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3,086,832

PROCESS FOR FINISHING DYEINGS

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It is known that cellulose fibers, such as cotton, can be dyed with advantage with dyestuffs which contain mobile reactive halogen atoms. It is also known that nitrogenous fibers, especially wool, can be dyed with the aforesaid dyestuffs in acid baths. However, the aforesaid dyestuffs are only partially suitable for this purpose. Some of these dyestuffs yield useful wool dyeings only in conjunction with certain assistants, which are hereinafter described. Generally, these dyestuffs have the disadvantage that they yield wool dyeings having unsatisfactory properties of wet fastness when the dyeing is carried out in the usual manner from an acid bath with or without one of the aforesaid additions. The properties of wet fastness, for example, the fastness to washing or perspiration, leave something to be desired not so much with respect to change in tint as with respect to bleeding on to or soiling fibrous materials that are undyed or differently dyed. This invention provides a process which enables this disadvantage to be largely or completely overcome.

Thus, the invention is based on the observation that by raising the pH-value of the acid dyebath after the dyestuff has been absorbed by the fiber the properties of wet fastness in relation to bleeding can be very substantially improved. Accordingly, this invention provides a process for finishing dyeings which have been produced on nitrogenous fibers with dyestuffs which contain at least one mobile halogen atom, in acid baths, wherein, after the fibers have absorbed the desired quantity of dyestuff, the pH-value of the dyebath is raised above 6.

The process is applicable to any nitrogenous fibers that have been dyed in the aforesaid manner, for example, silk or fibers of a polyamide obtained from ϵ -caprolactam or from adipic acid and hexamethylene diamine. However, the process is especially advantageous for wool dyeings.

The dyestuffs with which the fibers are dyed must contain at least one mobile halogen atom, that is to say a halogen atom capable of reacting with the fibrous material, for example, a bromine atom or advantageously a chlorine atom. In other respects the dyestuffs may belong to a very wide variety of classes of dyestuffs, for example, there may be mentioned stilbene dyestuffs, nitrodyestuffs, triphenylmethane dyestuffs, water-soluble phthalocyanine dyestuffs and above all acid anthraquinone or azo-dyestuffs, including metal-free and metallizable or metalliferous mono- or poly-azo-dyestuffs. In order that they can be dyed from acid baths, the dyestuffs must be soluble in such baths and therefore usually contain at least one sulfonic acid group.

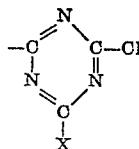
The mobile halogen atom may be bound, for example, to the acyl radical of an acid containing at least one acid group of the constitution



for example, to an acyl radical of cyanuric acid or of an aliphatic carboxylic acid. In the case of the acyl

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radical of cyanuric acid the dyestuffs contain at least one halogen atom bound to a 1:3:5-triazine ring, for example, a monochlorotriazine radical of the formula

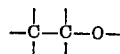


in which X represents an alkyl, aryl, aralkyl, alkylmercapto or arylmercapto group, or more especially an amino group which may be substituted or a hydroxyl group which is advantageously substituted; or a dichlorotriazine radical.

The halogen-containing acyl radicals of aliphatic carboxylic acids advantageously contain few carbon atoms, for example, two or three carbon atoms. As examples there may be mentioned the chloroacetyl group, the α - or β -chloropropionyl group and above all the α : β -dichloropropionyl group.

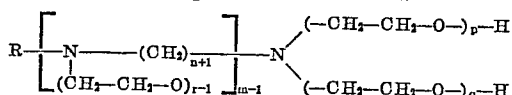
A large number of such dyestuffs is known or can be made by methods in themselves known, for example, from dyestuff components which contain the mobile halogen atoms, or by introducing by methods in themselves known radicals which contain mobile halogen atoms. Thus, by reacting an azo-dyestuff or anthraquinone dyestuff which contains a reactive hydroxy, mercapto or preferably a free amino group with chloroacetyl chloride, β -bromo- or β -chloro-propionyl chloride, chloropropionic anhydride or α : β -dichloropropionic acid chloride or anhydride, cyanuric chloride or a primary condensation product of cyanuric chloride which contains two chlorine atoms and, instead of the third chlorine atom, a free amino group or an organic radical, there are obtained valuable condensation products, which contain a mobile chlorine or bromine atom and are suitable for use in the process of this invention.

As stated above, some of these dyestuffs, especially those containing three or more than three sulfonic acid groups, when used for dyeing wool from acid baths yield weak, unlevel (skippery), practically useless dyeings. However, valuable level dyeings are produced with the aforesaid dyestuffs by dyeing wool in an aqueous bath in the presence of a compound which contains at least one basic nitrogen atom, to which is bound at least one radical containing a polyglycol ether chain, and the molecule contains at least three



groups (advantageously $\text{—CH}_2\text{—CH}_2\text{—O—}$ groups) and at least four carbon atoms that do not belong to such a group. In finishing dyeings by the process of this invention it is therefore of advantage, when these disadvantageous dyestuffs are used for dyeing, to add a nitrogen compound of the above constitution.

These nitrogen compounds apart from the fact that they must possess the characteristics defined above, may have a wide variety of constitutions. It will suffice herein to mention, as compounds especially suitable for this purpose, nitrogen compounds of the formula



in which R represents an advantageously unbranched aliphatic hydrocarbon radical containing at least 12 and preferably 16–20, carbon atoms, m and n each represents the whole number 1 or 2, and p , q and r each represents a whole number and the sum of $p+q+(m-1)(r-1)$ is at least 3, for example, 6 to 16.

Instead of the compounds containing free hydroxyalkyl groups, there may be used as assistants in the present process esters of these hydroxyalkyl-compounds with polybasic acids, for example, phosphoric acid or sulfuric acid, or water-soluble salts of these acids, for example, alkali metal salts or salts with ammonia or amines. Furthermore, in some cases skippery dyeings can be avoided by adding to the dyebath a cation-active compound, for example, cetyltrimethylammonium bromide, and also advantageously a polyglycol ether of an aliphatic alcohol of high molecular weight.

The dyeings with which the present process is concerned are dyeings that have been produced in acid baths, and for this purpose the dyeing is advantageously carried out in an acetic acid medium, that is to say, the dyebath has an acetic acid reaction at least at the beginning of the dyeing operation. It is therefore of advantage to incorporate in the dyebath advantageously at the beginning of the dyeing operation at least sufficient acetic acid to produce the desired pH-value, account being taken of the fact that both the fibrous metal and the dyestuff which is usually present in the form of an alkali metal salt consume a certain amount of acid. In general it is of advantage to add sodium sulfate to the dyebath.

As is usual in dyeing nitrogenous fibers, especially wool, the dyeing is carried out at a raised temperature, advantageously by commencing the dyeing process proper at about 50° C. to 80° C., and then heating the dyebath to the boiling temperature and continuing the process and completing it at that temperature. However, it has been found that in dyeing wool by the process of this invention it is not necessary to work at the boiling temperature of the dyebath or very close to that temperature. Usually equally good results are obtained by carrying out the dyeing process at a temperature distinctly below the boiling temperature, for example, at a temperature within the range of 80° C. to 90° C. When the dyeing is carried out in the presence of one of the aforesaid nitrogenous compounds, it is of advantage to enter the goods into the bath, which contains the acid and the assistant, that is to say the nitrogenous compound, and if desired sodium sulfate, at room temperature or at most a moderately raised temperature, then to raise the temperature of the bath and when the bath is hot, for example, at 50° C. to 80° C., to add the dyestuff in the form of an aqueous solution. If desired, the dyeing may be carried out in a suitable apparatus at a temperature above 100° C., at about 107° C.

The pH-value of the bath is then raised above 6. In order to raise the pH-value of the bath almost any water-soluble compound of alkaline reaction can be used.

However, in order to avoid damaging the fibers, especially in the case of wool dyeings, it is of advantage to add a compound of alkaline reaction of which an excess can be added without raising the pH value higher than about 9, and advantageously the pH is raised to a value within the range of 6.5 to 8.5. For this purpose it is of advantage to use nitrogenous bases, for example, amines such as ethanolamines. In some cases ammonia is quite suitable, and especially suitable is hexamethylene tetramine.

Alkali metal ortho-phosphates or polyphosphates or bicarbonates are also of advantage.

Only a relatively short time is required for the treatment at the higher pH-value, for example, about 10–30 minutes. It is preferably carried out at about the same temperature as that at which dyeing was carried out. For example, the dyebath may be maintained at the boiling temperature during the after-treatment, or the temperature may be allowed to fall slightly, for example, by discontinuing the supply of heat after the pH-value has been raised. Finally, the dyeings can be rinsed in the usual manner with warm and/or cold water and dried.

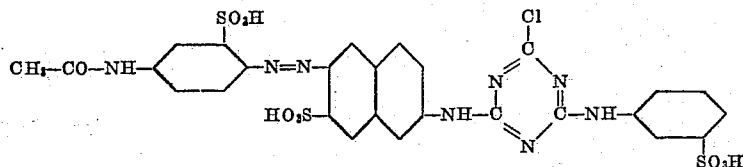
When dyeing is carried out in an acid bath in the presence of a nitrogenous compound of the kind referred to above, a considerable amount of the nitrogen compound remains adhering to the wool after rinsing and drying. This may cause a change in the feel of the wool, a change in the behaviour of wool piece goods in after-dressing treatments, or, due to the increased slip of the material, may affect the spinning properties of loose wool or combed wool, and a change in the speed of drying of the wet wool is frequently observed. These usually undesirable phenomena are avoided by raising the pH-value because the nitrogenous compounds are retained by the wool only under acid conditions, whereas they remain in solution in neutral baths or return to the dyebath when the wool surface is neutralized.

The process of this invention is especially suitable for dyeing mixtures of nitrogenous fibers with cellulose fibers, for example, so-called half-wool, since it can be carried out in a 2-stage process in a single bath. The wool component of the mixed fibers is first dyed in the manner described above, the cellulosic component remaining substantially undyed. After raising the pH-value, for example, by means of ammonia, there are added, advantageously without the further supply of heat, first sodium sulfate and then a direct-dyeing cotton dyestuff. It is of advantage to use a dyestuff which does not dye wool at all or only very slightly in the vicinity of 100° C. The dyeing is then continued until the cellulose fibers have attained the desired tint, for example, for about ½ hour, and then the dyeing is finished in the usual manner. In order to improve the properties of wet fastness of the dyed cellulose fibers it may be of advantage to subject them to an after-treatment in known manner with an agent capable of improving the properties of wet fastness, for example, the condensation product of dicyandiamide and formaldehyde.

The following examples illustrate the invention, the parts being by weight:

Example 1

100 parts of knitting wool, 3000 parts of water, 10 parts of crystalline sodium sulfate, 6 parts of acetic acid of 40% strength and 0.5 part of the addition compound from oleylamine and ethylene oxide described below are heated to 80° C. A solution of 2 parts of the dyestuff of the formula



in a small amount of water is added to this bath. In the course of ½ hour the bath is raised to the boil, and dyeing at the boil is carried on for 1 hour. The dyebath, which by then is practically exhausted, is treated with 3 parts of hexamethylenetetramine, and the whole is boiled for a further 30 minutes. The wool is then rinsed and dried. A very pure scarlet dyeing is obtained. The fastness of this dyeing to wetting, more especially insofar as bleeding into cotton is concerned, is subsequent increase of the pH value. Before the addition of hexamethylene-

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tetramine the pH is about 4.8, and the addition raises it to about 7.2.

The addition compound of ethylene oxide is prepared in the following manner:

100 parts of commercial oleylamine are mixed with 1 part of finely disintegrated sodium, the whole is heated to 140° C. When the ethylene oxide is being absorbed rapidly, the reaction temperature is reduced to 120 to 125° C., and the introduction of ethylene oxide is continued until 113 parts thereof have been absorbed. The reaction product obtained in this manner gives a practically clear solution in water.

Instead of the above ethylene oxide adduct the following products may be used:

(a) N-alkyl-propylenediamine (whose alkyl radicals correspond to the radical of tallow fatty acid)+8 mols of ethylene oxide;

(b) Dodecylamine+3 mols of ethylene oxide;

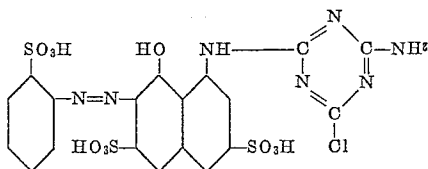
(c) Dodecylamine+3 mols of propylene oxide (this product can be prepared thus: 24 parts of commercial dodecylamine are heated to 160° in the presence of 0.13 part of finely disintegrated sodium in a current of nitrogen. Gaseous propylene oxide is then introduced until 19.5 parts thereof have been absorbed);

(d) The acid sulfuric acid ester obtained as follows: 79 parts of a mixture of fatty amines (0.3 mol) consisting of 30% of hexadecylamine, 25% of octadecylamine and 45% of octadecenylamine are reacted with ethylene oxide in the presence of 0.8 part of sodium until 106 parts (2.4 mols) of ethylene oxide have been absorbed.

The reaction temperature is at first 140 to 150° C. and can be gradually reduced to 120 to 125° C. 30.75 parts (0.05 mol) of the resulting ethylene oxide adduct are mixed in a stirring flask at 60° C. within 15 minutes with 5.4 parts of urea and then within 30 minutes with 5.4 parts of sulfamic acid (0.05 mol+10%) and kept for 5 to 6 hours under nitrogen on a boiling water bath. The resulting product (41 parts) is readily soluble in water and is of neutral reaction.

Example 2

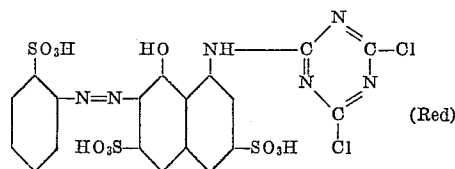
A piece of wool (100 parts) is immersed at 60° C. in a dyebath containing in 4000 parts of water 5 parts of acetic acid of 40% strength, 10 parts of crystalline sodium sulfate, 0.25 part of the ethylene oxide adduct described in the 2nd paragraph of Example 1 and 2 parts of the dyestuff of the formula



The whole is raised to the boil within ½ hour and dyeing is carried on at the boil for 1 hour. The heating is then discontinued, and 3 parts of aqueous ammonia of 25% strength are added. After 15 minutes the wool is removed from the dyebath, immediately rinsed in water and dried. A level red dyeing is obtained having a fastness to wetting which is much better than when no ammonia is subsequently added. The addition of ammonia raises the pH value from about 5.0 to 8.0.

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Instead of the dyestuff of the above formula there may be used the dyestuff of the formula

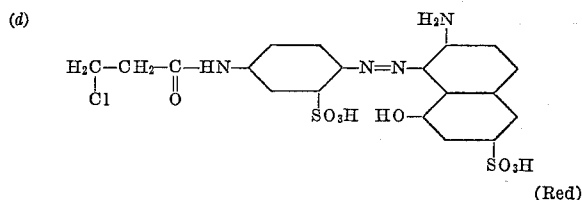
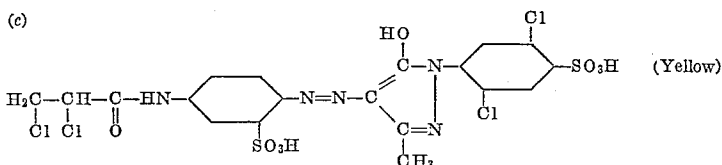
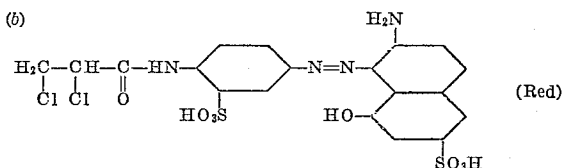
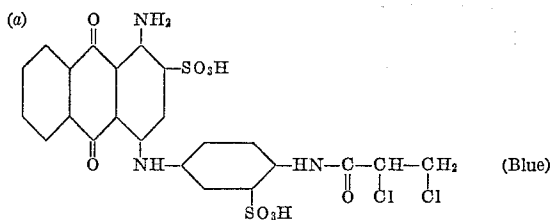


Practically identical dyeings are obtained when, after the addition of the dyestuff, the bath temperature is raised only to 85° C., dyeing being continued at this temperature for 1 hour.

Instead of with ammonia the raising of the pH value towards the conclusion of the dyeing operation may be achieved with triethanolamine or sodium bicarbonate.

Example 3

Dyebaths are prepared containing in 2000 parts of water, 6 parts of acetic acid of 40% strength and 1 part each of the dyestuffs of the formulae:



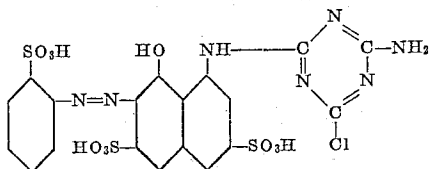
At 60° C. 100 parts of wool tops are immersed in the dyebath which is raised to the boil within ½ hour, and dyeing is carried out at the boil for 1 hour. The heating is then discontinued and 2.5 parts of trisodium phosphate are added. After 15 minutes, the wool is taken out of the dyebath, rinsed and dried. The resulting dyeings have much better fastness to wetting than when the subsequent addition of trisodium phosphate is omitted. This addition raises the pH value of the dyebath from about 4.7 to about 6.7.

Example 4

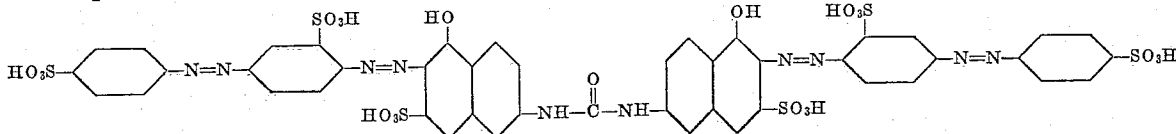
100 parts of a blended yarn of equal parts of wool and regenerated cellulose (staple fibers) are immersed at 50° C. in a dyebath containing in 4000 parts of water 5 parts of acetic acid of 50% strength, 0.5 part of the

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ethylene oxide adduct described in the 2nd paragraph of Example 1 and 1 part of the dyestuff of the formula



The whole is raised to the boil within ½ hour and dyeing is continued for ½ hour at the boil. The heating is then discontinued, and 3.5 parts of aqueous ammonia of 25% strength, 30 parts of crystalline sodium sulfate and 1.5 parts of the dyestuff of the formula



are added. The temperature is allowed to drop to about 80° C. within ½ hour. The dyeing is rinsed in cold water and dried. A very level, pure red dyeing is obtained.

To improve the wet fastness properties of its cellulose fibers, the material dyed in this manner can be after-treated in known manner with a condensation product from 2 mols of formaldehyde and 1 mol of the reaction product from 1 mol of ethylenediamine dihydrochloride with 2 mols of dicyandiamide.

What is claimed is:

1. A process for finishing a dyeing produced on nitrogenous fibers in an acid bath with a dyestuff containing at least one mobile halogen atom, which comprises raising the pH value of the bath above 6 when the fibers have absorbed the desired quantity of dyestuff.
2. A process for finishing a dyeing produced on wool in an acid bath with a dyestuff containing at least one mobile halogen atom, which comprises raising the pH value of the bath above 6 when the fibers have absorbed the desired quantity of dyestuff.
3. A process for finishing a dyeing produced on wool with a dyestuff selected from the group consisting of a dyestuff containing a chloropropionyl radical and a dyestuff containing a chlorotriazine radical in a bath which is acid with acetic acid at the beginning of the dyeing operation, which process comprises raising the pH value of the bath above 6 when the fibers have absorbed the desired quantity of dyestuff.
4. A process for finishing a dyeing produced on wool with a dyestuff containing a chlorotriazine radical in a bath which is acid with acetic acid at the beginning of the dyeing operation, which process comprises raising the pH value of the bath above 6 by addition of a nitrogenous base when the fibers have absorbed the desired quantity of dyestuff.
5. A process for finishing a dyeing produced on wool with a dyestuff containing a chlorotriazine radical in a bath which is acid with acetic acid at the beginning of the dyeing operation, which process comprises raising

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the pH value of the bath above 6 by addition of ammonia when the fibers have absorbed the desired quantity of dyestuff.

6. A process for finishing a dyeing produced on wool with a dyestuff containing a chloropropionyl radical in a bath which is acid with acetic acid at the beginning of the dyeing operation, which process comprises raising the pH value of the bath above 6 by addition of ammonia when the fibers have absorbed the desired quantity of dyestuff.
7. A process for finishing a dyeing produced on wool with a dyestuff containing a chlorotriazine radical in a bath which is acid with acetic acid at the beginning of the dyeing operation, which process comprises raising the

pH value of the bath above 6 by addition of hexamethylene tetramine when the fibers have absorbed the desired quantity of dyestuff.

8. A process for finishing a dyeing produced on wool with a dyestuff containing a chloropropionyl radical in a bath which is acid with acetic acid at the beginning of the dyeing operation, which process comprises raising the pH value of the bath above 6 by addition of hexamethylene tetramine when the fibers have absorbed the desired quantity of dyestuff.
9. A process for finishing a dyeing produced on the wool part of a mixture of wool and cellulose fibers in an acid bath with a dyestuff containing at least one mobile halogen atom, which process comprises raising the pH-value of the bath above 6 when the wool fibers have absorbed the desired quantity of dyestuff and then dyeing the cellulose fibers in the same bath with a substantive dyestuff.
10. A process for finishing a dyeing produced on the wool part of a mixture of wool and cellulose fibers with a dyestuff containing at least one mobile chlorine atom in a bath which is acid with acetic acid, which process comprises raising the pH-value of the bath above 6 when the wool fibers have absorbed the desired quantity of dyestuff and then dyeing the cellulose fibers in the same bath with a substantive dyestuff.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 11,647	Schaeffer	Feb. 1, 1898
654,864	Wilson	July 31, 1900
2,719,104	Westerberg	Sept. 27, 1955
2,723,262	Guasco	Nov. 8, 1955
2,773,871	Brassel et al.	Dec. 11, 1956
2,895,785	Alsberg et al.	July 21, 1959
2,900,218	Gray	Aug. 18, 1959
2,903,324	Hirsbrunner	Sept. 8, 1959
2,914,531	Staeuble et al.	Nov. 24, 1959
2,940,812	Denyer et al.	June 14, 1960