

UNITED STATES PATENT OFFICE

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PROCESS OF DYEING GLASS FIBERS

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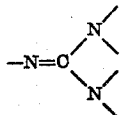
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Fibers are known which as such have no affinity for dyestuffs on account of their composition. Numerous experiments have been made in order to dye such products, such as fibrous materials from glass or vinyl polymerisation products, for example, Vinyon or Pe-Ce fibers, with organic dyestuffs. Up to now it has however not been possible to solve this problem satisfactorily.

The surprising observation has now been made that soluble products produced by the interaction of formaldehyde and compounds which contain at least once the atom grouping



are not of cyclic character and which consist of elements the atomic weight of which is not greater than 16 and which contain in their molecule in relation to carbon less oxygen than urea, for example transformation products of cyanamide, such as dicyandiamide or dicyandiamidine or guanidine, possess the characteristic property of precipitating onto fibrous materials having as such no affinity for dyestuffs, thus imparting to the treated material a remarkable affinity for water-soluble organic dyestuffs.

This unexpected property forms the basis of a new process for dyeing fibers, such as fibers from glass or vinyl polymerisation products, which consists in pretreating these fibers first of all with the above described reaction products and then treating the material, either immediately after the pretreatment or after rinsing or drying at ordinary or raised temperature, with water-soluble organic dyestuffs containing at least one sulfonic acid group.

The fibrous material can be used as such or after desizing; it can also be subjected to a pretreatment with acids or alkalis prior to the treatment with the above described reaction products. For example, glass fiber can be pretreated with hydrofluoric acid.

Depending on the nature of the reaction product from formaldehyde, the treatment with said reaction product can be performed in an acid, neutral or weakly alkaline medium. The operation is carried out at ordinary temperature; as a rule a single reaction of short duration is sufficient. The material is then rinsed in cold water, dried at ordinary or raised temperature and dyed. It can also be introduced into the dyebath after the treatment, the temperature of the bath being selected so as to suit the properties of the respec-

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tive fiber. In the case of glass fiber it is appropriate to work in a warm bath, for example at 75-90° C., in the case of fibers which do not endure higher temperatures such as fibers from vinyl polymerisation products, dyeing cannot be effected at the boil, and it is advantageous to work at an average temperature of for example 50° C.

The dyestuff is relatively rapidly absorbed by the fiber. The material is then rinsed and dried. If deeper shades are desired, the whole dyeing process (pre-treatment and dyeing) can be repeated, the intensity of the dyeings being dependent on the quantity of the formaldehyde product fixed onto the fiber. The dyeings obtained with the present process are fast to water; they can also be fast to light when suitably selecting the dyestuffs.

The lustre of the artificial fiber is generally reduced by dyeing the vinyl polymerisation products. The lustre can be easily restored by subjecting the dyed material to a treatment with suitable swelling agents. This treatment is appropriately carried out in an aqueous medium, for example with aqueous solutions of the known swelling agents for vinyl polymerisation products, for example phenol, resorcin, diethyleneglycol, acetone, and the like.

Dyestuffs suitable for dyeing these materials are quite generally water-soluble dyestuffs containing at least one sulfonic acid group, it being immaterial whether they are acid wool dyestuffs or direct dyeing cotton dyestuffs. Dyestuffs containing metal in complex union can also be used. If dyestuffs are used which can be after-treated with agents yielding metal, e. g. copper compounds, the dyed materials can also be after-treated.

Of the reaction products from formaldehyde characterized in the second paragraph of column 1 it is known that they are capable of improving the wet fastness properties of dyeings produced on cellulose material with aid of water-soluble dyestuffs. However, it could not be anticipated in any way that they would have affinity for a material such as glass or vinyl polymerisation products. Moreover, the affinity for soluble dyestuffs of a material treated in such a manner is also surprising.

The following examples illustrate the invention, the parts being by weight:

Example 1

A fabric consisting of glass or Vinyon fiber is treated for ¼ hour at room temperature in a

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solution containing for 1000 parts of water 10 parts of a water-soluble product produced by the interaction of formaldehyde and dicyandiamidine and 1 part of ammonia, and after drying introduced into an aqueous solution of 0.5 per cent strength of Benzyl Violet 5BN (Colour Index No. 698) at 75 or 50° C. and dyed for 5 minutes. The material is then rinsed in cold water until the washing water is entirely clear. An intensive violet dyeing is obtained.

After treating with the reaction product from formaldehyde, the material can also be rinsed and introduced in the dyebath without previous drying.

The water-soluble product produced by the interaction of formaldehyde and dicyandiamidine has been dissolved according to the following prescription:

4 parts of the product were introduced into 4 parts of water of 35° C., while stirring, a thick paste being thus obtained. 16 parts of water of 35° C. containing 0.12 part of formic acid were added to this paste. The water-soluble product produced by the interaction of formaldehyde and dicyandiamidine can be prepared by allowing formaldehyde to act on dicyandiamidine in an alkaline medium.

Yellow, red to green dyeings are obtained with the following dyestuffs:

Amido Yellow E (Colour Index No. 11)

Kiton Fast Red 4BL (Colour Index, Supplement, page 44)

Brilliant Kition Red B (Colour Index No. 748)

Wool Green S (Colour Index No. 737)

Similar results are obtained when replacing the dicyandiamidine product by a reaction product from guanidine, cyanamide or dicyandiamide (cf. British Patent 515,847.)

The decrease of the lustre of the Vinyon fiber brought about by the product produced by the interaction of formaldehyde and dicyandiamidine and subsequent dyeing can be restored by treating the fiber in a cold bath containing per liter 40 grams of phenol.

Example 2

A fabric consisting of glass or Vinyon fiber is pretreated as indicated in Example 1 and after drying introduced into an aqueous solution of 0.5 per cent strength of Direct Fast Orange SE (Colour Index No. 326) at 75 or 50° C., and dyed for 5 minutes. The material is then rinsed in cold water until the washing water is entirely clear. A deep orange dyeing is obtained. The replacement of Direct Fast Orange SE by Direct Fast Scarlet SE (Colour Index No. 326), Direct Brown M (Colour Index No. 420), Direct Sky Blue green shade (Colour Index No. 518), Cotton Blue N (Colour Index No. 502), Melantherine BH (Colour Index No. 401) leads to red to blue or brown dyeings.

Example 3

A fabric consisting of glass or Vinyon fiber is pretreated as indicated in Example 1 and after drying introduced into an aqueous solution of 0.5 per cent strength of the complex copper compound of the azo-dyestuff from 2 mols of diazotized 1-amino-4-hydroxybenzene - 5 - sulfamide and 1 mol of 5:5'-dihydroxy-2:2'-dinaphthylamine-7:7'-disulfonic acid at 75 or 50° C., and dyed for 5 minutes. The material is dyed in cold water until the washing water is entirely clear. A strong violet dyeing is obtained.

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Brown dyeings which are fast to light are obtained with the complex copper compound of the trisazo dyestuff obtained by mixing the so-called intermediate product from 1 mol of tetrazotized 4:4'-diaminodiphenyl and 1 mol of salicylic acid with 1 mol of the monoazo dyestuff from resorcin and diazotized 1-amino-2-hydroxybenzene-4-sulfonic acid.

Example 4

A fabric consisting of glass or Vinyon fiber is pretreated as indicated in Example 1 and after drying introduced into an aqueous solution of 0.5 per cent strength of the complex chromium compound of the azo-dyestuff from diazotized 1-amino-2-hydroxybenzene-4-sulfamide and 1-(3'-sulfamide)-phenyl-3-methyl-5-pyrazolone at 75 or 50° C., and dyed for 5 minutes. The material is then rinsed in cold water until the washing water is entirely clear. A deep orange dyeing is obtained.

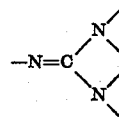
An orange dyeing is also obtained with the chromium compound of the azo-dyestuff from diazotized 1-hydroxy-2-amino-4-nitrobenzene-2-sulfonic acid and 1-methyl-3-methyl-5-pyrazolone; a rose colored dyeing is obtained with the chromium compound of the azo dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and the 1-(3'-sulfamide)-phenyl-3-methyl-5-pyrazolone; and a green dyeing is obtained with the chromium compound of the azo-dyestuff from diazotized 1-hydroxy-2-amino-5-nitrobenzene and 2-aminonaphthalene-6-sulfonic acid.

The complex copper compound of the azo-dyestuff from 1-phenyl-3-methyl-5-pyrazolone and the diazo compound of the leuco triphenylmethane dyestuff obtained itself by condensing 2 mols of dimethylaniline with 1 mol of meta-hydroxybenzaldehyde, disulfonating, nitrating and reducing the condensation product, leads also to a green dyeing.

Any loss of lustre of the Vinyon fiber can be restored by treating the fiber with phenol, as described in Example 1.

What I claim is:

1. A process of dyeing artificial fibrous material made of glass which as such has no affinity for dyestuffs, which comprises treating the said fibrous material with unhardened soluble products produced by the interaction of formaldehyde and a compound which contains not more than six hydrogen atoms, only one atom grouping



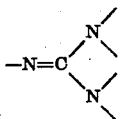
is not of cyclic character and which consists of elements the atomic weight of which is not greater than 16 and which contains in its molecule in relation to carbon less oxygen than urea, and then, while maintaining the unhardened character of the said products, treating the material with a water-soluble organic dyestuff which contains at least one sulfonic acid group.

2. A process of dyeing artificial fibrous material made of glass which as such has no affinity for dyestuffs, which comprises treating the said fibrous material with unhardened soluble products produced by the interaction of formaldehyde and dicyandiamidine, and then, while maintaining the unhardened character of the said products, treating the material with a water-soluble

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organic dyestuff which contains at least one sulfonic acid group.

3. Artificial fibrous material made of glass which as such has no affinity for dyestuffs and which has been treated first with unhardened soluble products produced by the interaction of formaldehyde and a compound which contains not more than six hydrogen atoms, only one atom grouping



is not of cyclic character and which consists of elements the atomic weight of which is not greater than 16 and which contains in its molecule in relation to carbon less oxygen than urea, and then, while maintaining the unhardened character of the said products, with a water-soluble organic dyestuff which contains at least one sulfonic acid group.

4. Artificial fibrous material made of glass which as such has no affinity for dyestuffs and which has been treated first with unhardened

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soluble products produced by the interaction of formaldehyde and dicyandiamidine, and then, while maintaining the unhardened character of the said products, with a water-soluble organic dyestuff which contains at least one sulfonic acid group.

HANS ROESTT.

REFERENCES CITED

- 10 The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,119,189	Widmer	May 31, 1938
15 2,169,546	Widmer	Aug. 15, 1939
2,189,918	Moncrieff	Feb. 13, 1940
2,257,076	Petke	Sept. 23, 1941
2,315,329	Hood	Mar. 30, 1943
20 2,317,965	Bestian	Apr. 27, 1943

FOREIGN PATENTS

Number	Country	Date
509,408	Great Britain	July 11, 1939
559,329	Great Britain	Feb. 15, 1944
25 768,282	France	May 14, 1934