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von der Eltz et al.

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[54] **PROCESS FOR SPACE-DYEING OF CELLULOSE FIBERS**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **8/14,** 8/46, 8/25

[51] **Int. Cl.** **D06p 1/12,** D06p 1/14

[58] **Field of Search** ..... 8/14, 1 XA, 1 S

[56] **References Cited**

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[57] **ABSTRACT**

Process for the space-dyeing of yarn or sliver made from cellulose fibers, wherein a wound package of the said textile material is first impregnated with an aqueous liquor containing an alkaline substance and at least one component capable of entering into azo coupling, then — at least at one selected portion of the bobbin — one or several acid aqueous solutions each containing at least one diazonium compound of an aromatic amine and at least one phthalocyanine dyestuff having quaternary ammonium groups are injected, and finally the goods so treated are exposed to the action of heat for fixation of the phthalocyanine dyestuffs and for development of the azo dyestuffs.

2 Claims, No Drawings

PROCESS FOR SPACE-DYEING OF CELLULOSE FIBERS

The present invention relates to a process for the space-dyeing of cellulose fibers.

From German Patent No. 1,244,104 it is known to dye yarn containing cellulose fibers with reactive dyestuffs irregularly in such a manner that no repetition of pattern occurs on the finished textile materials after the yarn thus dyed has been woven or knitted. According to this dyeing method known as "space-dyeing", an alkaline reactive dyestuff solution is injected into the wound-up fibrous material at different places and the wound package is then allowed to dwell until the dyestuff has reacted with the cellulose.

This known process, however, has the disadvantage that the reactive dyestuffs dissolved in the alkaline medium are stable for only a limited period of time since the formation of the dyestuff/fiber-linkage is accompanied by a secondary reaction of the reactive component of these dyestuffs with the hydroxyl ions of the aqueous dyebath. The products thus formed by hydrolysis, however, can no longer enter a convalent bond with the cellulose and, therefore, the color yield is appreciably reduced. Moreover, for the same reason, the remaining dyebath must not be stored for a prolonged period of time but has to be prepared freshly for each injection.

Another disadvantage is the long dwelling time which is required, according to the prior art, for the fixation of the dyestuffs on the fiber.

Finally, the use of reactive dyestuffs generally involves relatively high dyestuff costs. If, on the contrary, the comparatively inexpensive direct dyestuffs are used for the injection solutions, as disclosed in Austrian Patent No. 104,379, the yarns which have been random dyed in this manner cannot be employed for certain textile articles since the dyeings produced with these dyestuffs have a poor fastness to wet processing. If, for this purpose, the ice color technique is applied, according to which the wound-up yarn is first impregnated with the coupling component dissolved in an alkaline medium, and the diazo components are then injected after or without intermediate drying, very fast dyeings are obtained, the dyestuff costs of which, especially for deep shades, are lower than those arising from the use of reactive dyestuffs; however, with this class of dyestuffs, it is very difficult — and partly impossible — to achieve fashionable intermediate shades by means of mixtures of the coupling or of the diazo components. Although this method for space-dyeing of yarn according to the ice color technique is novel, it is not claimed as the subject of the present invention.

It has now been found that yarn or sliver made from cellulose fibers can be space-dyed by injection of dyeing liquid into the fibrous material at least at one selected portion of the wound package, with dyeing solutions that are more stable than the dyebaths according to German Patent No. 1,244,104, without long dwelling periods for the fixation of the dyestuffs, to yield dyeings having fashionable shades of good fastness to wet processing, by first impregnating a bobbin of the said textile material with an aqueous liquor containing an alkaline substance and at least one component capable of entering into azo coupling, then injecting one or several acid aqueous solutions containing at least one diazonium compound of an aromatic amine and at least one phthalocyanine dyestuff having quaternary ammonium groups, and finally exposing the goods thus treated to the action of heat for fixation of the phthalocyanine dyestuffs and for development of the azo dyestuffs.

In the course of the above-disclosed process, the azo dyestuffs applied according to the ice color technique yield, in the yarn bobbins, dyeings which are tinged by the phthalocyanine derivatives.

According to the process of the invention, pretreatment of the wound-up yarns with the impregnation baths containing the alkaline substances and the coupling components is advantageously carried out in a dyeing apparatus, for example a device for dyeing cross-wound bobbins. This process step ensures simultaneous impregnation of a large number of bobbins and thus does practically not reduce the production rate, especially since the second lot can be already impregnated while the bobbins of the first lot are injected with the solution of the diazo component and the phthalocyanine derivative. Moreover, the wound packages pretreated with alkali and coupling component can be stored and taken to use at any time and in any amount since the impregnated bobbins, after drying, are stable upon storage for an almost unlimited period of time if care is taken that any access of moisture is prevented.

For the impregnation of the wound-up yarn, the coupling components are used, preferably those of substantive nature toward the fibrous material. These are compounds which couple in vicinal position to a hydroxy group and do not have any solubilizing group, especially arylamides of aromatic or heterocyclic o-hydroxy-carboxylic acids or of acylacetic acids, as well as other aromatic or heterocyclic hydroxy compounds and compounds containing an enolizable or enolized ketomethylene group in a heterocyclic ring. Such substances are, for example, the arylamides of 2,3-hydroxy-naphthoic acid, 2-hydroxy-anthracene-3-carboxylic acid, 4-hydroxy-diphenyl-3-carboxylic acid, 2-hydroxy-carbazole-3-carboxylic acid, 3-hydroxy-diphenylene-oxide-2-carboxylic acid, 3-hydroxy-diphenylene-sulfide-2-carboxylic acid, acetoacetic acid or of benzoylacetic acid. Furthermore, hydroxybenzenes, polyhydroxy-benzenes, hydroxy-naphthalenes and pyrazolones have proved suitable among others, which may be substituted by non-ionic radicals.

As alkaline agents, any inorganic alkaline substance may be used in the impregnation baths; preferably sodium hydroxide solution. These baths may also contain commercial-type nonionic or anionic wetting agents for a better penetration of the yarn; for example wetting agents on the basis of the reaction products of alkylene oxides with alkyl phenols, of mixtures consisting of high-molecular oxyalkylation products of alkanols or alkyl-phenols and alkyl-sulfuric acid esters of alkane- or alkyl-aryl-sulfonic acids, or of naphthalene-sulfonic acid derivatives. The alkaline agent applied together with the impregnation liquor serves equally for the fixation of the phthalocyanine dyestuffs to be injected subsequently.

The fibrous material is treated with the impregnation bath for 10 to 40 minutes, preferably for 30 minutes, at a temperature of from 20° to 70°C, preferably of from 30° to 50°C.

After impregnation, the bobbins are centrifuged or sucked and can immediately be conducted to injection

while still moist. Intermediate drying of the pre-treated goods is not necessary but it results in a higher liquor absorption during the subsequent injection since the fibrous material has a better absorptive power when dry.

The phthalocyanine dyestuffs to be used jointly with the diazo components for the injection of the yarn bobbins according to the invention have been disclosed in detail in the technical literature. They are metal-containing phthalocyanine derivatives containing two to four quaternary ammonium groups linked via methylene bridges to the benzene nuclei of the molecule. In these products, the complex-bound metals are nickel, cobalt and especially copper. The quaternary nitrogen atom of the salt-binding radical carries identical or different lower alkyl-or hydroxy-alkyl groups; the aniomic constituent is the hydroxyl ion or the anion of an inorganic or organic acid, preferably acetate. Compounds of this type have, for example, been disclosed in German Patent No. 1 220 065. Such phthalocyanine derivatives which are soluble in water owing to the salt-like substituents are split within their side chains by action of heat in the presence of alkaline agents and, optionally of reducing agents, and therefore can be converted into an unsoluble pigment which can be fixed as such on the cellulose fiber.

As diazonium compoinds for the development of the azo dyestuffs, any primary aromatic amine may be used, which yields water-insoluble mono-, dis- or polyazo dyestuffs with the above-specified coupling components, thus the tetrazonium compounds of aromatic diamines and the fast color salts obtainable by stabilization from the corresponding amines, too. The said suitable amines, among them amino-azo dyestuffs, have no ionic substituents and are known as diazo components from the ice color technique.

According to the process of the invention, the acid solution of the phthalocyanine dyestuff and of the diazonium compound is injected under pressure into the package that has been pre-treated with the coupling component, at least at one selected portion of the wound material. The coloring liquid thus spreads out along the limited injection zone, so that along the length of the yarn of the wound package, dyed and undyed areas of varying lengths are produced at quite irregular intervals. The amount of the mixture of phthalocyanine derivative and of diazo component injected may, of course, be varied. It depends on the desired ratio of dyed and undyed yarn. The injection of the dyeing liquor at several locations may be carried out separately or simultaneously. To obtain a definite non-repeating pattern the injection positions must, of course, be selected in a suitable manner. In order to produce a multi-color spotted yarn according to the invention, dyeing liquors of a different shade may also be injected into the package side by side, either separately or simultaneously.

The injection mechanism contains as the most essential element a hollow injection needle which has a perforated shaft (for more details see Astrodyed (registered trademark) Technical Manual, Astro Dye Works, Inc., Calhoun, Ga. 30701/USA, page 12, FIG. 14). The length of the needle approximately corresponds to the thickness of the wound package to be treated. The position of the injection needle support can be rearranged so that the point of the injection needle can penetrate the package from the outside yarn layer to a desired position inside the thickness of the winding, whereupon the inflow of the dyeing liquor sets in. The flow of the liquor may be stopped again by a reversed motion of the needle support.

According to the novel process, generally acid aqueous solutions of the diazo component and the phthalocyanine dyestuff are injected into the wound-up fibrous material. The pH value of these solutions is adjusted to 4.5 –6.9 by means of known buffer mixtures or weak acids, especially acetic acid. In this connection, it is advantageous to feed the substances used as alkali-binders at such a rate that the pH of the bobbins, after the injection of the solution of the dyestuff and the diazo compound, is beyond the neutral point within a weakly acid range. In some cases, it is suitable to add commercial-type non-ionic dispersants, for example on the basis of the reaction products of alkylene oxides with cresol-camphor resins, or of mixtures consisting of oxyalkylated fatty alcohols and high-molecular-weight polyglycol ethers, to the injection solutions. In most cases, injection liquors or about room temperatures are used.

After injection of the dyeing solutions, the goods are exposed to the action of heat continuously or batchwise at a temperature of 100° to 130°C, preferably by steaming for 30 seconds to 10 minutes, preferably for 1 – 4 minutes, at 100°to 110°C, preferably at 102° – 106°C, for fixation of the phthalocyanine derivatives and for development of the azo dyestuffs. The bobbins are finally after-treated in a boiling aqueous liquor and dried. The dyeings produced according to the invention show the good fastness properties typical of the phthalocyanine dyestuffs and the ice colors.

The textile articles dyed according to the process of the invention may contain the cellulose fibers in a natural or regenerated form. What has been said for the dyeing of yarn is also true for the dyeing of sliver.

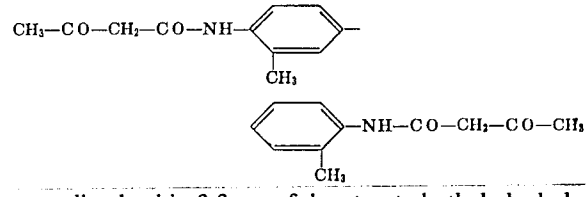
The following Example serves to illustrate the invention.

EXAMPLE

Seven hundred twenty Grams of wound-up cotton yarn were treated at 35°C for 30 minutes in a dyeing apparatus, at a goods-to-liquor ratio of 1:25, with the impregnation bath hereinafter disclosed. The wound package was then sucked and dried. At different locations of the bobbin, the below-indicated injection solutions (a), (b), (c), and (d) were injected into the ball of yarn thus impregnated, the liquor absorption of the fibrous material being 150%, calculated on the weight of the dry goods. The material thus dyed was then steamed for 1 to 2 minutes at 103°C for the fixation of the dyestuff and subsequently after-treated at the boil in a dyeing apparatus with an aqueous liquor with the addition of a non-ionic synthetic detergent and finally dried.

Impregnation bath

3.3 Grams of the compound of the formula



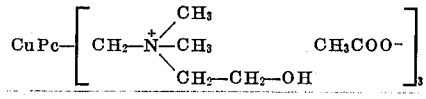
were dissolved in 3.3 cc. of denaturated ethyl alcohol, 3.3 cc. of sodium hydroxide solution of 38°Be and 6.6 cc. of hot water. 5 Grams of a wetting agent on the

basis of mixtures consisting of high-molecular-weight oxyalkylation products of alkanols or alkyl-phenols and alkyl-sulfuric acid esters of alkane- or alkylaryl-sulfonic acids, were added to the solution thus obtained and the liquor was adjusted to 1 liter by diluting with cold water.

Injection solution (a) :

1 Liter of water contained

30 g of the dyestuff of the formula



(CuPc = copper phthalocyanine)

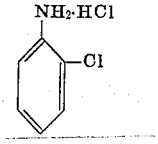
and 3 cc. of acetic acid (of 50% strength).

Injection solution (b)

1 Liter of water contained

30 g of the dyestuff corresponding to solution (a),

10 g of the amine of the formula



which had been diazotized by means of sodium nitrite and hydrocholoric acid and the diazonium salt solution obtained had been neutralized by adding sodium acetate,

6.5 cc. of acetic acid (of 50% strength) and

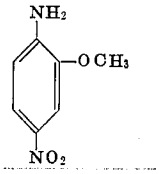
1 g of a dispersing agent on the basis of mixtures of oxyalkylated fatty alcohols and high-molecular-weight polyglycol ethers.

Injection solution (c)

1 Liter of water contained

30 g of the dyestuff corresponding to solution (a),

9 g of the amine of the formula



which had been diazotized by means of sodium nitrite and hydrochloric acid and the diazonium salt solution obtained was neutralized by adding sodium acetate,

5.4 cc. of acetic acid (of 50% strength) and

1 g of a dispersing agent as indicated for solution (b).

Injection solution (d)

1 Liter of water contained

9 g of the amine corresponding to solution (c), which had been diazotized as indicated above and the diazonium salt solution obtained had been neutralized in an analogous manner,

5.4 cc. of acetic acid (of 50% strength) and

1 g of a dispersing agent corresponding to solution (b).

A bobbin was obtained, the yarn of which showed, at the injections positions, a brilliant intense turquois shade with the soution (a), an intense verdigris green shade with the solution (b), an olive shade with the solution (c) and a brilliant golden orange shade with the solution (d).

Corresponding results as those of the preceding Example can be obtained using cellulose sliver for the dyeings instead of yarn.

What we claim is:

1. In a process for the space-dyeing of yarn or sliver made from cellulose fibers by injection of dyeing liquid into the fibrous material at least at one selected portion of the wound package, the improvement which comprises: first impregnating a bobbin of the said textile material with an aqueous liquor containing an alkaline substance and at least one coupler component capable of entering into azo coupling, then injecting one or several acid aqueous solutions each containing a mixture of at least one diazonium compound of an aromatic amine and at least one basic-modified, metalliferous phthalocyanine dyestuff having quaternary ammonium groups, said dyestuff being one wherein from two to four short chain alkyl-short chain hydroxy alkyl substituted quaternary ammonium groups are linked to a benzene nuclei of the dyestuff molecule via methylene bridges, and finally exposing the goods so treated to the action of heat for fixation of the phthalocyanine dyestuffs and for development of the azo dyestuffs.

2. A process as claimed in claim **1**, wherein the fixation of the dyestuffs is carried out by steaming.

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