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AGENT FOR DYEING ANIMAL FIBRES AND METHOD OF MAKING SAME

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2 Claims. (Cl. 260—123.7)

The process according to the present invention enables animal fibres, and particularly wool to be dyed with chrome dyes, in total times of operation reduced by 50%, and with the boiling time reduced by 85% compared with the times deemed indispensable for said operations heretofore. Moreover, the treatment with chromium salts subsequent to acid dyeing, is carried out at a temperature below boiling and in a period of time about 40% shorter than that universally prescribed and applied in this operation, which heretofore has been habitually carried out in a boiling bath for at least 30 to 40 minutes.

The terms "chrome dyes" and "acid dyes" as used in this specification mean any known chrome and acid dyestuffs, since this invention is applicable without exception to the dyeing of wool with all kinds of chrome and acid dyestuffs. As defined in the Encyclopaedia Britannica, acid dyestuffs are salts of colored compounds containing acidic groups and they dye animal fibres directly from an acidified solution, owing their affinity towards animal fibres to the sulphonic or other acid groups they contain, which enter into combination with the amino groups of the protein molecules. Mordant and chrome dyes are defined in the Encyclopaedia Britannica as colored compounds containing particular groups, usually —OH or —COOH groups, capable of forming stable colored lakes with metallic hydroxides, particularly those of chromium, aluminum, iron and copper.

Examples of well known acid dyestuffs given in the Encyclopaedia include fast yellow, metanil yellow, orange II, acid scarlets, fast reds, naphthalene blacks, acid magenta, soluble and alkali blues, patent blues, acid violets, acid greens etc.; the eosines, acid rhodamines, fast acid violets, the nigrosines, indolines, wool fast blues, wool fast violets, indocyanines, alizarine saphirol, alizarine irisol, alizarine emeraldol, alizarine cyanine green and alizarine direct blues.

Examples of chrome dyes given in the Encyclopaedia include dyes of the anthraquinone class, such as alizarine, purpurine, alizarine blue, alizarine cyanines, anthragallol etc.; the galloxyanines, eriochrome blacks, solochrome browns, reds and blacks, the eriochrome azurols and cyanines, gallein, coeruleine and ultraviridine, and the brilliant alizarine blues.

When dyeing with acid dyes, the total time and the duration of the boiling are proportionally diminished as specified hereinafter.

The dyeings thus obtained are characterized by excellent penetration and homogeneity.

The abbreviated dyeing time, the greatly reduced boiling time, the elimination of boiling during chrome-developing, and a particular chemical effect, which prevents the harmful oxidizing action of bichromate upon wool, have as a logical consequence a much better preservation of the fibre, which in addition to its improved suitability for spinning, also provides the following advantages:

(a) The yield of wool after dyeing is improved (owing to the reduced formation of soluble wool degradation

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products produced when wool is boiled for a long time, and owing to decreased deterioration during chrome-developing). The absolute yield of the yarn is always improved due to the decreased formation of waste in preparing and in spinning.

(b) The dynamometric resistance and elongation (elasticity) are always definitely improved.

(c) The percentage of breakages, defects in the yarns, and loss of weight by fulling of the respective fabrics are always decreased substantially.

(d) The deterioration of the wool dyed with this method in dilute alkaline solutions (with washing subsequent to dyeing) is decreased due to lower solubility and hence greater stability against oxidation, reduction, proteolytic enzymes etc.

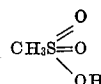
Dyeing operations which are speeded up by 50% allow for a corresponding increase in production and proportional to reduction of the general dyeing expenses; the boiling times being reduced by 85% save steam.

The further possibility of obtaining exceptional penetration and homogeneity on difficult material and with difficult dyes, eliminates many burdensome and poor dyeing results.

To make such dyeing process possible, an accelerating agent is used, which also has the property of imparting homogeneity and penetration to the dye bath, formed by the reaction of animal fibres, and specifically wool, with alkyl-alpha-oxysulfonic acids or with dialkyl sulfites, followed by a second reaction with alkyl-boric esters, in this way a product of considerable acidity is obtained, which is conveniently neutralized with sodium or ammonium hydroxide, to provide a stable product of determinable characteristics.

One example of obtaining the accelerating agent contemplated in the present invention, is as follows:

1 kg. of waste wool containing about 13% of cystin, is treated for 45 minutes at boiling temperature in a reflux apparatus with 10 litres of water to which 96 g. of methyl sulfonic acid



are added, which is derived as an ester from the asymmetric form of sulfurous acid. In this way and during this time, the breaking of the disulfide bond of the cystin is effected, as is evidenced by the strong swelling and partial colloidal solution of the wool. The mass is then cooled down to 15° C., 205 g. of methyl boric ester (B(OCH₃)₃, obtained by heating boric anhydride with methyl alcohol) are added and in a very rapid reaction the wool is almost completely dissolved while the acidity of the solution rapidly rises to pH=3.5. The solution is then neutralized to pH=7 with sodium hydroxide or with ammonium hydroxide and it is concentrated under vacuum at a maximum temperature of 42° C., to obtain a total product of partial salt form which is sufficiently stable and has a melting point of about 47° C. To bring this product to a convenient concentration for use and to increase the preservation and stability of its solutions, sodium sulfate, dextrines, amides etc. may be added, as a buffer.

This product imparts to the dye baths a powerful equalizing and penetrating action, without retarding the exhaustion of the dye solutions (in contrast to many dye assistants, which act by retarding action) in a manner similar to old acid dyeing baths. On the contrary, it accelerates visibly the exhaustion of the dye baths and, owing to its equalizing power, it allows with dyes of difficult homogeneity, to be dyed with the initial addition of the desired quantity of acids, without recourse, as is common, to re-

tarded additions of acid in order to exhaust the bath gradually during the course of dyeing.

Moreover, this product, which is a good selective acceptor for oxygen, catalyzes strongly the chromating (subsequent to dyeing) of chrome dyes, which is rendered possible without prolonged boiling any other deterioration of the wool by violent oxidation; hitherto prolonged boiling was necessary.

Examples

(A) *Chrome dyes*.—To the dye bath, heated to about 30° C., is added the 0.5–1–2% respectively for clear, medium and full colours, of the accelerating agent of this invention, of the kind hereinbefore described, then the required initial quantity of acetic or formic acid together with the required quantity of acid for exhausting the bath (e. g. sulfuric acid, formic acid, etc.) and finally the dye. The temperature is raised to boiling temperature in 30 minutes and is allowed to boil for a further 15 minutes (instead of 60 minutes as heretofore). Then the bath is exhausted and is cooled down at once rapidly as is customary, i. e., in about 5 minutes, the required quantity of K or Na bichromate is added, and the bath is heated to 90° C. The steam is cut off and the bath allowed to act for 30 minutes; this is in contrast to the usual 50–60 minutes of which 30–40 minutes of continuous boiling was indispensable heretofore.

The actual dyeing time is 75 minutes as against 150 minutes conventional time. The actual boiling time is 15 minutes as against 100 minutes conventional minimum.

(B) *Monochrome dyes*.—The accelerating agent of this invention is added at the beginning of the dyeing and then the method proceeds as conventionally prescribed

for this dyeing method. However, it is sufficient to boil for only half of the conventional time, to obtain perfectly solid and resistant dyeings.

(C) *Acid dyes*.—The accelerating agent of this invention is added at the beginning of the dyeing, the temperature is raised to boiling in the usual time and then boiled only 15 minutes boiling, whereupon the dyeing process is generally finished and one can thus sample starting at once the eventual shading which too proceeds with great rapidity and homogeneity.

(D) *Metallized dyes*.—As with acid dyes, but it is necessary to boil during a longer time for obtaining a well completed dyeing. Usually however half the boiling time suffices as compared with the conventionally indispensable very long boiling time necessary to obtain a good result with conventional dyeing methods.

What I claim is:

1. The method of preparing an accelerating agent for the acid and chrome dyeing of animal fibres, which comprises treating wool under reflux for about 45 minutes with methyl sulphonic acid and water, in the proportions of about 1 kg. wool, 10 litres of water and 96 g. of methyl sulphonic acid, cooling the reaction mixture to room temperature, adding methyl borate in the proportion of about 205 g., neutralizing the resulting solution with alkali, and concentrating the neutral solution under vacuum.

2. The acid- and chrome-dyeing accelerating agent prepared by the method defined in claim 1.

References Cited in the file of this patent

Blackburn et al.: *Biochem. Journal*, vol. 38, No. 1, pp. 25–29 (1944).