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2,903,324

PROCESS FOR THE DYEING OF WOOL

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Copending application Serial No. 410,433, filed February 15, 1954, now abandoned, discloses a quick process for the dyeing of wool, if desired of wool mixed with other textile fibres in particular with synthetic polypeptide fibres which are similar to wool. The dyestuffs used in this process are complex heavy metal compounds of monoazo and azo methine dyestuffs which contain 2 dyestuff molecules to 1 heavy metal atom, and with the exception of any carboxyl groups present taking part in the complex formation, which contain no acid water solubilising groups. This process consists in putting the goods to be dyed direct into a hot dyebath prepared with the above named heavy metal compounds of dyestuffs, the pH value of the bath being at least 7.5, and completing the dyeing at the boil and sinking pH value while strongly circulating the liquor or moving the goods well. Dependent on the depth of the shade and the type of dyestuff used and the agent used to lower the pH value, in this manner completely even, fully developed dyeings which have good fastness properties are obtained in the very short time of from 10 to 30 minutes.

The best results are obtained with this process in a weakly alkaline pH range by which the pH value of the liquor can be kept under that limit of alkalinity which would cause considerable damage to the wool.

Although the pH conditions to be observed in this process can be regarded as really not injurious to the material, it has been noticed when dyeing wool, even in only weakly alkaline baths, that the goods have a rather bad feel and cannot be spun so easily. In particular for loose wool, slubbing and in some cases also for knitting wool, there is a need, therefore, for a quick acid dyeing process.

It is known however, that in the acid pH range, particularly however, in hot acid baths, the affinity of these heavy metal containing dyestuffs to natural and synthetic polypeptide fibres is so great that, because of too quick exhaustion of the baths, only uneven dyeings are obtained which technically are unusable. Up to now, it has been attempted to overcome this difficulty by either entering the goods into the liquor containing the dyestuff at a low temperature or by adding the dissolved dyestuff to the dyebath at low temperatures of 40° to 60°. The dyeing then proceeded at a relatively long drawn out warming and dyeing time under exact temperature control, whilst in particular the critical temperature of from 70 to 80° C. was very slowly passed, if necessary by completely halting the increase in temperature. For this purpose an acid buffer mixture from alkali acetate and acetic acid has proved to be greatly superior to the

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sodium sulphate-sulphuric acid mixture usual in wool dyeing.

In contrast to this method, it was a great technical advance when a quick acid dyeing process was found which enabled wool, if desired in a mixture with other fibres similar thereto, to be dyed evenly and quickly with complex heavy metal compounds, in particular with complex chromium and cobalt compounds of monoazo and azo methine dyestuffs of the type described above. This process according to Patent No. 2,817,575, patented on December 24, 1957, consists in pre-treating the wool—preferably in the dyebath—in the absence of the dyestuff, in a hot circulating liquor which contains so much of a polybasic strongly dissociating mineral acid that the final pH value of the liquor is constant between 4.0 and 6.0 whereupon the dyestuff is added at a temperature of over 80°, advantageously dissolved in water, and dyeing is continued in the presence of capillary active polyglycol ethers containing no nitrogen, at the boil while circulating the liquor or moving the goods well until the bath is exhausted to all intents and purposes.

On further work being done on this subject, it has been found that if dyeing is performed in closed vessels under pressure advantageously at temperatures of up to about 110°, particular advantages are attained with regard to the shortness of the dyeing time and evenness of the dyeings and, under these conditions, even with regard to the presence in the dyebath of a polyglycol ether to retard the drawing of the dyestuff.

The present invention concerns a further development of the process for the dyeing of wool with complex heavy metal compounds of monoazo and azo methine dyestuffs which contain two dyestuff molecules to one heavy metal atom, preferably a chromium or a cobalt atom bound in complex linkage and—with exception of any carboxyl groups present in complex linkage—which contain no acid dissociating groups which form hydroxonium ions in water, according to the aforesaid Patent No. 2,817,575. This process is characterized by pre-treating the wool first in a hot, acid dye liquor not containing any dyestuffs but containing so much of a strongly dissociating polybasic mineral acid that the final pH value is from 3 to 6, and preferably from 4 to 5, then adding the dyestuff and dyeing in a closed vessel under pressure. It is of advantage to add the dyestuff in aqueous solution to the warm, or preferably, hot dyebath. The temperature of the apparatus is then rapidly raised to about 110° C. and dyeing is performed at this temperature while constantly circulating the liquor well until the bath is exhausted.

Chiefly sulphuric acid and phosphoric acid can be used as polybasic strongly dissociating mineral acids. The amount of acid necessary is dependent on the pre-treatment of the wool and is preferably determined by previous trials for a certain type of goods. In a hot dye liquor, generally a few minutes are sufficient for the pre-treatment, e.g. the time from the entering of the goods into the apparatus to the beginning of the actual dyeing. As in the process according to the aforesaid Patent No. 2,817,575, here also care must be taken to ensure that the liquor circulates well both during the acid treatment and during the actual dyeing process. The well dissolved dyestuff is advantageously added to the closed apparatus which has been previously put under pressure with gases,

after the desired temperature at which to begin dyeing has been reached. It is particularly advantageous to begin the dyeing in the region of the normal boiling point of water and at a final pH value of the acid pre-treatment liquor of 5 and more. The temperature of the apparatus is kept between 100 and 115° C. while dyeing is continued. It should never exceed this figure as, according to Justus' trials, the wet tensile strength of wool quickly begins to fall when dyeing in liquors of over 110° C. (see Deutscher Färbekalender, 1954, pp. 62-65). The preferred temperature is one lying between 100 and 106° C. although good results are obtained at temperatures even a little below 100° C. provided dyeing is performed in the presence of compressed gases. At the preferred temperature of 100 to 106°, level dyeings are obtained in 5 to 15 minutes. Retarding polyglycol ethers, e.g. those of higher fatty alcohols, can either be not used or, in contrast to the amounts given in the aforesaid Patent No. 2,817,575, very much reduced. If desired, also other dyeing auxiliary agents such as e.g. naphthalene mono-sulphonic acid-formaldehyde condensation products, can be added to the dye liquor. Dyeing can be completed in a not over-heated liquor at the boil under normal pressure. The dyeing time can thus be as long as normal without any injurious effects. Dyeing under compressed gases in a not over-heated liquor is particularly recommended if shading additives have to be used. Otherwise, the particulars and conditions given in the aforesaid Patent No. 2,817,575 pertain.

It is surprising that, while overcoming justified prejudices, in the process according to the present invention, it is possible to dye perfectly evenly on to wool heavy metal containing dyestuffs which contain no sulphonic acid groups and no carboxyl groups not taking part in the complex formation from a mineral acid bath by a quick method. It is also particularly characteristic of the inventive nature of the new method that not so perfect results can be obtained with the organic acids chiefly used up to the present such as e.g. with acetic acid or also with formic acid, even when working under the same conditions.

The following examples illustrate the invention without limiting it in any way. The parts are given as parts by weight and the temperatures are in degrees centigrade.

The following examples were performed in a high temperature dyeing apparatus of the Thies type.

This works according to the principle of stationary material and circulating liquor and consists of an autoclave, an expansion vessel and a centrifugal pump worked by an electric motor. The autoclave serves as container for the goods, the expansion vessel as pressure compensating chamber. On heating, the enclosed air is compressed so that there is static pressure on the bath. Additional static pressure which is independent of temperature can also be attained by compressed gases, e.g. nitrogen or air. The expansion vessel serves as container for additives and dyestuffs, so that it is possible for the whole liquor to be heated in the expansion vessel before dyeing. The dyestuff solution is entered into the expansion vessel by means of a communicating tube; the dyestuff can be added while the apparatus is working under static pressure. The liquor is drawn from the expansion vessel into the pump and from there into the autoclave and back into the expansion vessel. A heating tube allows of the heating or cooling of the liquor. Tubes can be screwed into the autoclave to hold the cylindrical and conical cheeses, loose wool and tops.

(a) Dyeing of conical worsted yarn cheeses: Conical worsted yarn cheeses are placed on to tubes serving to hold the goods which are screwed into the liquor container. The liquor is pressed alternately from the inside to the outside and sucked from the outside to the inside of the cheeses.

Example 1

100 parts of woollen worsted yarn are dyed as follows: 1500 parts of soft water are poured in, the pump is set in motion, 0.54 part of sulphuric acid (98%) is added and then the bath is heated with indirect steam to 85° within 5 to 15 minutes. The pH value of the liquor is then measured, it should be about 5.0. The apparatus is closed and a static pressure of 3 atm. is attained by the introduction of nitrogen into the expansion vessel. At 85°, 1.5 parts of the grey complex metal compound from 2 mols of the monoazo dyestuff 2-aminophenol-4-ethyl sulphone→acetylaminonaphthol-(1.7) co-ordinated with 1 chromium atom well dissolved in hot water are then added. The bath is heated within 10 minutes to 106°, kept at this temperature for 15 minutes and at the end of this time, dyeing is finished by quickly cooling to 90° and opening the dyeing autoclave. On completion of the dyeing, the liquor has a pH value of 5.1.

In this way, very level fully penetrated cheeses of an even grey colour are obtained.

Example 2

The dyebath is prepared according to the information given in Example 1. Dyeing is performed with 1 part of the grey complex metal compound from 2 mols of the monoazo dyestuff 2-aminophenol sulphonic acid methylamide→acetylaminonaphthol-(1.7) co-ordinated with 1 chromium atom and 0.2 part of the wine red complex metal compound from 2 mols of the azo dyestuff from 2-aminophenol-4-sulphonic acid methylamide→β-naphthol, co-ordinated with 1 cobalt atom. Dyeing is performed as in the previous example under 3 atm. pressure but the temperature is raised only to 98° within 5 minutes and dyeing is completed at this temperature after 30 minutes.

In this way, very level well penetrated cheeses of an even silver grey colour are obtained.

Example 3

The procedure as in Example 1 and the dyestuff mixture as in Example 2 are used; instead of sulphuric acid however, 0.54 part of phosphoric acid (84%) is added. During dyeing, which is also performed at static pressure, the pH value rises from 5.3 to 5.5.

In this way, very level well penetrated cheeses of an even silver grey colour are obtained.

(b) Dyeing of woollen slubbing on tops: The apparatus is prepared by placing the tops on perforated tubes which serve to hold the goods which are screwed into the liquor container. The liquor is forced from the inside to the outside of the tops by means of the circulation pump.

Example 4

1500 parts of water are poured in, the circulation pump is set in motion and the bath is heated with indirect steam to 60°. While heating, 1.08 parts of sulphuric acid (98%) are added. On reaching 60°, the steam is turned off; the liquor is continuously pumped to attain a constant pH value and after 15 minutes this pH value is measured. The apparatus is then closed and nitrogen is introduced into the expansion vessel until there is a pressure of 3 atm. Then, while continuously pumping, 0.5 part of the yellow complex metal compound from 2 mols of the monoazo dyestuff 2-aminophenol-4-methyl sulphone→acetoacetic acid-o-chloranilide co-ordinated with 1 cobalt atom is added. The liquor is pumped for a further 5 minutes at 60°, then the steam valve is opened and the temperature is raised in 15 minutes to 106°. The dyeing is finished according to the data given in Example 1. During the dyeing process the pH value of the liquor remains constant at 3.5.

In this way, very level well penetrated tops of an even yellow colour are obtained.

Further dyestuffs which can be dyed in a manner anal-

ogous to those described in the previous examples are given in the following table.

complex heavy metal compounds of dyestuffs selected from the group consisting of monoazo and azo methine

No.	Complex metal compound of the azo dyestuffs	Metal	Acid	pH	Colour of the wool dyeing
1-----	2 mols of azo methine dyestuff from 2-aminophenol-4-sulphamide → 3,5-dichloro-2-hydroxybenzaldehyde.	Cr	H ₂ SO ₄	4.2-4.5	yellow.
2-----	2 mols of dyestuff 2-aminophenol-5-sulphonic acid amide → 1-phenyl-3-methyl-5-pyrazolone.	Cr	H ₂ SO ₄	5.2-5.5	yellow red.
3-----	2 mols of dyestuff 2-aminophenol-4-sulphonic acid amide → 2-naphthol.	Co	H ₂ PO ₄	4.8-4.9	bordeaux red.
4-----	2 mols of dyestuff 4-chloro-2-aminophenol → 2-naphthol-6-sulphonic acid amide.	Cr	H ₂ SO ₄	5.7	violet.
5-----	mixed chromium complex of the dyestuffs 2-aminophenol-4-methyl sulphone → 2-naphthol and 5-nitro-2-aminophenol → 2-naphthol.	Cr	H ₂ SO ₄	3.6-3.8	blackish navy blue.
6-----	2 mols of dyestuff 2-aminophenol-4-sulphamide → 1-phenyl-3-methyl-5-pyrazolone.	Cr	H ₂ SO ₄	4.9-5.1	orange.
7-----	2 mols of dyestuffs 5-nitraminophenol → 1-phenyl-3-methyl-5-pyrazolone.	Cr	H ₂ SO ₄	3.2-3.3	red.
8-----	2 mols of dyestuff 4-nitro-2-amino-1-hydroxybenzene → 1-(3'-chlorophenyl)-3-methyl-5-pyrazolone.	Cr	H ₂ SO ₄	5.0-5.1	orange.
9-----	2 mols of azo methine dyestuff from 2-aminophenol-4-sulphamide → 5-chloro-2-hydroxybenzaldehyde.	Cr	H ₂ SO ₄	5.9	yellow.
10-----	2 mols of dyestuff 2-aminobenzoic acid → 1-phenyl-3-methyl-5-pyrazolone.	Cr	H ₂ SO ₄	3.9-4.1	greenish yellow.
11-----	2 mols of dyestuff 5-nitro-2-aminophenol → β-naphthylamine.	Co	H ₂ SO ₄	4.7	blue-grey.

What I claim is:

1. A method for the dyeing of wool with water-soluble complex heavy metal compounds of dyestuffs selected from the group consisting of monoazo and azo methine dyestuffs of the type containing two dyestuff molecules co-ordinated with one heavy metal atom and which, with the exception of carboxylic acid groups participating in complex formation do not contain any acid water solubilising groups, which comprises pre-treating wool in circulating hot water with a strongly dissociating polybasic mineral acid, adjusting the acid reaction of said hot water to a constant pH value of from 4 to 6, then adding an aqueous solution of the dyestuff and dyeing in a closed dyeing vessel under static gas pressure of at least 3 atmospheres, beginning below the boiling point and finishing at a temperature of from 90° to 115° C.

2. The process of claim 1 wherein the solution of the dyestuff is added to the dyeing vessel which is already under the said static gas pressure and charged with the wool.

3. A method for the dyeing of wool with water-soluble complex heavy metal compounds of dyestuffs selected from the group consisting of monoazo and azo methine dyestuffs of the type containing two dyestuff molecules co-ordinated with one chromium atom and which, with the exception of carboxylic acid groups participating in complex formation do not contain any acid water solubilising hot water with sulphuric acid, adjusting the acid reaction of said hot water to a constant pH value of from 4 to 6, then adding an aqueous solution of the dyestuff and dyeing in a closed dyeing vessel under static gas pressure of at least 3 atmospheres, beginning below the boiling point and finishing at a temperature of from 90° to 115° C.

4. A method for the dyeing of wool with water-soluble

dyestuffs of the type containing two dyestuff molecules co-ordinated with one cobalt atom and which, with the exception of carboxylic acid groups participating in complex formation, do not contain any acid water solubilising groups, which comprises pre-treating wool in circulating hot water with sulphuric acid, adjusting the acid reaction of said hot water to a constant pH value of from 4 to 6, then adding an aqueous solution of the dyestuff and dyeing in a closed dyeing vessel under static gas pressure of at least 3 atmospheres, beginning below the boiling point and finishing at a temperature of from 90-115° C.

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