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PROCESS OF TREATING ANIMAL FIBERS

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This invention deals with a process of treating animal fiber, especially wool, whereby to increase its affinity for various organic compounds as more fully defined below.

In the copending application of one of us, Serial No. 329,108, it has been shown that if wool is treated with certain specified agents it acquires increased affinity for indigo and other vat dyes, as a result of which wool may be dyed with said dyestuffs from an alkaline bath in a sufficiently short time to avoid substantial injury to the animal fiber by the alkaline liquors.

In copending application of G. T. Hug, Serial No. 403,074, filed July 18, 1941, a further development of this invention is described wherein the pre-treated wool is then dyed with azo dyes of the so-called "ice-color" class.

The details of procedure as set forth in the earlier of said copending applications consisted essentially of treating woolen material by padding it through a solution or suspension of a sulfur-containing compound selected from a specified group, squeezing the textile material to remove excess solution, running the same into a steam-ager wherein it was exposed to steam at atmospheric pressure for a short time, then rinsing the material with warm water and running it directly into the vat containing the indigo or similar dye.

We now find that superior results both from the chemical viewpoint and from the viewpoint of mechanical manipulation are obtained if the steaming and rinsing steps are omitted and replaced preferably by a drying step, whereby the wool is substantially rid of moisture prior to its entry into the alkaline dyeing bath. The said drying step, which may be carried out at a temperature between 200 and 300° F., appears to increase the rate of penetration of the wool by the alkaline liquors and seems further to increase the degree of dyeing or impregnation which it is desired to effect by said liquors. The ultimate result is a stronger and more uniform dyeing, as well as greater strength in the fiber itself.

Moreover, whereas in said prior process it was necessary to enter the wool into the dye bath promptly after the pretreatment, as otherwise the effect of the pretreatment would be weakened or lost, we find now that when the steaming step is replaced by a drying step the effect of the pretreatment becomes much more stable, and further treatment may be delayed in some cases for several hours or even days.

As treating agents for the purpose stated the following were mentioned in said prior application: formamidine-sulfinic acid, hydrosulfite, the aldehyde sulfoxylates, the bisulfites and the water-soluble sulfides. All these were classed under the single heading of sulfur-containing, vat-reducing agents. Not all of these, however, are satisfactory in our present improved process.

More particularly, we find that for the purpose of the improved process of this application it is better to limit the treating agent to that subgroup which dissolves in water with a mildly acid reaction. The alkali-metal bisulfites and the water-soluble hydrosulfites (e. g. sodium- or zinc-hydrosulfite) are suitable examples of such agents, and at the concentrations preferred for this invention (1 to 4 ounces per gallon) they give the pre-treatment bath a pH value somewhere between 3.5 and 4.5. Also, it is desirable for the purpose of our invention that the drying be effected at elevated temperature. No critical lower limit has been found by us for this temperature, but it should apparently be high enough to cause decomposition of the treating agent within the fiber. Of course, it should be low enough to avoid carbonization of the wool fiber. The range of 160 to 300° F. may be taken as useful for practical purposes.

In all other details the pre-treatment of the animal fiber according to this invention and the subsequent dyeing operation may follow the details set forth in the prior applications above referred to, and may be followed by dyeing according to either of said copending applications.

Our invention accordingly consists of an improved process for treating animal fiber, such as wool, whereby to endow it with improved affinity for indigo, anthraquinone vat-dyes, naphthols, and in general for any organic compound which does not dissolve in water except after transformation into an —ONa compound or an equivalent —OM compound, M being an alkali-metal. By this we mean that the compound has to be transformed into one which has one or more ONa groups (or OM groups) attached to carbon in its nucleus.

As additional typical examples of such organic compounds may be mentioned alpha- and beta-naphthol, 2,3-hydroxy-naphthoic acid, and the various arylides of 2,3-hydroxy-naphthoic acid which are well known in the art of dyeing textiles by means of the so-called "ice colors." These compounds are not soluble in neutral or weakly acid water, but they dissolve readily in alkaline aqueous baths, presumably by forming an OM compound in solution by direct action of the alkali on the phenolic OH group.

The vat dyes of the anthraquinone or indigoid series likewise dissolve in water by virtue of transformation into OM-compounds. These dyestuffs, as is well known, are characterized by their content of ketonic groups (CO) in the molecule, and by their insolubility in water. They may be brought into solution however by "vatting", that is treating them with an aqueous bath containing both alkali and a reducing agent. The accepted theory of this phenomenon is that the



group is reduced into a



group (the so-called "leuco-form") which is instantly neutralized by the alkali present into the form ≡C—ONa, or equivalent form ≡C—OM, depending on the particular alkali selected.

The increased affinity above mentioned which animal fiber acquires for OM-type compounds when pre-treated according to this invention, expresses itself in an increased speed of absorption of such compounds from their alkaline solution, as well as in a stronger ultimate dyeing. As a result of these factors, our improved process enables the development of continuous processes for treatment of animal fiber in the form of piece goods.

This development itself is of tremendous practical value inasmuch as it renders vat dyes and "ice-colors" applicable to wool in economical manner, whereas hitherto such colors could be applied to such fiber only under special and costly procedures, if at all.

Without intent to limit our invention thereby, the following examples are given to illustrate our preferred mode of operation. Parts mentioned are by weight.

A. Indigo and Vat Dyes

Example 1

In a continuous operation, wool flannel is padded through an aqueous solution containing 2½ ounces per gallon of sodium bisulfite at 130–140° F. The time of immersion is approximately 3 seconds (operative range 1 to 10 seconds) and the squeezing rollers are adjusted to permit the material to retain 100 to 150% of its weight of moisture. The material is then thoroughly dried at a temperature of 240–275° F. The treated flannel is then run through a vat containing 3 ounces per gallon of reduced indigo 20% paste. The indigo is first reduced according to normal procedure with hydrosulfite and caustic soda and the bath is rendered alkaline with ammonia. Time of immersion in the indigo vat is 3 minutes at 125–130° F. After dyeing, the cloth is squeezed to remove excess moisture and oxidized according to normal procedure.

The dyeings so obtained are at least 50% stronger in shade than if untreated wool is dyed in an indigo vat of the same strength.

Example 2

Wool flannel is padded through a solution containing 2½ ounces per gallon of sodium hydrosulfite at 100–110° F. The time of immersion is approximately 3 seconds and the squeezing rollers are adjusted to permit the material to retain 100 to 150% of its weight of moisture. The impregnated material is then thoroughly dried at 240–275° F.

The pretreated flannel can now be dyed in a bath containing reduced indigo 20% paste as described in Example 1. Very much heavier shades are obtained than if untreated flannel is dyed in a bath of equal strength.

Example 3

Wool crepe is pretreated by padding through a solution containing 2½ ounces per gallon of sodium hydrosulfite and dried as described in Example 2. It is then passed through a bath, for 2 minutes at 125° F., containing one ounce per gallon of reduced Ponsol red BN double paste (Color Index #1162). The vat dye is first reduced with hydrosulfite and caustic soda as commonly employed in the dyeing of cotton. To prevent an undue deleterious action of the alkali on the wool, however, only two-thirds of the normal amount of caustic soda is to be used for reduction. After passage through the dye bath the wool crepe is squeezed to remove excess moisture and oxidized by chemical means. The dyeings on the pretreated material are at least 50% stronger than dyeings on untreated crepe.

Example 4

Wool flannel is pretreated with sodium bisulfite as described in Example 1 and dyed as described in Example 3, the color selected being sulfanthrene blue 2BD paste (Color Index #1184). The pretreated material becomes dyed very much heavier than untreated wool.

B. Azoic Dyes

Azoic colors are very rarely, if at all, applied to wool due to the deleterious effect of the alkali, necessary to dissolve the derivatives of beta-hydroxynaphthoic acid, on the fiber. It has been found, however, that a pretreatment with sodium bisulfite or sodium hydrosulfite, followed by drying, as described previously under Indigo, increases the affinity of wool for azoic colors. It therefore, becomes possible to obtain full, bright shades of excellent fastness in a continuous operation on pretreated woolen piece goods by immersing for 2 minutes in an alkaline solution of a derivative of beta-hydroxynaphthoic acid at 80–100° F., drying and coupling for 1 to 10 minutes in a solution containing a diazotized amino compound.

The short immersion time, as well as the low temperature used, prevents any damage to the wool resulting from the alkalinity of the baths. The details of the subsequent dyeing, including composition of dyeing bath, concentration of each reagent, temperature, etc. may follow in general the similar established practice in the case of cotton materials.

Example 5

In a continuous operation, wool flannel is padded through an aqueous solution containing 2½ ounces per gallon of sodium bisulfite at 130–140° F. The time of immersion is approximately 3 seconds (operative range 1 to 10 seconds) and the squeezing rollers are adjusted to permit the material to retain 100 to 150% of its weight of moisture. The impregnated material is then thoroughly dried at a temperature of 240–275° F.

The pretreated woolen material is then run through a bath containing 1⅓ ounces per gallon of the anilide of 2,3-hydroxynaphthoic acid, previously dissolved by pasting with alcohol and adding the necessary amount of caustic soda. In

place of alcohol, Turkey Red oil may be used, but in either case the procedure followed is exactly the same as is commonly practiced in cotton dyeing. Time of immersion is 2 minutes at 80–100° F.

Following this treatment the cloth is squeezed to remove excess moisture and is dried at 240–275° F. The cloth is then run through a bath containing one-quarter ounce per gallon of 4-nitro-2-amino-anisole, previously dissolved and diazotized according to standard procedure with the necessary amounts of hydrochloric acid and sodium nitrite. Time of immersion in this bath is approximately 3 minutes at 70–80° F. The dyed cloth is then passed between squeeze rollers to remove excess moisture, rinsed and soaped at 140–180° F.

The shades so obtained are very much fuller and brighter than when untreated wool is dyed in a bath of the same strength.

Example 6

Wool flannel is padded through an aqueous solution containing 2½ ounces per gallon of sodium hydrosulfite at 100–110° F. The time of immersion is approximately 3 seconds and the squeeze rollers are adjusted to permit the cloth to retain 100–150% of its weight of moisture. The material is then thoroughly dried at 240–275° F.

Immediately after drying the pretreated cloth is passed through a bath containing one ounce per gallon of the naphthylamide of 2,3-hydroxynaphthoic acid, previously dissolved with alcohol and the necessary amount of caustic soda according to common procedure. Time of immersion is approximately 2 minutes at 80–100° F. Following this treatment the cloth is again squeezed, dried at 240–275° F. and run through a bath containing one-half ounce per gallon of m-nitro-aniline, previously dissolved and diazotized according to standard procedure. Time of immersion in this bath is approximately 2 minutes at 70° F. The dyed cloth is then passed between squeeze rollers to remove excess moisture, is rinsed and soaped at 140–180° F.

The shades so obtained are at least 50% stronger and much brighter than if untreated wool is dyed in a bath of equal strength.

Example 7

Wool crepe is pretreated with sodium bisulfite as described in Example 5. After drying, the pretreated cloth is immersed for 2 minutes in a bath containing one ounce per gallon of the anilide of 2,3-hydroxynaphthoic acid. Following squeezing to remove excess moisture and drying, the material is run through a bath containing one-half ounce per gallon of 4-carbomethoxyamino-2,5-diethoxyaniline, which was previously dissolved and diazotized according to common procedure. Time of immersion is approximately 5 minutes at 70–80° F. The cloth is then squeezed, rinsed and soaped.

The dyeing so obtained is very much stronger and brighter than that obtainable on untreated wool.

Example 8

Wool flannel, pretreated with sodium bisulfite as described in Example 5 is passed through a bath containing one ounce per gallon of the o-toluidide of 2,3-hydroxynaphthoic acid, previously dissolved with alkali according to common procedure. Time of immersion is 2 minutes at approximately 85° F. After squeezing and drying, the prepared cloth is run through a bath containing one-half ounce per gallon of diazotized 4-nitro-2-amino-toluene. Time of immersion is 2 minutes at 70° F. Following squeezing and rinsing, the dyed cloth is soaped at 140–180° F.

Very much heavier and brighter shades are obtained than if untreated cloth is dyed in a bath of equal strength.

Example 9

Wool flannel, pretreated with sodium hydrosulfite as described in Example 6 is passed through a bath containing one-quarter ounce per gallon of the beta-naphthylamide of 2,3-hydroxynaphthoic acid, previously dissolved with alkali according to standard procedure. Time of immersion is 2 minutes at 80–100° F. Following squeezing and drying, the prepared cloth is passed through a bath containing one-half ounce of the diazonium compound obtained from 4-chloro-2-amino-toluene hydrochloride. Time of immersion is 4 minutes at 70° F. The dyed material is then squeezed, rinsed and soaped.

Very much fuller and brighter shades are obtained than if untreated wool is dyed in a bath of equal strength.

It will be understood that the above examples are merely illustrative, and that the details of procedure may be varied within wide limits without departing from the spirit of this invention.

We claim:

1. A process for treating animal fiber whereby to increase its affinity for organic compounds which dissolve in water only after transformation into an OM-type compound, wherein M stands for an alkali-metal, which comprises impregnating said animal fiber with a reagent selected from the group consisting of the water-soluble bisulfites and water-soluble hydrosulfites, the quantity of agent employed being less than that which would reduce the wool to a rubber-like condition, and drying the fiber at a temperature not less than 160° F.

2. A process for treating animal fiber whereby to increase its affinity for organic compounds which dissolve in water only after transformation into a compound having OM groups attached to carbon, M being an alkali-metal, which comprises impregnating said animal fiber with an aqueous solution of a reagent selected from the group consisting of the water-soluble bisulfites and water soluble hydrosulfites, the concentration of said reagent in the solution being not greater than 4 ounces per gallon, and then drying the fiber at a temperature between 200 and 300° F.

3. A process for treating animal fiber whereby to increase its affinity for organic compounds which dissolve in water only after transformation into a compound having at least one ONa group attached to carbon, which comprises impregnating said animal fiber with an aqueous solution of an alkali-metal bisulfite at a concentration of from 1 to 4 ounces per gallon, and then drying the fiber at a temperature between 240 and 275° F.

4. A process for treating animal fiber whereby to increase its affinity for organic compounds which dissolve in water only after transformation into a compound having at least one ONa group attached to carbon, which comprises impregnating said animal fiber with an aqueous solution of an alkali-metal hydrosulfite at a concentration of 1 to 4 ounces per gallon, and then

drying the fiber at a temperature between 240 and 275° F.

5. A process of dyeing wool fiber with a dyestuff selected from the group consisting of indigoid and anthraquinone-type vat dyes which comprises impregnating said wool, in the absence of alkali, with an aqueous bath of a sulfur-containing reagent selected from the group consisting of the water-soluble bisulfites and the water-soluble hydrosulfites, drying the wool at a temperature between 200 and 300° F., and then treating the same with an alkaline vat containing said color in reduced form.

6. A process of dyeing wool fiber with azoic colors of the so-called "ice-color" series, which comprises impregnating said wool, in the absence of alkali, with an aqueous bath of a sulfur-containing reagent selected from the group consisting of the water-soluble bisulfites and the water-soluble hydrosulfites, drying the wool at a temperature between 200 and 300° F., and then treating the same with an alkaline aqueous solution of an "ice-color" coupling component, drying the fiber and further treating the same with an aqueous solution of a diazonium compound to develop an azo dye on the fiber.

7. A continuous process for dyeing wool piece goods, which comprises treating said goods in an aqueous bath containing an alkali-metal bisulfite in quantity of from 1 to 4 ounces per gallon but containing no added alkali; drying the piece goods at a temperature between 240 and 275° F., and then treating the same with an alkaline vat containing the reduced form of a dyestuff selected from the group consisting of indigoid and anthraquinone-type vat dyes, and finally subjecting the dyed fabric to an oxidation treatment to oxidize the vat dye on the fiber.

8. A continuous process for dyeing wool piece goods, which comprises treating said goods in an aqueous bath containing an alkali-metal bisulfite in quantity of from 1 to 4 ounces per gallon but containing no added alkali; drying the piece goods at a temperature between 240 and 275° F., and then treating the same with an alkaline aqueous bath containing an azoic coupling component, and finally treating the fabric with a diazo bath to develop an azo dye on the fiber.

9. A process for dyeing wool fabric with indigo, which comprises treating the fabric with an aqueous solution of sodium bisulfite containing the latter in a concentration of 2 to 3 ounces per gallon, drying the fabric at a temperature between 240 and 275° F., and then running the same into an alkaline vat containing indigo in reduced form and subjecting the dyed fabric to oxidation whereby to regenerate the indigo dye on the fiber.

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