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PROCESS FOR CHLORINATING TEXTILES COLORED WITH DYESTUFFS SENSITIVE TO CHLORINE

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It is known to color cellulose fibers, such as cotton or regenerated cellulose, on a large scale with dyestuffs which do not withstand treatment with chlorine. Such dyestuffs are for example the great majority of the direct dyeing dyestuffs and of the dyestuffs which are developed on the fiber either by diazotizing and uniting with coupling components or by after-treatment with diazo compounds. Moreover it is known that most of the sulfur dyestuffs are not fast to chlorine. This deficient fastness to chlorine excludes the textiles colored with such dyestuffs from a series of important applications, even if the other fastness properties, such as for example the fastness to light or to washing, would meet higher requirements.

On the other hand, it is known that textile materials can be improved by finishing them with water-insoluble condensation products, for example from formaldehyde and urea or phenols. This finishing operation can be carried out in such a manner that these condensation products exist in or on the fiber in coherent form or in the form of separate particles. In the one case there are obtained for instance finishing effects such as anti-creasing properties of stiffening finishes, the fixation of dyestuffs and the like; in the other case there are obtained matting effects.

It has now been found that cellulose textile materials, such as cotton, linen, regenerated cellulose, for example in the form of viscose rayon or staple fibres, which have been colored with dyestuffs sensitive to chlorine, can be treated in baths containing chlorine without destroying the dyestuffs by producing insoluble condensation products from formaldehyde and urea compounds, or products which behave similarly, on the colored textiles previous to the chlorination, this treatment being effected in the well-known manner, which leads to condensation products formed on or in the fiber in coherent form. Among urea compounds or products which behave similarly are included quite generally products which may form water-insoluble, resinous condensation products with formaldehyde, that is to say for instance urea and particularly thiourea, further products like biuret, phenylurea, melamine, phenols, aniline and the like.

The formation of the insoluble condensation product may take place in such a manner that the colored textile materials are impregnated with mixtures of the above indicated compounds and formaldehyde or with water-soluble addition products and condensation products, respectively, of formaldehyde with the indicated compounds, it being advantageous to add a catalyst, for instance an ammonium salt of a strong acid, to the impregnating bath. The impregnated fabric is then subjected to a treatment which produces the formation of the insoluble coherent condensation product. This may be brought about for example by drying the impregnated fabric at a moderate or higher temperature before the insoluble condensation product which forms under the influence of the catalyst has precipitated in substantial quantities in discrete, pigment-like form, however, it is advantageous to subject the treated textile materials to a short heat treatment at 120–150° C.

The present chlorinating process is particularly valuable if colored textile materials consisting of mixtures of wool and cellulose fibers are to be treated in such a manner that the wool remains resistant towards felting and shrinking. Such a treatment may consist of chlorinating the wool with an acidified hypochlorite solution. If the new textile materials consisting of wool and cellulose colored with dyestuffs sensitive to chlorine and finished with coherent insoluble condensation products from formaldehyde and urea compounds are treated with an acidified hypochlorite solution, the color of the cellulose is not destroyed.

The new process may also find application in cases where undyed cellulose fibers must be bleached beside colored fibers.

If, for example, a colored fabric, consisting of cotton in which the colored yarns have been dyed with dyestuffs sensitive to chlorine, is chlorinated, the color of the cellulosic portion is more or less destroyed. However, when using colored yarns which have been finished with the insoluble, coherent condensation products, the chlorination of the new fabrics consisting of undyed celluose and cellulose colored with dyestuffs sensitive to chlorine and finished with the insoluble, coherent condensation products from formaldehyde and urea compounds, may be effected unhesitatingly, even if the cellulose has been dyed with azo dyestuffs or sulfur dyestuffs which under other conditions are sensitive to chlorine.

In mixed fabrics or yarns the finishing of the colored portion with the insoluble condensation products takes place preferably prior to the production of the fabric. The manufacture of such textile materials as well as the materials themselves, i. e. mixed fibers containing cellulose fibers which have been colored with dyestuffs sensitive to chlorine and which have been finished with insoluble, coherent condensation products from formaldehyde and urea compounds, which repre-

sent valuable new products, form also the subject of the present invention.

In a time where mixed yarns or fabrics are used more and more, the new process constitutes an important technical progress. Its success is entirely surprising, since other resinous condensation products which have attained great technical importance and are also used for the finishing of textile materials, such as for example the vinyl resins, do not lead to the desired end.

The following examples illustrate the new process without however limiting the same:

Example 1

Viscose staple fiber which has been dyed with 2.5 per cent of Direct Brown M (Colour Index No. 420) is impregnated with a solution which has been prepared as follows:

50 grams of thiourea are heated in a reflux apparatus with 95.5 grams of a formaldehyde solution of 40 per cent strength which has been made feebly alkaline with sodium carbonate until solution has taken place. The clear solution pH=6 is standardized with cold water to 1000 cc. 10 grams of ammonium chloride are added to the impregnation bath thus prepared. The viscose impregnated therein is centrifuged, and dried in a drying chamber or hardened at 120° C.

The viscose thus prepared is worked up into the finished yarn with equal parts of dyed wool.

This yarn is given anti-shrink and non-felting properties by treating for 20 minutes with a chlorine solution which contains 1.5 per cent of active chlorine (as sodium hypochlorite solution) and 4 per cent of sulfuric acid, calculated on the weight of the fiber, the ratio of goods to liquor being 1:40. The yarn is then rinsed, aftertreated with 5 cc. of bisulfite solution of 72° Tw. per liter and again rinsed. The brown coloring of the regenerated cellulose has not been destroyed by the chlorine treatment.

Similar effects are obtained when using mixtures of dimethylolurea and dimethylolthiourea instead of pure dimethylolthiourea.

Example 2

Loose viscose staple fiber intended to be mixed with wool for hosiery yarn, is dyed with 2.5 per cent of Direct Fast Scarlet SE (Colour Index No. 326) in a neutral Glauber's salt bath. The staple fiber is then rinsed and impregnated with a solution containing per liter 100 grams of dimethylolurea and 10 grams of ammonium chloride as well as 1 gram of a mixture of the sulfonated and unsulfonated monocetyl ester of phthalic acid. The material is hydroextracted and dried in a drying chamber or hardened at 120° C., and is then mixed with loose wool which has been dyed with 2 per cent of Cloth Fast Red (Colour Index, page 347). The mixed yarn produced from this mixture can be made resistant to felting by acid chlorinating, as indicated in Example 1.

Example 3

Cotton yarn which has been dyed with 15 per cent of Pyrogene Indigo 5G (Colour Index No. 961) is after-treated with the thiourea-formaldehyde compound of Example 1 and used as fancy yarn in a cotton fabric. The color of the fancy yarn is changed only slightly by a cold bleach with an alkaline hypochlorite solution containing 1 to 2 grams of active chlorine per liter (ratio of goods to liquor: 1:20), whereas untreated yarns lose their color entirely in the chlorine bath.

Also here the thiourea may be replaced entirely or partially by a urea compound.

Similar effects are obtained when the Pyrogene Indigo is replaced by other sulfur dyestuffs, for example Progrene Deep Black T (compare Colour Index No. 978), Pyrogene Blue 2R (Colour Index No. 956), Indocarbon CL (Colour Index Suppl. page 43), Pyrogene Green 3G (Colour Index No. 1006) and the like.

Example 4

Viscose staple fiber is dyed with 3 per cent of Melantherine BH (Colour Index No. 401) and then aftertreated with a solution containing per liter 100 grams of dimethylolurea, 75 grams of dimethylolthiourea, 10 grams of ammonium chloride, 1 gram of a mixture of the sulfonated and unsulfonated monocetylester of phthalic acid. The material is then centrifuged, dried in a drying chamber and the temperature is kept at 110° C. for 40 minutes. The staple fiber thus treated may serve in the manufacture of yarn which is used as fancy yarn in cotton fabrics which are chlorinated with sodium hypochlorite solution according to the data of Example 3. The treated fiber may also be used with advantage for mixing with loose wool for the manufacture of hosiery yarns which are then acid chlorinated according to the method of working of Example 1. The color withstands the chlorinating process in both cases.

Here too the urea derivative may be replaced entirely or partially by the thiourea derivative, or the latter may be replaced entirely or partially by the urea derivative.

The dyestuffs used in Examples 1, 2 and 4 may be replaced also by other dyestuffs, for example by Direct Fast Red F (Colour Index No. 419), Direct Sky Blue green shade (Colour Index No. 518) Cotton Yellow CH (Colour Index No. 365).

Dyeings may also be used, the fastness properties of which on the fiber have been increased by other treatments, as is the case for example with Rosanthrene BN (Colour Index No. 324a), Rosanthrene Bordeaux B (Colour Index No. 324a), or Para Black R (Colour Index No. 339) either by diazotizing on the fiber and coupling with β-naphthol, or by after-treating with diazotized para-nitraniline.

Example 5

Viscose rayon yarn, after having been dyed with 3 per cent of Direct Sky Blue green shade (Colour Index No. 510) and rinsed, is impregnated with a solution prepared as follows: 63 grams of melamine, 136 cc. of formaldehyde of 40 per cent strength by volume, 34 cc. of water are boiled for a short time, cooled and diluted with 800 cc. of cold water. To this solution are added 23.5 grams of dimethylolthiourea, further 11.7 grams of ammonium chloride and 1.2 grams of a mixture of the sulfonated and unsulfonated monocetylester of phthalic acid (the last three substances dissolved in water) and the whole is made up with water to 1170 cc.

After impregnating, the treated viscose rayon is centrifuged, dried and hardened for 40 minutes at 110° C. This yarn is woven with an undyed viscose rayon yarn to a colored fabric and is then subjected to a bleaching process for 30 minutes at ordinary temperature with a sodium hypochlorite solution containing 2 grams of active chlorine per liter. The color withstands this bleaching process.

Rayon yarn which has been dyed before the treatment in the indicated manner with Direct Scarlet WS (Colour Index Suppl. page 39), Melantherine BH (Colour Index No. 401) Direct Fast Orange SE (Colour Index No. 326) or with similar direct dyestuffs or sulfur dyestuffs, such as Pyrogene Indigo 5G (Colour Index No. 961), behaves similarly.

What I claim is:

1. A process for the production of mixed textile fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine, which process comprises dyeing the fibers of another component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with insoluble coherent condensation product selected from the class consisting of melamine-formaldehyde condensation product, formaldehyde-urea condensation product, formaldehyde-thiourea condensation product and mixtures of the latter, working the said component parts into mixed fiber form, and then chlorinating the mixed fibers, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

2. A process for the production of mixed textile fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine, which process comprises dyeing the fibers of another component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with an insoluble coherent condensation product from formaldehyde and urea, working the said component parts into mixed fiber form, and then chlorinating the mixed fibers, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

3. A process for the production of mixed textile fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine, which process comprises dyeing the fibers of another component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with an insoluble coherent condensation product from formaldehyde and thiourea, working the said component parts into mixed fiber form, and then chlorinating the mixed fibers, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

4. A process for the production of mixed textile fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine, which process comprises dyeing the fibers of another component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with insoluble coherent condensation product consisting of a mixture of formaldehyde-urea and formaldehyde-thiourea, working the said component parts into mixed fiber form, and then chlorinating the mixed fibers, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

5. A process for the production of mixed textile fibers which include wool fibers as one component part and cellulosic fibers of non-animal origin as another component part, which process comprises dyeing the fibers of the other component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with insoluble coherent condensation product selected from the class consisting of melamine-formaldehyde condensation product, formaldehyde-urea condensation product, formaldehyde-thiourea condensation product and mixtures of the latter, and working the said component parts into mixed fiber form, and then chlorinating the mixed fibers whereby the wool fibers are rendered resistant to felting and shrinking while the said dyed other component part remains unaffected.

6. A process for the production of mixed textile fibers which include wool fibers as one component part and cellulosic fibers of non-animal origin as another component part, which process comprises dyeing the fibers of the other component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with an insoluble coherent condensation product from formaldehyde and urea, and working the said component parts into mixed fiber form, and then chlorinating the mixed fibers whereby the wool fibers are rendered resistant to felting and shrinking while the said dyed other component part remains unaffected.

7. A process for the production of mixed textile fabrics which include wool fibers as one component part and cellulosic fibers of non-animal origin as another component part, which process comprises dyeing the fibers of the other component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with an insoluble coherent condensation product from formaldehyde and thiourea, and working the said component parts into mixed fiber form, and then chlorinating the mixed fibers whereby the wool fibers are rendered resistant to felting and shrinking while the said dyed other component part remains unaffected.

8. A process for the production of mixed textile fibers which include wool fibers as one component part and cellulosic fibers of non-animal origin as another component part, which process comprises dyeing the fibers of the other component part with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs, impregnating the fibers of the said dyed component part with insoluble coherent condensation product consisting of a mixture of formaldehyde-urea and formaldehyde thiourea, and working the said component parts into mixed fiber form, and then chlorinating the mixed fibers whereby the wool fibers are rendered

resistant to felting and shrinking while the said dyed other component part remains unaffected.

9. A process of the character described which comprises the step of chlorinating mixed fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine and another component part consisting of fibers dyed with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs and impregnated with insoluble coherent condensation product selected from the class consisting of melamine-formaldehyde condensation product, formaldehyde-urea condensation product, formaldehyde-thiourea condensation product and mixtures of the latter, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

10. A process of the character described which comprises the step of chlorinating mixed fibers including at least one component part consisting of wool fibers and another component part consisting of cellulosic fibers of non-animal origin dyed with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs and impregnated with insoluble coherent condensation product selected from the class consisting of melamine-formaldehyde condensation product, formaldehyde-urea condensation product, formaldehyde-thiourea condensation product and mixtures of the latter, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

11. A process of the character described which comprises the step of chlorinating mixed fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine and another component part consisting of fibers dyed with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs and impregnated with insoluble coherent formaldehyde-urea condensation product, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

12. A process of the character described which comprises the step of chlorinating mixed fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine and another component part consisting of fibers dyed with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs and impregnated with insoluble coherent formaldehyde-thiourea condensation product, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

13. A process of the character described which comprises the step of chlorinating mixed fibers including at least one component part consisting of fibers whose properties are modified upon treatment thereof with chlorine and another component part consisting of fibers dyed with a dyestuff which is sensitive to chlorine and is selected from the class consisting of the direct dyeing dyestuffs, the azo dyestuffs and the sulfur dyestuffs and impregnated with a mixture of insoluble coherent formaldehyde-urea and formaldehyde-thiourea condensation product, whereby the properties of the first-named component part are modified while the said dyed other component part remains unaffected.

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