United States Patent Office 3,363,971 Patented Jan. 16, 1968

3,363,971

PROCESS FOR DYEING WITH SULFUR DYESTUFFS

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No Drawing. Filed June 2, 1965, Ser. No. 460,840
Claims priority, application Switzerland, June 5, 1964, 7,336/64
9 Claims. (Cl. 8—37)

The application of sulfur dyestuffs, especially to woven fabrics, is nowadays carried out continuously or intermittently. The continuous application generally required technically highly developed expensive apparatus, for example in the pad steam, standfast or pad roll process. For the intermittent application there may be used the traditional method performed in inexpensive apparatus, e.g. on a dye jig or in a winch vat. However, in the dyehouse the latter methods are often accompanied by considerable difficulties. There is obvious need for a dyeing method that can be performed with moderate plant and is yet simple and reliable.

It has now been found that fibrous materials can be dyed advantageously with sulfur dyestuffs with simple means without damaging the fiber when

(a) an alkaline preparation of the dyestuff is applied continuously at room temperature to the fibrous material,
(b) preparations are used that contain as reducing agent a water-soluble salt of hydrogen sulfide and
(c) the impregnated material is stored for at least one hour at room temperature in a closed system, which contains as little oxygen as possible.

Suitable fibrous materials are both natural and synthetic polyhydroxylated materials. For the series of the natural cellulosic materials there may be mentioned as examples linen and cotton, whereas synthetic materials are mainly regenerated cellulose such as rayon (viscose), spun rayon or Polynosic fabrics. From among all these materials the native cellulosic substrates, especially cotton, are the most suitable.

Dyestuffs suitable for use according to the invention are sulfur dyestuffs. As a rule, they are as such insoluble in water and are converted into a water-soluble form only when subjected to alkaline reduction; in this water-soluble form they are adsorbed by the material to be dyed and fixed by reoxidation either under the action of air or of mild oxidants, thus resuming their original, water-insoluble form. Apart from these insoluble sulfur dyestuffs there may also be used their water-soluble non-substantive derivatives obtained by esterification of the reduced form. In an alkaline solution these derivatives undergo hydrolysis, whereupon their capacity of becoming adsorbed on to the fibrous material is restored.

When the dyestuffs are applied to the fibrous material in their insoluble form, special attention must be paid to their degree of dispersion. To achieve satisfactory results, the dyestuffs must be used in a fine dispersion.

The alkalinity of the dyestuff preparation is achieved by inorganic acid acceptors, above all by an alkali metal hydroxide or an alkaline salt such as an alkali metal carbonate.

As reducing agent a water-soluble salt of hydrogen sulfide is used, especially one of the normal or acid ammonium or alkali metal salts of this acid. There may be mentioned especially sodium sulfide (Na_2S) and sodium bisulfide (NaHS).

The amount of reducing agent required may vary within rather wide limits and ranges in general from 1 to 15%, preferably from 5 to 10%, calculated from the weight of the preparation as a whole.

Particularly good results have been obtained with certain combinations of reducing agent and acid acceptor; inter alia, it has been observed that sodium sulfide in a liquor alkalinized with an alkali metal hydroxide, and sodium hydrogen sulfide in a liquor alkalinized with an alkali metal carbonate, give the best results.

The dyestuff preparation is applied at room temperature continuously, preferably on a padder, to the material to be dyed. The substrate impregnated in this manner is then stored at room temperature for a varying length of time, while making sure that the dyed material cannot dry even partially. Accordingly, the material is preferably stored in a closed system containing a minimum of oxygen e.g. in a securely closed vat which is filled with nitrogen or has been evacuated, or by wrapping the dyed material airtight in a plastic foil or in a rubber blanket.

All stages of the present process are performed at room temperature, that is to say at the ambient temperature or at a temperature only little above or below it. In this connection it is as such immaterial whether the temperature is high or low; on an average it will be about 20° C. If it is higher the storing time is correspondingly shortened, whereas if it is lower the storing time must be extended. The minimum storing time is one hour, but it can be lengthened at will, keeping in mind that after a certain time an optimum is reached. This optimum varies from dyestuff to dyestuff and, as will be readily understood, it depends also largely on the temperature so that no generally applicable data can be given. At any rate, a storing time exceeding 48 hours will be necessary only very rarely. Storing beyond the optimum has no harmful effect on the dyeing.

The dyestuff preparation may also contain further additives e.g. thickeners, dispersants, wetting agents and the like.

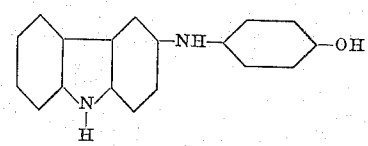
On completion of the storing the dyeings are finished off in the conventional manner used with sulfur dyestuffs. Thus, the reoxidation may be carried out by suspending the dyed material in airy rooms, by an air passage of differing duration or by treatment with a mild oxidant. Afterwards, the material is vigorously rinsed in hot and in cold water.

By the present process high quality dyeings are obtained by technically simple methods and a minimum of energy consumed. The aspect of the dyed material is very good, that is to say the dyeings are level and are not skittery because even irregularities in the material are extensively covered. The degree of dyestuff exhaustion is very high, which is of special advantage with dark shades. Mixed fabrics from cotton and polyester fibers display a particularly good reserve for the synthetic fiber.

Parts and percentages in the following examples are by weight. The dyestuffs are used in the form of a finely dispersed, pulverulent standard product of 50% strength.

Example 1

30 parts of the finely dispersed dyestuff C.I. Vat Blue 43 (Colour Index 53630), obtained by sulfurizing the compound of the formula



are dispersed in 450 parts of water, then 300 parts of N-sodium hydroxide solution and 250 parts of a 20% solution of sodium sulfide are added, and the whole is made up with water to 1000 parts. A mercerized cotton fabric is impregnated in this dyebath, then expressed to a weight increase of 80% and reeled.

The reel is placed in a cylindrical vessel which is then

evacuated to about 40 mm. Hg pressure. After having remained in this vessel for 12 hours at room temperature the reel is taken out, passed through air to reoxidise the dyestuff. The dyeing is completed by rinsing the fabric first in cold and then in hot water and drying it. A level dark-blue dyeing of good penetration is obtained.

If the impregnated reel is wrapped as firmly and airtight as possible in a plastic foil or placed in a vessel filled with nitrogen, and dyeing is performed otherwise as described above, similar good results are obtained.

When the dyestuff used above is replaced by 100 parts of C.I. Sulfur Black 11 (Colour Index 53290) or 100 parts of C.I. Sulfur Black 6 (Colour Index 53295), proceeding otherwise as described above, handsome, full black tints are obtained. With 30 parts of C.I. Solubilized Sulfur Blue 7 (Colour Index 53440) a blue tint is obtained which likewise possesses excellent properties.

When in the above padding liquor the sodium hydroxide solution is replaced by equal parts of a 10% solution of sodium carbonate, and the sodium sulfide is replaced by equal parts of a 20% solution of sodium hydrogen sulfide proceeding otherwise in identical manner, similar results are obtained in all variants referred to above.

Example 2

60 parts of the dyestuff C.I. Solubilized Sulfur Green 2 (Colour Index 53571) are dissolved in 500 parts of water. 30 parts of a 10 N-sodium hydroxide solution and 50 parts of sodium sulfide are then added, and the solution is made up with water to 1000 parts. A spun rayon fabric is padded with this solution, expressed to a weight increase of 80% and reeled. The reel is then enveloped with a tightly fitting plastic bag, evacuated for a short time, nitrogen is injected and the wrapped reel is stored for 12 hours at room temperature. The dyed fabric is then rinsed in a sodium bicarbonate bath of about 0.1% strength and oxidized in a hydrogen peroxide bath of about 0.1% strength, then once more rinsed and finally dried.

The finished green dyeing is level and of good penetration.

Similar results are obtained by dyeing under identical conditions other woven fabrics from regenerated cellulose, e.g. Polynosic (registered trade name).

What is claimed is:

1. Process for dyeing polyhydroxylated fibrous material, which comprises applying to said material in a continuous manner at room temperature an aqueous alkaline preparation containing at least one sulfur dyestuff and a water-soluble salt of hydrogen sulfide and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

2. Process for dyeing cellulosic textile fibers, which comprises applying to said material in a continuous manner at room temperature an aqueous alkaline preparation containing at least one sulfur dyestuff and a water-soluble salt of hydrogen sulfide and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

3. Process for dyeing cellulosic textile fibers, which comprises applying to said material in a continuous manner at room temperature an aqueous alkaline preparation containing at least one sulfur dyestuff and an alkali metal salt of hydrogen sulfide and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

4. Process for dyeing cellulosic textile fibers, which comprises applying to said material in a continuous manner at room temperature an aqueous preparation containing at least one sulfur dyestuff, sodium sulfide and sodium hydroxide and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

5. Process for dyeing cellulosic textile fibers, which comprises applying to said material in a continuous manner at room temperature an aqueous preparation containing at least one sulfur dyestuff, sodium hydrogen sulfide and sodium carbonate and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

6. Process for dyeing cellulosic textile fibers, which comprises padding said material at room temperature with an aqueous preparation containing C.I. Vat Blue 43 (C.I. 55630) sodium sulfide and sodium hydroxide and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

7. Process for dyeing cellulosic textile fibers, which comprises padding said material at room temperature with an aqueous preparation containing C.I. Sulfur Black 11 (C.I. 53290), sodium sulfide and sodium hydroxide and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

8. Process for dyeing cellulosic textile fibers, which comprises padding said material at room temperature with an aqueous preparation containing C.I. Solubilized Sulfur Blue 7 (C.I. 53440), sodium hydrogen sulfide and sodium carbonate and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

9. Process for dyeing cellulosic textile fibers, which comprises padding said material at room temperature with an aqueous preparation containing C.I. Sulfur Black 6 (C.I. 53295), sodium hydrogen sulfide and sodium carbonate and then storing the fibrous material so treated for at least one hour at room temperature in a closed system poor in oxygen.

References Cited

UNITED STATES PATENTS

3,043,650	7/1962	Wegmann et al.	8—54.2
3,110,541	11/1963	Weber et al.	8—34
3,208,990	9/1965	Benz et al.	8—43 X
3,223,470	12/1965	Boedeker et al.	8—54 X

FOREIGN PATENTS

657,820	3/1938	Germany.

OTHER REFERENCES

E. Koster, Melliand Textilberichte, vol. 24, June 1943, pp. 265–266.

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