it is possible to improve the crease resistance of the dyed fabric in a wet state and to improve the wash and wear property of the fabric by allowing the padded fabric for a short period of time at 80° to 90° C. or overnight at room temperature.

For the purpose of regulating the hand temper of the dyed fabric or imparting water resisting property to the fabric, conventional softner or water repellents may be employed together with the resin treating agent.

The acid catalyst should not be one which may cause the aggregation of the color followed by its precipitation which makes impossible a uniform impregnation of dyes. The catalysts of high acidity, therefore, are not desirable. We have found that the most preferable acid catalysts which may be used in the process of the present inven-

tion are hydrochlorides of organic amines and zinc nitrate and a mixture thereof.

The baking may be carried out under customary resin treatment conditions. For example, it may be carried out at 120° to 150° C. for 3 to 8 minutes. If the baking is carried out with superheated steam, it is possible to improve further the fastnesses of a heavy color dyeing.

The present invention is illustrated but not limited by the following examples. In the examples fastness to washing was tested according to JIS (Japanese Industrial Standards) L–1045 corresponding to ISO Method MC–2, and fastness to rubbing according to JIS L–1048 corresponding to AATCC 8–1961, Crock-meter method, and crease resistance according to JIS L–1003 corresponding to AATCC 66–1959, Clerk's method.

Example 1

A hank of cuprammonium rayon of 75 deniers/54 filaments was immersed for one minute in a treating solution having the following composition:

	G./l.
A direct black dye	15
Resin treating agent [1]	200
Zinc nitrate	5
N-octadecyl-N-ethylene urea [2]	8

[1] The resin treating agent was prepared by adding 5% sodium hydroxide to 1,540 cc. of 40% formalin to give a pH of 8 and then adding one kg. of urea thereto and heating the mixture at 80° C. for 20 minutes with stirring and cooling the resultant product.

[2] The material is a softener and water repellent. The treated hank was immediately centrifuged and then wrapped in a vinyl chloride sheet. After standing at room temperature for two hours, the hank was dried at 70° C.

A taffeta was woven by employing the above dyed yarn as warp and then baked at 140° C. for four minutes.

Thus a uniformly dyed fabric was obtained having excellent fastnesses and good crease resistance as shown in the following Table 1.

TABLE 1

Composition of treating bath	Fastness to washing	Fastness to rubbing	Crease resistance, percent
Example 1	5	5	65
Ex. 1 without resin treating agent	1	1	38

Example 2

Scoured 100 deniers/40 filaments viscose rayon taffeta was padded with a treating solution having the following composition:

	G./l.
A direct blue dye [1]	10
Resin treating agent [2]	180
Zinc nitrate	5

[1] The padded fabric obtained 72% wet pick-ups and is immediately rolled up and wrapped in a vinyl chloride sheet. After standing at room temperature for two hours, the treated fabric was dried at 80° C. and then baked at 140° C. for five minutes.

[2] The treating agent was prepared by adding 8 cc. of 5 percent sodium hydroxide to 800 cc. of 40 percent formalin to give a pH of 9 and then adding 500 grams of melamine thereto and heating the mixture at 80° C. for 30 minutes and cooling the resultant product.

Thus a uniformly blue dyed fabric was obtained having excellent fastnesses and good crease resistance as shown in the following Table 2.

TABLE 2

Composition of treating bath	Fastness to washing	Fastness to rubbing	Crease resistance, percent
Example 2	4	4	60
Ex. 2 without resin treating agent	1	1	39

Example 3

Tricot half of 50 deniers/38 filaments cuprammonium rayon was padded with a treating solution having the following composition:

	G./l.
C.I. Direct Red 95	3
Resin treating agent [1]	200
Zinc nitrate	5
Silicone emulsion	10

[1] The resin treating agent was prepared in the same manner as in Example 1.

The fabric is squeezed by a padded mangle to obtain 92 percent mangle expression, and immediately put into a covered box. After standing at room temperature for two hours, the fabric was baked with a pin tenter at 150° C. for five minutes.

Thus a uniformly dyed fabric was obtained having excellent fastnesses and a low shrinkage percentage as shown in following Table 3.

TABLE 3

Composition of padding bath	Fastness to washing	Fastness to rubbing	Washing shrinkage, percent	
			Coarse	Well
Example 3	5	5	0.5	1.5
Ex. 3 without resin treating agent	1	1	4.8	9.7

Example 4

Scoured twill of 75 deniers/33 filaments viscose rayon was padded at 40° C. with a treating solution having the following composition:

	G./l.
C.I. Direct Yellow 50 (C.I. 29025)	18
Dimethylethylene urea	70
2-amino-2-methyl-1-propanol hydrochloride	15

The material is squeezed by a padding mangle to obtain 70% wet pick-ups and is immediately allowed to stand in a room having a humidity of 80 percent and a temperature of 70° C. for 30 minutes. The fabric was then dried and baked with superheated steam at 130° C. for three minutes. Thus a uniformly dyed fabric was obtained having a fastness to washing of grade 5 and a good crease resistance.

Example 5

Cotton calico which had been previously scoured and bleached by a usual method was at 50° C. padded with a treating solution having the following composition:

	G./l.
C.I. Direct Black 19 (C.I. 35255)	20
Dimethylol hydroxyethylene urea	60
Trimethoxymethyl melamine	25
2-amino-2-methyl-1-propanol HCl	10
Zinc nitrate	4
Silicone emulsion	8

The padded material obtained 65 percent wet pick-ups, and is immediately allowed to stand in a room having a relative humidity of 85 percent and a temperature of 80° C. for one hour. The fabric was then dried at 70° C. and baked at 140° C. for four minutes. Thus a uniformly dyed fabric was obtained having a good crease resistance and a fastness to washing of grade 5.

Example 6

Scoured viscose rayon staple fiber muslin fabric was padded at room temperature with a treating solution having the following composition:

	G./l.
C.I. Direct Blue 71 (C.I. 34,140	15
Trimethylolmelamine	100
Zinc nitrate	5

The wet pick-ups of the padded fabric regulated 85% of the dried fabric, and is immediately rolled up and wrapped in a vinyl chloride sheet. After standing at room temperature for 12 hours, the fabric was dried at 70° C. and then baked at 140° C. for four minutes. Thus a uniformly dyed fabric was obtained having a good wet crease resistance and a fastness to washing of grade 5.

Example 7

A cake of 75 deniers/33 filaments viscose rayon was charged into a cake dyeing machine, and a treating solution having the following composition:

	G./l.
C.I. Direct Black 76 (C.I. 35,865)	6
Dimethylolurea	50
Monomethylolurea	60
2-amino-2-methyl-1-propanol hydrochloride	20
N-octadecyl-N-ethylene-urea (a softener)	20

was passed through the inside of the cake at a pressure of 10 meters water with the pump of the dyeing machine for five minutes. Then the cake was dehydrated by a one cake type centrifuge. The wet pick-ups of the treated cake was 85% of the dried cake, and was immediately wrapped in a vinyl chloride sheet. After standing for three hours at room temperature the cake was dried at 60° C. Twill was woven from thus dyed yarn. The resultant fabric was then baked at 140° C. for four minutes to obtain a uniformly dyed fabric having an excellent crease resistance and good fastnesses.

Example 8

6,000 ends of cuprammonium rayon yarns of 75 deniers/54 filaments which had been warped on a beam, was padded in 80 percent wet pick-up with a treating solution having the following composition:

	G./l.
C.I. Direct Red 95	8
Dimethylol ethylene erea	100
2-amino-2-methyl-1-propanol HCl	10
Silicone emulsion	20

Yarns were rewound on another beam, and the padded yarns on the rewound beam were wrapped in a vinyl chloride sheet. After standing at room temperature for two hours, the yarns were dried by passing them through a drying machine. Twill was woven from these yarns as warp and the 75 deniers/54 filaments cuprammonium rayon as shown in Example 1 as filling yarns, and the fabric was then baked at 140° C. for five minutes to obtain a uniformly dyed fabric having a good crease resistance and excellent fastnesses.

What we claim is:

1. A process for concurrent dyeing and resin treatment comprising the steps of:
   (a) padding cellulosic fibrous materials with an aqueous solution of a direct dye containing an aminoplast precursor treating agent and an acid catalyst and then allowing the padded fiber to stand in a wet state, while suppressing the evaporation of water,
   (b) baking the said materials thus treated with either dry heat or superheated steam.

2. A process according to claim 1, wherein said cellulose fiber is selected from the group consisting of viscose rayon, cuprammonium rayon, polynosic rayon, cotton, and hemp fibers.

3. A process according to claim 1 wherein said amino resin treating agent is selected from the group consisting of methylolurea, methylolmelamine, methylol ethylene urea, methylol hydroxyethylene urea, methylolurone and methyl etherified products thereof and a mixture thereof.

4. A process according to claim 1, wherein said acid catalyst is selected from the group consisting of hydrochlorides of organic amines and zinc nitrate and a mixture thereof.

5. A process according to claim 1 wherein said aqueous solution of a direct color further contains a conventional fiber softener or water repellent.

6. A process according to claim 1 wherein the padded fiber is allowed to stand in a wet state by rolling up and wrapping it in a plastic sheet.

7. A process according to claim 1, wherein the padded fiber is allowed to stand in a wet state by packing it in a covered box.

8. A process according to claim 1, wherein the padded fiber is allowed to stand in a wet state by introducing it into a room of a high humidity.

9. A process according to claim 1 wherein the padded fiber is allowed to stand in a wet state at ordinary temperature for 1 to 3 hours.

10. A process according to claim 1 wherein the padded fiber is allowed to stand in a wet state at 80° to 90° C. for a period of time shorter than one hour.

11. A process according to claim 1 wherein said baking is effected at a temperature of 120° to 150° C. for 3 to 8 minutes.

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