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DYEINGS

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The present invention relates to a process of improving dyeings with wool dyestuffs, which are of insufficient fastness to wet treatment, on animalized cellulosic material.

It is known that the affinity of all kinds of cellulosic material, for instance fibers, bands and films of natural or regenerated cellulose or cellulose derivatives, to wool dyestuffs can be increased by incorporating with the material a basic substance. Since thereby the material, in its behaviour towards dyestuffs, is rendered more or less similar to animal fibers, this method of increasing the affinity to wool dyestuffs is commonly called "animalizing" and the basic substances incorporated with the cellulose material to produce the said effect are called "animalizing agents."

Animalizing may be performed, for instance, by incorporating with the material a compound containing basic nitrogen, phosphorus or sulfur. This may be done in any suitable stage of the production or treatment of the material. Among the compounds which may and have been used for this purpose there may be mentioned, for instance, polyalkylenepolyamines, polyalkylenimine, derivatives of urea and guanidine, basic condensation products from phenol, formaldehyde and aliphatic mono- or diamines, reaction products of halogenated aliphatic or aromatic hydrocarbons, esters, ketones, polymerisates, etc. with primary, secondary or tertiary amines of polyamines. Moreover, high molecular ammonium, phosphonium and sulfonium compounds and also reaction products of esters of polyalcohols with mono- or polybasic aliphatic or aromatic acids, for instance toluene sulfonic acid ester of starch with nitrogen containing compounds come into question.

Sometimes it is preferable not to incorporate the animalizing agents in the ready-made state with the material, but to produce the animalizing agent from suitable reactive components in and on the material itself, for instance by reacting suitable reactive compounds with nitrogen-, phosphorus- or sulfur-containing compounds. For instance, there may be added to the spinning solution of cellulose or cellulose derivatives halogenated substances like halogenated paraffin, halogenated polymerisates, or esters like the toluene sulfonic ester of starch, and the filaments, fibers, bands, films or the like precipitated from these solutions may be treated with basic substances like pyridine, ethylenediamine, polyalkylenepolyamines etc.

By all these methods it is possible to more or less increase the affinity of the cellulosic material to wool dyestuffs.

However, it has been a serious practical disadvantage of these processes that the dyeings produced on the material thus animalized were often not sufficiently fast towards wet treatments, for instance towards water, washing, fulling, potting, perspiration etc. This was especially the case with the best known animalizing agents which themselves do not sufficiently take on the fiber, i. e. which are not sufficiently substantive. Generally, therefore, dyeings produced on animalized cellulosic material, lacked the good fastness to wet treatments possessed by dyeings with the same dyestuffs on wool.

It is an object of our invention to avoid these disadvantages and to furnish a method which will allow to produce dyeings on animalized cellulosic material which are of similar fastness towards wet treatments as the dyeings produced on wool even when animalizing agents of insufficient substantivity have been used. This and other objects of our invention will be apparent from the following description thereof.

Broadly speaking, our invention consists in applying to the cellulosic material, besides the said animalizing agent or agents, a practically colorless, non-basic organic substance being of the character of a mordanting agent. By the term "mordanting agent" as used in the description of our invention and the claims annexed thereto, as customary in the art, such agents are meant which are capable of forming insoluble compounds with basic dyestuffs and which are suitable, therefore, in the art of dyeing as mordants for applying basic dyestuffs to the cellulosic fiber. As such compounds there may be specifically mentioned, for instance, tannin, gallnut extract, other natural or synthetic tanning agents, tannin substitutes like phenol/sulfur condensation products and the metal compounds thereof, condensation products of phenols with phenol sulfonic acids, of phenols or hydroxyarylsulfones with aldehydes like formaldehyde, of phenols with acetylene, and many more like compounds.

The mordanting agents according to our invention may be incorporated with the cellulosic material at any stage of the manufacture thereof, before, together with or after the incorporation of the animalizing agent. The mordanting agents may be applied in any suitable way from neutral, alkaline or acid solution or emulsion. They may also be incorporated with spinning solutions of cellulose or cellulose derivatives. The

treatment of the material with the mordanting agents may be performed at room temperature or preferably at higher temperatures, up to boiling temperature. In many cases it is advantageous to use, besides the mordanting agent, other compounds which are known to promote its going on the fiber, for instance, organic or inorganic salts.

The amounts of animalizing and mordanting agents to be used may vary over a relatively large range. Of course, the exact amounts of both agents depend on the kind of material to be treated and of the kind of dyeing one wants to produce. In case the mordanting agent does not possess sufficient substantivity, like for instance in the case of tannin, it is advantageous to treat the material in the usual way with a fixing agent for the mordanting compound, for instance, in the case of tannin with tartar emetic.

The dyeings produced on the material thus treated with wool dyestuffs are of improved fastness towards water, perspiration, fulling, potting, steaming, washing, etc., in comparison with dyeings on material which has not been treated according to the present invention with a substance of mordanting character.

In some cases the affinity of the animalized material to dyestuffs is slightly changed by the treatment with the mordanting agent; it may be increased or lessened. This is especially apparent when simultaneously dyeing the animalized material and wool, for instance, in mixed yarns or mixed fabrics, and may be used in order to obtain more level dyeings. It was also observed that on dyeing such mixed material with dyestuff mixtures a much better tone-in-tone coloration was obtained on the material treated according to the present invention.

The invention is further illustrated by the following examples without being restricted thereto, the parts being by weight:

Example 1

3.5% of a condensation product of chlorinated paraffin and ethylenediamine according to British specification No. 359,001 are added to a spinning solution of cuprammonium cellulose. 100 parts of the resulting cellulose are impregnated at 80 to 90° C. for 2 minutes in a bath containing 5 to 10 parts of a phenol-sulfur compound prepared according to British specification No. 173,313 and 2 to 5% sodium carbonate. The rinsed and dried fiber is dyed as usual with Wool Fast Blue BL (Schultz, Dyestuff Tables, vol. I, 1931, No. 974).

The dyeing shows increased fastness to all kinds of wet treatment when compared with cellulose which has been animalized in the same way, but not after-treated.

The fibers can also be treated with the phenol-sulfur compound at low temperature, for instance at 20 to 30° C. when it is advantageous to prolong the treatment or to add an electrolyte. The treatment may be carried out subsequent to spinning process in a continuous manner. On subsequently dyeing, in any case dyeings of better fastness to wet treatment are obtained.

Similar results are obtained when dyeing with other acid wool dyestuffs; as for instance Anthralan Yellow G (Schultz, Dyestuff Tables, 1st sup. vol., 1934, page 68), Supra Light yellow GL (Schultz, Dyestuff Tables, vol. I, 1931, No. 736), Anthralan Red B (Schultz, Dyestuff Tables, 1st sup. vol., 1934, page 68), Supranol Brilliant Red B. (Schultz, Dyestuff Tables, vol. II, 1932, page 204), Supramine Bordo B (Schultz, Dyestuff

Tables, vol. II, 1932, page 203), Supramine Violet R (Schultz, Dyestuff Tables, vol. II, 1932, page 204), Anthralan Violet 3B (Schultz, Dyestuff Tables, 1st sup. vol., 1934, page 68), Anthralan Blue, G (Schultz, Dyestuff Tables, 1st sup. vol., 1934, page 68), Alizarine Light Grey BBLW (Schultz, Dyestuff Tables, vol. II, 1932, page 12), Diamond Black P2B (Schultz, Dyestuff Tables, vol. I, 1931, No. 234).

Example 2

If, instead of cuprammonium cellulose, viscose cellulose or viscose artificial silk is employed, the fastness properties of the dyeings with acid wool dyestuffs are considerably improved by the treatment according to Example 1.

Example 3

When dyeing cellulose or cuprammonium cellulose together in the same dyeing bath or as mixed yarn, mixed fabrics or mixed tissues with wool according to Example 1 or 2, for instance, in the proportion 50:50, the dyeing is also improved in comparison with the non-treated material.

Example 4

When using a condensation product of polyethyleneimine and alkylhalogenides, for instance octadecylbromide, instead of the animalizing agent of Example 1, on dyeing, for instance with Anthralan Red BBT (Schultz, Dyestuff Tables, 1st sup. vol., 1934, page 68) a considerable improvement of the fastness properties is obtained.

Example 5

A spun viscose fiber is animalized with 3% octadecylbiguanide in the usual manner and subsequently treated with a phenol sulfur compound as described in Example 1. The fiber dyed together with wool, for instance with the dyestuff of Example 1 shows an improved fastness to water, washing and perspiration.

Example 6

Cuprammonium cellulose is animalized with 5% of a condensation product of ethylenediamine with a higher fatty acid chloride. On aftertreating the same with tannin or a tannin substitute the dyeings are further improved.

Example 7

A cellulose artificial fiber animalized according to Example 1 is treated in an aqueous liquor at 75° C. for some minutes with 1% its weight of tannin, squeezed off and treated with ½% tartar emetic in an aqueous liquor for several minutes, rinsed and dried. On dyeing the fiber in the usual manner with the dyestuff mentioned in Example 1 the dyeing is faster than without the tannin-tartar-emetic treatment.

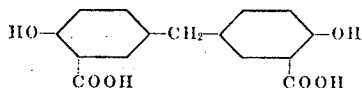
The affinity of the fiber is somewhat less than by only animalizing, i. e., by the aftertreatment a certain reserving of the animalized fiber is effected.

Example 8

Acetate artificial silk is treated with the animalizing agent of Example 1 and with a sulfonated condensation product of chlorinated benzyl chloride and phenol in an acid or neutral bath according to British Specification No. 332,960. The dyeings obtained with the dyestuffs of Example 1 show a better fastness to washing than those made on non-treated animalized acetate silk.

Example 9

Animalized staple fiber prepared as described in Example 1 from a cuprammonium cellulose solution is treated at about 90° C. for 3 minutes in a bath containing 5 to 10 parts methylenedisalicylic acid of the formula:



Dyeings on this material with wool dyestuffs are of better fastness to wet treatments, for instance to washing, than dyeings on animalized staple fiber which has not been treated with the mordanting agent.

Instead of methylenedisalicylic acid, a condensation product of salicylic acid and formaldehyde according to German Patent 358,401, Example 1, may be employed with a similar result.

Example 10

The staple fiber animalized as described in the foregoing example is treated similarly as above described with a condensation product from dihydroxydiphenylsulfone and formaldehyde (obtainable according to German Patent 464,088). Dyeings with wool dyestuffs on this material, besides showing better fastness to wet treatment, are also of better fastness to light in comparison with dyeings on material which has not been treated with the mordanting agent.

Example 11

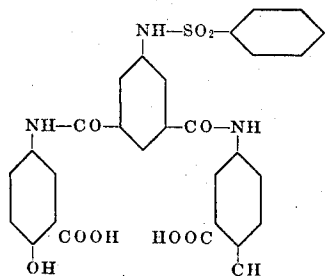
To a cuprammonium cellulose solution with which an animalizing agent has been incorporated as described in Example 1 there are added 1 to 3% of a phenol-sulfur compound (see British Specification No. 173,313), and the mass is well kneaded. Staple fiber prepared from this solution is dyed with excellent fastness to wet treatments by wool dyestuffs.

Example 12

A viscose spinning solution is prepared, similarly as described in the foregoing example, by first adding the animalizing agent and thereupon the mordant. Fibers produced from this solution are dyed by wool dyestuffs with excellent fastness, exceeding the fastness of dyeings on material containing no mordant.

Example 13

Animalized staple fiber prepared as described in Example 9 from a cuprammonium spinning solution is treated as described in Example 1 with a mordanting compound of the formula:



Dyeings with wool dyestuffs on this material are of improved fastness when compared with dyeings which have been produced in the absence of a mordant.

Example 14

To a spinning solution for cuprammonium anti-

ficial fibers there are added 5% of a product obtainable by precipitating the animalizing agent of Example 1 (chlorinated paraffin+ethylenediamine) from its acid aqueous solution by adding a phenol-sulfur condensation product (compare British Specification 173,313). Dyeings with acid dyestuffs on such material are of improved fastness to wet treatments.

Example 15

Staple fiber from viscose prepared similarly as described in Example 1 with addition of an animalizing agent to the spinning solution is dyed with Anthralan Violet 3B (see Example 1) and aftertreated with a soda-solution of the phenol-sulfur condensation product of Example 1. The fastness of the dyeing to wet treatments is increased thereby.

Example 16

Staple fiber is spun from a cuprammonium cellulose solution containing 3% of a phenol-sulfur condensation product. The material is then treated with an aqueous emulsion of the animalizing agent mentioned in Example 1, and dyed with Anthralan Blue G (see Example 1). The dyeing is of improved fastness when compared with the dyeing on material containing no mordant.

Example 17

Staple fiber animalized and mordanted as described in Example 1 is dyed in the presence of an equal quantity of wool with the following wool dyestuffs:

Rhodamine B extra (Schultz, Dyestuff Tables, vol. 1, 1931, No. 864),
Turkise Blue BB (Schultz, Dyestuff Tables, vol. 1, 1931, No. 757),
Victoria Blue B (Schultz, Dyestuff Tables, vol. 1, 1931, No. 822).

A good tone-intone coloration is obtained. Animalized staple fiber which has not been treated with the mordanting agent is not or only slightly dyed with insufficient fastness by the said dyestuffs.

Example 18

50 parts of staple fiber from cuprammonium cellulose animalized as described in Example 1 are treated for 5 minutes at 90 to 100° C. in an aqueous bath containing per liter 7.5 gs. of a alkali-soluble phenolformaldehyde resin (prepared by condensing the components in an acid medium) and 5 ccms. of caustic soda lye of 32% strength. The material is then squeezed, treated for a short time in a bath containing 5 ccms. glacial acetic acid per liter, rinsed and dried. The material is then dyed in the usual manner alone or in the presence of wool with acid wool dyestuffs like

2% Supra Light Yellow GGL (Schultz, Dyestuff Tables, vol. 1, 1931, No. 736),
8% Diamond Black P2B (Schultz, Dyestuff Tables, vol. 1, 1931, No. 234),
2% Palatine Fast Blue BN (Schultz, Dyestuff Tables, 1st sup. vol., 1934, page 117).

Instead of the above-mentioned condensation product from phenol, also similar condensation products from the homologues of phenol, for instance from cresols, may be employed.

The treatment of the staple fiber with the mordanting agent may be performed during any stage of its manufacture, before or after the final drying of the fibers.

Example 19

If instead of the phenolaldehyde condensation product of the foregoing example an equal quantity of an alkali soluble reaction product from phenol and acetylene (compare the German Patent 642,886, Example 1) is used, the fibers are dyed by wool dyestuffs with better fastness to wet treatments than if the fibers were not treated with the phenol-acetylene condensation product.

We claim:

1. A process of improving the fastness to wet treatment of dyeings with wool dyestuffs on shaped animalized cellulosic material which comprises treating said material at any stage of its manufacture with an organic mordanting agent for basic dyestuffs and dyeing the mordanted material with an acid dyestuff.

2. A process of improving the fastness to wet treatment of dyeings with wool dyestuffs on animalized cellulosic material which comprises treating the material after precipitation from a spinning solution containing an animalizing agent with an organic mordanting agent for basic dyestuffs and dyeing the mordanted material with an acid dyestuff.

3. A process for improving the fastness to wet treatment of dyeings with wool dyestuffs on animalized cellulosic material which comprises incorporating an animalizing agent and an organic mordanting agent for basic dyestuffs with a spinning solution of the cellulosic material, precipitating and dyeing the precipitated material with an acid dyestuff.

4. A process of improving the fastness to wet treatment of dyeings with wool dyestuffs on animalized cellulosic material which comprises treating said material after precipitation from a spinning solution having incorporated therein an animalizing agent, at temperatures from 50-100° C. with an aqueous alkaline solution of about 10 to 15% of an organic mordanting agent for basic dyestuffs and dyeing the mordanted material with an acid dyestuff.

5. A process of improving the fastness to wet

treatment of dyeings with wool dyestuffs on animalized cellulosic material which comprises treating said material after precipitation from a spinning solution having incorporated therein a condensation product from chlorparaffin and ethylenediamine, at temperatures of from 50-100° C. with an aqueous alkaline solution of about 10 to 15% of a phenolformaldehyde mordanting agent for basic dyestuffs and dyeing the mordanted material with an acid dyestuff.

6. A process of improving the fastness to wet treatment of dyeings with wool dyestuffs on animalized cellulosic material which comprises treating the material after precipitation from a spinning solution having incorporated therein a condensation product from chlorparaffin and ethylenediamine, at temperatures of from 50-100° C. with an aqueous alkaline solution of about 10 to 15% of a phenolsulfur mordanting agent for basic dyestuffs and dyeing the mordanted material with an acid dyestuff.

7. Cellulosic fibers having incorporated therewith an animalizing agent and an organic mordanting agent for basic dyestuffs, said fibers being dyed with an acid dyestuff.

8. Fibers from regenerated cellulose having incorporated therewith an animalizing agent and an organic mordanting agent for basic dyestuffs, said fibers being dyed with an acid dyestuff.

9. Fibers from regenerated cellulose having incorporated therewith a condensation product from chlorparaffine and ethylenediamine and a phenol-formaldehyde mordanting agent for basic dyestuffs, said fibers being dyed with an acid dyestuff.

10. Fibers from regenerated cellulose having incorporated therewith a condensation product from chlorparaffine and ethylenediamine and a phenol-sulfur-mordanting agent for basic dyestuffs, said fibers being dyed with an acid dyestuff.

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