Cl. 8

Published Apr. 27, 1943

Serial No. 275,399

# ALIEN PROPERTY CUSTODIAN

## DYEING CELLULOSE ESTERS

Robert Schnegg, Dormagen, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 24, 1939

The present invention relates to the art of dyeing cellulose esters, and more especially, to a process for dyeing shaped articles like fibres, films, bands, and so on of highly acetylated cellulose, i. e. cellulose acetate having an acetate content of above 59%; such cellulose acetates are for the most part soluble in chloroform.

It is known that highly esterified cellulose acetate is not easily dyed even with such dyestuffs which are usually employed in dyeing the lower cellulose acetates. The same holds true when trying to increase the affinity of highly esterified cellulose acetate towards other dyestuff classes, for instance, acid wool dyestuffs by animalizing. This great resistance of highly esterified cellulose acetate to all kinds of dyestuffs is presumably due to the fact that the articles manufactured therefrom possess a rather horny surface free of pores which would allow the dyestuff particles, which are mostly high molecular, to wander into the interior.

It is known that similar difficulties, but on a lesser scale, are encountered when dyeing common acetate artificial silk which is less highly esterified and is soluble, not in chloroform, but in acetone, and that it has been tried to overcome the difficulties by adding certain swelling agents to the dye-baths for such artificial silk.

However, when trying to apply the processes used in dyeing acetone-soluble acetate artificial silk to the problem in question, the result is not successful. It was rather unexpected, therefore, when I found that nevertheless also articles from highly esterified cellulose acetate can be very easily dyed when the articles are previously brought into a highly swollen condition and are dyed in this state. In order to achieve this result, I have found it to be necessary to treat the articles with at least 40% aqueous acetic acid or a swelling agent of at least equal swelling action; furthermore, it is preferable to carry out this swelling treatment at high temperatures, for instance, temperatures of above 50° C. It may be noted that under such conditions the common acetone-soluble artificial silk is completely dissolved or at least destroyed to an extremely high degree. Contrary thereto, the mechanical properties of the articles of highly esterified cellulose acetate, for instance, resistance to break and elongation at break, are practically unimpaired by the present process.

After the treatment with one of the swelling agents, the articles can be dyed directly in deep and full shades; the dyeings so obtained have good fastness properties. It is especially possible to dye animalized articles after the said swelling treatment with acid wool dyestuffs and to obtain dyeings of excellent fastness. Before dyeing, the swelling agent may be removed from the articles by washing with water, without practically losing the property of being easily dyed. This property is only lost when the articles are dried before dyeing.

I have now furthermore found that by a suitable treatment it is even possible to dry the articles having been treated with one of the above strong swelling agent in a manner that they retain the property of being easily dyed. In order to achieve this result, I treat the articles which have been brought into the strongly swollen condition, if desired after removal of the swelling agent by washing, with a fixing agent selected from the group consisting of aqueous solutions of salts of organic or inorganic acids and wetting agents, which are free from sulphonic acid groups; these fixing agents may be employed alone or in admixture with each other. Apparently by this treatment the swollen condition of the cellulose acetate articles which is necessary for their being easily dyed is fixed to some extent. After the said fixing treatment the articles may be dried. They remain easily dyeable thereafter and may be stored for any length of time or shipped to the customer without being impaired with regard to their dyeing properties. If before or during dyeing the fixing agents are washed out from the articles, the cellulose acetate will again pass into the unswollen state whereby the dyestuff particles are very strongly fixed in the interior of the material so that the dyeings produced in this way show excellent fastness properties. For instance, dyeings with acid wool dyestuffs on animalized cellulose material having been produced according to my invention are faster in many respects, for instance, against fulling and washing than the same dyeings on wool. As I have mentioned in several instances, the process according to my invention is of special value in dyeing animalized material of highly esterified cellulose acetate with acid wool dyestuffs. Such material is produced in known manner, for instance, by incorporating basic substances like nitrogen bases with the material, for instance, by adding a suitable nitrogen base to a spinning solution for artificial fibres from highly acetylated cellulose. It is possible in this way, for example, to prepare artificial fibres from cellulose having an acetic acid content of above 59% which can be dyed alone or together with wool in equal shades as wool. For example, cellulose

triacetate fibres are prepared which contain a basic nitrogen containing resin, the fibres are treated with at least 40% aqueous acetic acid or a swelling agent of similar strength, are then treated with one of the above mentioned fixing agents and thereupon dyed with an acid wool dyestuff. The fibres may then be worked up into a mixed fabric together with wool and, by aftertreating with the same dyestuff, may be uniformly dyed. It is self-understood that in a similar way two-colored effects may be produced. It is furthermore possible to work up animalized cellulose triacetate fibres together with wool to slivers, yarns, skeins, fabrics and so on, and to treat these materials with a swelling agent which will not impair the wool. Thereupon the materials may be dyed in one on the same bath in uniform shades with acid wool dyestuffs. As above mentioned the fastness of the dyeings on the cellulose acetate articles surpass that of the same dyeings on wool, especially as regards the fastness to washing and fulling.

Of course the process is also applicable to textile printing. For instance, a fabric from cellulose triacetate fibres or animalized cellulose triacetate fibres may be printed with one of the above strong swelling agents and thereupon may be dyed with a suitable dyestuff, if desired, after having been treated with one of the said fixing agents. In both cases dyed patterns on a white ground or vice versa may be obtained.

*Example 1*

Fibres which have been prepared from chloroform-soluble cellulose acetate (acetic acid content: 59–61%) according to a wet-spinning process are continuously passed through a bath containing 60% aqueous acetic acid. The fibres swell strongly. Thereupon the fibre bundle is deacidified by washing with water and dyed with a water insoluble cellulose acetate dyestuff. By using, for instance, Cellit Fast Blue B (Schultz, Dyestuffs Tables, 1st suppl. vol., 1934, page 75), a deep blue shade is obtained whereas without the said swelling treatment the fibres are practically not dyed.

When trying to treat common acetate artificial silk (acetic acid content: 54–55%) in the same way, the fibres are completely dissolved.

*Example 2*

Fibres swollen and washed as described in example 1 are cut into staples and brought into a bath containing 10–30% of an inorganic or organic salt. The following salts, if their solubility permits so, may be used: chlorides, bromides, iodides, sulfates, nitrates, borates, phosphates, sulfites, thiosulfates, thiocyanates of the alkali and alkaline-earth metals, furthermore, alkali and alkaline-earth metal salts of the lower fatty acids, and mixtures of the said salts. After the swollen fibres have been treated for 5–10 minutes in a salt bath, for instance, a 20% solution of common salt, they are centrifuged and dried. After shortly washing the fibres are dyed as usual with celculose acetate dyestuffs, for instance, Celliton Fast Black BTN (Schultz, Dyestuff Tables, 1st suppl. sol., 1934, page 76). Contrary to the untreated fibres, they are dyed in deep and full shades.

The usual softening and finishing agents may be added to the salt bath.

*Example 3*

Instead of a salt bath as described in the foregoing example, there may be used an aqueous solution of 5–50 g per litre of a wetting agent which is free from sulphonic acid groups, for instance, a reaction product of a reactive tertiary amine with the anhydride of a substituted succinic acid, or a condensation product of oleyl alcohol or of castor oil with an excess of ethylene oxide.

*Example 4*

Fibres having been subjected to a swelling treatment as described in example 1 are aftertreated with a bath containing 2–10% of a salt and 0.05–0.5% of wetting agent which is free of sulphonic acid groups. The results are similar to those obtained according to examples 1–3.

*Example 5*

Cellulose acetate artificial silk (acetic acid content: 59%) prepared by a dry spinning process is treated in skein form for 15–120 seconds at a temperature of 30° C in a 50% aqueous acetic acid. After having been washed with water, the silk is dyed with Celliton Fast Black BTN in a deep black shade, whereas the untreated silk is hardly dyed. Of course, it is possible to add an aftertreatment of the swollen fibres as described in examples 2–4.

*Example 6*

To a raw solution of cellulose triacetate, there are added 5–15% (calculated on cellulose acetate) of a reaction product of starch benzene sulfonate with an amine as described in the application Ser. No. 180,157, filed December 16, 1937, and the solution is spun into fibres. In spite of the presence of the nitrogenous compounds, these fibres are but scarcely dyed with acid wool dyestuffs.

The fibres are then continuously passed through a bath containing 60% aqueous acetic acid at a temperature of 20° C for 15–120 seconds, thereupon washed with water and are dyed, while still wet, with acid wool dyestuffs, for instance, Amido Yellow E (Schultz, Dyestuffs Tables, vol. 1, 1931, No. 16). The deep dyeings obtained in this manner are especially distinguished by their fastness. For example, the fastness against fulling is 4–5 (Normen der Deutschen Echtheitskommission 1935), whereas a corresponding dyeing on wool has a fastness against fulling of 1–2. A series of other acid wool dyestuffs act in the same way, for instance, Quinoline Yellow (Schultz, Dyestuffs Tables, vol. I, 1931, No. 918), Brilliant Crocein B (Schultz, Dyestuff Tables, 1st suppl., vol., 1934, No. 539), Alizarine Rubinol R. (Schultz, Dyestuff Tables, vol., I, 1931, No. 1210), Wool Fast Violet B (Schultz, Dyestuff Tables, vol. I, 1931, No. 974), Alizarine Direct Blue A (Schultz, Dyestuff Tables, vol. II, 1932, page 9), Azo Acid Black 3 BL special (Schultz, Dyestuff Tables, 1st suppl. vol., 1934, page 70), and so on.

*Example 7*

A solution of cellulose triacetate in glacial acetic acid is mixed with an animalizing agent, for instance, a reaction product of chlorinated paraffin with ethylene diamine, and is spun by the wet-spinning process; the fibres obtained therefrom are swollen in a 60% aqueous acetic acid at 60° C for 15 seconds washed with water, and treated for 5 minutes in a salt bath containing 5% sodium acetate, 2% ammonium thiocyanate, 2% of a finishing agent and 0.5% isododecenyl-succinic acid-diethyl amino-methyl ester. The centrifuged and dried fibre is excellently dyed by acid wool dyestuffs.

*Example 8*

A fibre bundle of cellulose triacetate being animalized as described in example 6 is swollen for 30 seconds at a temperature of 10° C in a 65% aqueous acetic acid which contains about 2% of a chromium compound, for instance, sodium bicromate or chromium acetate and, if desired, a reduction agent like formaldehyde or glucose. The bundle is freed from acid and cut into staples. The fibres are after-treated in a salt bath (containing 8% sodium acetate, 1% of a wetting agent free of sulfo groups and 2% of a usual preparation), dried and worked up with wool to a yarn or textile fabric. The mixture is uniformly dyed with acid wool dyestuffs. Especially suitable are chromable dyestuffs. The dyeings on the artificial fibres are not only of the same fastness to washing, fulling and perspiration, but are equal to the dyeings on pure wool regarding the fastness to light.

*Example 9*

Triacetate artificial silk containing an animalizing agent is worked up with wool in the relative proportion 1:1. The mixture is treated in a bath containing 60% aqueous acetic acid and 2% glucose for 15 seconds at 20° C, centrifuged, washed and dyed in the wet state with wool dyestuffs such as, for example, Anthralane Blue B (Schultz, Dyestuff Tables 1st suppl., vol., 1934, page 68). The dyeings obtained are uniform on both kinds of fibres. Dyeings of particular fastness are obtained by using salts of the acid sulfuric acid esters of leuco vat dyes, which also dye both kinds of fibres equally and with the same fastness properties.

*Example 10*

On working as described in example 9, but inserting, after the swelling, a salt treatment, similar dyeings are obtained as those of example 9.

*Example 11*

A fibre produced as described in example 8 is dyed with a water-insoluble cellulose acetate dyestuff, for instance, a Celliton Fast Dyestuff. By the presence of the animalizing substance, the affinity of the triacetate against such dyestuffs is not as one should have believed, diminished, but even considerably increased, so that, for instance, the dye baths are almost completely exhausted and the dyeings are deeper than on acetate artificial silk having an acetic acid content of 54–55%.

*Example 12*

Fibres of chloroform-soluble cellulose acetate produced by the dry- or wet-spinning process are locally printed with 60% aqueous acetic acid, if desired, in the presence of a thickening agent and thereupon dyed, or treated with salt and after drying dyed with cellulose acetate dyestuffs at 70–80° C. Thereby fibres are obtained which show interesting two-colour effects, because the untreated places do not or practically not absorb the dyestuff, whereas the treated fibres absorb the same very strongly.

*Example 13*

Fibres of triacetate having incorporated therewith an animalizing agent are spun and treated as described in example 12. Flamed fibres may be obtained with cellulose acetate dyestuffs or with acid wool dyestuffs, chrome dyestuffs and so on.

*Example 14*

A fabric prepared of cellulose triacetate fibres is printed in patterns with a paste containing 65% aqueous acetic acid, washed and dyed, or washed, treated with a salt as described in example 7 and then dyed. With suitable dyestuffs, for instance, with Cellit Fast Blue B, dark patterns on a white ground are obtained.

*Example 15*

A fabric of triacetate artificial silk having incorporated an animalizing agent is printed as described in example 14. On dyeing with cellulose acetate dyestuffs, similar effects as in example 14 are obtained. By dyeing with acid wool dyestuffs or with chrome dyestuffs which reserve acetate silk, coloured patterns on a white ground are obtained.

ROBERT SCHNEGG.