

1

3,387,913

METHOD FOR COLORING FIBERS WITH THIOSULFURIC ACID DERIVATIVES OF SULFUR DYES

Leon Tigler, Charles D. Weston, and Gordon A. Geselbracht, Charlotte, and Laszlo A. Meszaros, Mount Holly, N.C., and Raphael E. Rupp, deceased, late of Charlotte, N.C., by North Carolina National Bank, executor, Charlotte, N.C., assignors to Martin-Marietta Corporation, a corporation of Maryland
No Drawing. Filed May 22, 1964, Ser. No. 370,401
4 Claims. (Cl. 8—37)

ABSTRACT OF THE DISCLOSURE

There is disclosed herein a method for producing dyeings and prints on cellulosic, polyester or polyamide fibers comprising the steps of applying to said fibers a composition comprising water, thiosulfuric acid derivative of sulfur dye, and a fixing agent selected from the group consisting of thiourea, ammonium thiocyanate, urea, acetyl thioureas, hexamethylenetetramine, 2-mercapto-benzothiazole, formic acid, and trisodium thiocyanurate; and fixing the dyestuff at an elevated temperature.

The present invention relates to a method for coloring fibers, and more particularly to a method for coloring fibers selected from the group consisting of cellulosic, polyester and polyamide with thiosulfuric acid derivatives of sulfur dyes.

The method of the present invention is particularly characterized in that it is a process for producing dyeings and prints on fibers selected from the group consisting of cellulosic, polyester and polyamide, which consists essentially of applying to said fibers a composition comprising water, thiosulfuric acid derivative of sulfur dye, and a fixing agent selected from the group consisting of thiourea, ammonium thiocyanate, urea, acetyl thioureas, hexamethylenetetramine, 2-mercapto-benzothiazole, formic acid, and trisodium thiocyanurate; and fixing the dyestuff at an elevated temperature. If desired, the fibers may then be rinsed and dried, or scoured and dried. Preferably, the fibers are pre-dried subsequent to application of the dye and prior to fixation.

Thiosulfuric acid derivatives of sulfur dyes are well known and are referred to as "C.I. Solubilised Sulfur Dyes" in the 1963 Supplement of the "Colour Index," published by the Society of Dyers and Colourists, Yorkshire, England. They are sometimes less precisely called "thiosulfonic" acid derivatives of sulfur dyes.

Thiosulfuric acid derivatives of sulfur dyes have been known since as early as 1895. It has also been known for many years that these dyes may be dyed on cellulosic textile fibers by the conventional chemical reduction-oxidation method, such as sulfide and bichromate, and this method is in vogue in several countries at the present time. However, the thiosulfuric acid derivatives of sulfur dyes have not achieved anywhere near the popularity of ordinary sulfur dyes. Sulfur dyes are produced in large quantity in the United States, but as late as 1963 thiosulfuric acid derivatives of sulfur dyes were not being made commercially in the United States.

The prior art chemical reduction-oxidation method for

2

continuous dyeing either thiosulfuric acid derivatives of sulfur dyes or sulfur dyes has a number of disadvantages, some of which follow. First, this method requires use of an expensive dyeing range, which occupies a large amount of valuable dye-house space. Second, labor costs for operating this method are high, as a great deal of personal attention is required to supervise and maintain proper conditions of temperature, concentration, nip pressures, etc. Third, numerous wet operations with intermediate washing and drying steps are involved, which has the disadvantages of heat and water costs, loss of color yield, and fiber shrinkage. Fourth, maintaining the correct shade throughout the run is a problem, and frequently undesirable surface dyeing or "bronzing" results. Finally, disposing of the waste effluent from the method, containing harsh chemicals such as excess reducing and oxidizing agents, causes problems.

It was suggested in the prior art, in 1957, that dyeings could be made by a process consisting of the steps of applying to cellulosic fibers an aqueous solution consisting of water and thiosulfuric acid derivative of sulfur dye, and thereafter heating the fibers. However, this suggestion is commercially impractical, as the color yield is so low that very weak dyeings result, and therefore the suggested process is totally unacceptable for commercial use and is not used commercially.

According to the method of the present invention, the above disadvantages and limitations of the prior art have been overcome, and additional advantages have been provided as follows.

It has been found, according to the method of the present invention, that thiosulfuric acid derivatives of sulfur dyes may be dyed or printed on cellulosic, polyester or polyamide fibers by applying to the fibers a composition comprising said dyes, water, and the fixing agents mentioned above, and thereafter heating the fibers to obtain fixation of the dyestuff. Excellent dyeings and prints, having wash fastness, light fastness and bleach fastness comparable to that obtained by the prior art reduction-oxidation method, result.

Additionally, dyeing equipment suitable for use in the present method is much less expensive and occupies much less space than that used in prior art reduction-oxidation systems, e.g. equipment for the present method may consist of a dye padder and curing device, such as curing oven, heated cylinders, or infra-red unit.

Labor costs are lessened in the present method because there are fewer operations to supervise and maintain. Heat and water costs are diminished and color yield and fiber shrinkage are improved because of fewer washing and drying steps. The problem of waste effluent disposal is minimized because the volume and harshness of the wash is lessened.

Moreover, the method of the present invention may be conducted at a more rapid rate than the chemical reduction-oxidation method, which rapidity is very important from the standpoint of economy.

Another important feature of the present invention is that the thermal fixation is so efficient that a saleable product emerges from the heat fixing device, no further wet processing being required. This is in marked contrast to the wet processing steps which are used subsequent to oxidation in conventional reduction-oxidation systems for dyeing thiosulfuric acid derivatives of sulfur dyes. Thus, after fibers emerge from the curer, they may be sold or

carried forward to resin finishing without the customary intermediates wet treatment and the expense thereof.

The dye composition which is applied to the fibers comprises water, thiosulfuric acid derivative of sulfur dye, and a fixing agent selected from the group consisting of thiourea, ammonium thiocyanate, urea, acetyl thioureas, hexamethylenetetramine, 2-mercapto-benzothiazole, formic acid, and trisodium thiocyanurate. The dye composition may additionally comprise a migration inhibitor, for example sodium alginate or an electrolyte such as sodium chloride or sodium acetate. For printing, the dye composition will be in the form of a printing paste and will also comprise a thickening agent.

Suitable compositions for making dyeings may comprise, by weight, about 0.5–150 parts concentrated thiosulfuric acid derivative of sulfur dye, 5–200 parts above fixing agent, and optionally 1–50 parts migration inhibitor, per thousand parts of aqueous dye composition. As the migration inhibitor, about 1–4 parts sodium alginate or 10–50 parts electrolyte may be used.

Suitable printing pastes may comprise, by weight, about 0.5–60 parts concentrated thiosulfuric acid derivative of sulfur dye, 5–200 parts above fixing agent, and 25–100 parts thickening agent per thousand parts of aqueous printing paste. Conventional thickening agents such as starch, converted starches, natural gums, starch tragacanth, synthetic polymer thickeners, etc., may be utilized. Water-in-oil emulsion thickeners may also be utilized, in which case the printing paste may comprise 0.5–60 parts thiosulfuric acid derivative of sulfur dye, 5–200 parts above fixing agent and water-in-oil emulsion thickener to 1,000 parts.

The dyeing solution or printing paste may be applied to the fibers by any convenient means, such as padder, engraved rollers, screen, spray, etc.

In the dyeing process, if desired, the wet padded fabric may be either batched and stored, or skyed, to assist in dye diffusion and leveling.

Following application of the dye composition, the fibers are preferably pre-dried, for reasons of economy and to assist in providing better levelness, although it is possible to omit the pre-drying step. The pre-drying conditions, such as time and temperature, will be governed by the type of pre-drying equipment used, the weight of the fabric, and the moisture content of the fibers entering the pre-drier. Preferably the fibers are pre-dried to about 5–15% moisture content. Housed sectional heated tenters are excellent for pre-drying, although such equipment as an infra-red unit, heated stainless steel cylinders, loop dryers and other conventional pre-dryers may be utilized.

The dyestuff is fixed on the fibers by means of an elevated temperature. Fixation may be achieved by subjecting pre-dried fibers to a temperature of 360°–450° F. for 5–0.1 minutes. When the fibers have not been pre-dried, somewhat longer will be required to achieve thermofixation. Thermofixation may be achieved by such means as hot flue, direct heating on heated cylinders, hot oil bath, molten metal bath, infra-red units (radiant heat), and dielectric heating.

Following thermofixation, the fibers may be, if desired, rinsed and dried or scoured and dried, although no steps subsequent to thermofixation are essential.

It will be recognized that the present method may be conducted continuously, and it may be conducted at very high speeds, such as 200 yards per minute.

The following non-limiting examples are set forth by way of illustration; all parts are by weight unless otherwise specified.

Example 1

A dye solution at 140° F. consisting of 13.5 parts concentrated C.I. Solubilised Sulphur Yellow 2 (C.I. 53121) dye, 100 parts urea, 50 parts thiourea, 2 parts sodium alginate and 834.5 parts water is padded onto woven cotton fabric weight 4 oz. per sq. yd.; the fabric is squeezed between nip rollers to 60% wet pick up based on fabric

weight; pre-dried to 10% moisture content; heated in a curing oven at 400° F. for 1 minute to fix the dye, and collected. A deep gold shade is obtained with good fastness to light and washing.

Example 2

A printing paste consisting of 13.5 parts concentrated C.I. Solubilised Sulphur Yellow 2 (C.I. 53121) dye, 50 parts thiourea, 150 parts urea, 262 parts 10% aqueous solution of starch-ether thickener, and 524.5 parts water is roller printed onto woven cotton fabric weighing 4 oz. per sq. yd., the fabric is pre-dried; heated in a curing oven maintained at 410° F. for 2 minutes, and collected.

Example 3

This example is the same as Example 1 above, except that the urea is omitted, the thiourea is increased to 100 parts, and the water is increased to 884.5 parts.

Example 4

A dye solution at 140° F. consisting of 22.5 parts concentrated C.I. Solubilised Sulphur Brown 10 (C.I. 53056) dye, 100 parts ammonium thiocyanate, and 877.5 parts water is padded onto cotton fabric weighing 4 oz. per sq. yd.; the fabric is nipped to 66% wet pick up; pre-dried by heating in a loop dryer at 170° F.; heated in a curing oven maintained at 410° F. for 1 minute, and collected. A bright reddish brown dyeing with good fastness properties is obtained.

Example 5

A printing paste consisting of 22.5 parts concentrated C.I. Solubilised Sulphur Brown 10 (C.I. 53056) dye, 100 parts ammonium thiocyanate, 292 parts 10% aqueous solution starch-ether thickener, and 585.5 parts water is printed onto cotton fabric in the manner described in Example 2 above.

Example 6

A dye solution at 140° F. consisting of 15 parts concentrated C.I. Solubilised Sulphur Yellow 2 (C.I. 53121) dye, 200 parts urea, 15 parts NaCl, and 770 parts water is padded onto cotton fabric; the fabric is nipped to 65% wet pick up; predried by passing it over a series of rotating heated cylinders; heated in a curing oven maintained at 410° F. for 2 minutes; rinsed in warm water and dried.

Example 7

A printing paste consisting of 15 parts concentrated C.I. Solubilised Sulphur Yellow 2 (C.I. 53121) dye, 15 parts NaCl, 200 parts urea, 100 parts corn starch thickener, and 670 parts water is printed onto cotton fabric; the fabric is pre-dried; and heated in a curing oven maintained at 410° F. for 1.5 minutes.

Example 8

A dye solution at room temperature consisting of 24 parts concentrated C.I. Solubilised Sulphur Brown 14 (C.I. 53248) dye, 50 parts S-acetyl-thiourea, and 926 parts water is padded onto cotton fabric; the fabric is nipped to 66% wet pick up; pre-dried; heated in a curing oven maintained at 400° F. for 1 minute; passed into a wash box containing 0.15 oz. soap per gallon of water at 185° F.; squeezed with nip rollers; passed through two wash boxes containing water at 145° F. and equipped with exit nip rollers; and dried. A deep brown dyeing with excellent fastness results.

Example 9

A printing paste consisting of 15 parts concentrated C.I. Solubilised Sulphur Brown 14 (C.I. 53248) dye, 50 parts S-acetylthiourea, 295 parts 10% aqueous starch-ether thickener, and 590 parts water is printed on cotton fabric in the manner described in Example 7.

Example 10

A dye solution at 140° F. consisting of 13.5 parts concentrated C.I. Solubilised Sulphur Yellow 2 (C.I. 53121)

5

dye, 40 parts N,N'-diacetylthiourea, 30 parts sodium acetate, and 946.5 parts water is padded onto cotton fabric; the fabric is nipped to 60% wet pick up; pre-dried by passing it through a three sectional closed housed heated tenter at 160°-200° F.; and heated in a curing oven maintained at 390° F. for 2 minutes.

Example 11

A printing paste consisting of 13.5 parts C.I. Solubilised Sulphur Yellow 2 (C.I. 53121) dye, 40 parts N,N'-diacetylthiourea; 315.5 parts 10% aqueous starch-ether thickener, and 631 parts water is printed onto cotton fabric; the fabric is pre-dried with infra-red lamps; and heated in a curing oven maintained at 410° F. for 1.5 minutes.

Example 12

A dye composition consisting of 18 parts concentrated C.I. Solubilised Sulphur Blue 7 (C.I. 53441) dye, 60 parts hexamethylenetetramine and 922 parts water is dyed on cotton fabric in the manner described in Example 1.

Example 13

A printing paste consisting of 18 parts concentrated C.I. Solubilised Sulphur Blue 7 (C.I. 53441) dye, 60 parts hexamethylenetetramine, 307 parts 10% aqueous starch-ether thickener, and 615 parts water is printed on cotton fabric in the manner described in Example 2.

Example 14

A dye composition consisting of 37.5 parts concentrated C. I. Solubilised Sulphur Black 1 (C.I. 53186) dye, 20 parts 2-mercapto-benzothiazole, and 942.5 parts water is dyed on cotton fabric in the manner described in Example 1.

Example 15

A printing paste consisting of 37.5 parts concentrated C.I. Solubilised Sulphur Black 1 (C.I. 53186) dye, 20 parts 2-mercapto-benzothiazole, 314 parts 10% aqueous starch-ether thickener, and 628.5 parts water is printed on cotton fabric in the manner described in Example 2.

Example 16

This example is the same as Example 12 above, except that 20 parts formic acid are substituted for the hexamethylenetetramine.

Example 17

This example is the same as Example 13 above, except that 20 parts formic acid are substituted for the hexamethylenetetramine.

Example 18

This example is the same as Example 1 above, except that a dye composition consisting of 22.5 parts concentrated C.I. Solubilised Sulphur Brown 10 (C.I. 53056) dye, 20 parts trisodiumthiocyanurate, 2 parts sodium alginate, and 955.5 parts water are substituted for the dye composition of Example 1.

Example 19

This example is the same as Example 2 above, except that a printing paste consisting of 20 parts C.I. Solubilised Sulphur Brown 10 (C.I. 53056) dye, 20 parts trisodium thiocyanurate, 320 parts 10% aqueous starch-ether thickener, and 640 parts water is substituted for the printing paste of Example 2.

Example 20

This example is the same as Example 1 above, except that thermo-fixation is effected by heating the fabric in an oil bath at 410° F. for 40 seconds, and except that the fabric is washed free of the oil prior to collection.

6

Example 21

This example is the same as Example 1 above, except that thermo-fixation is effected by contacting the fabric with rotating heated cylinders having a surface temperature of 425° F. for 8 seconds.

Example 22

A water-in-oil emulsion printing may be made by roller printing a printing paste consisting of 227 parts Varsol ® (straight petroleum aliphatic solvent), 98.6 parts 50% xylene solution ethylcellulose, 463.4 parts water, 148 parts urea, 49 parts thiourea, and 14 parts concentrated C.I. Solubilised Sulphur Brown 14 (C.I. 53248) onto cotton fabric; pre-drying the fabric; and heating the fabric in a curing oven maintained at 410° F. for 1.5 minutes.

In the foregoing examples rayon, polyester or polyamide fabrics may be substituted for the cotton fabric. Also, similar prints and dyeings may be made on yarns, ball warps, knit goods and other fibers as well as on woven fabrics. Raw stock may be dyed according to the present invention using continuous raw stock dyeing equipment.

Moreover, union prints and dyeings, e.g. wherein blends of different types of fibers are colored, may be made according to the method of the present invention. For example, a blend of cotton and polyester fabric or blended nylon and cotton fabric may be substituted for the cotton fabric in the foregoing examples, in which case the solubilised sulphur dye fixes on the three types of fibers.

Also, when making union prints and dyeings, other types of dyes may be added to the dye composition to achieve an equal degree of coloration on both types of fibers in the blend. For example, disperse type dyes may be added to the solubilised sulphur dye composition in the dyeing of cotton/polyester blends, in which case the disperse dye colors the polyester and the solubilised sulphur dye colors both the cotton and the polyester.

Example 23

Fabric dyed according to Example 1 above, without any further wet processing or dyeing subsequent to dye fixation and prior to resin padding, is padded with a resinous composition consisting of 10% dimethylol ethylene urea resin, 2% magnesium chloride catalyst and 88% water, nipped to 60% wet pick up based on fabric weight, pre-dried, and cured in an oven at 350° F. for 2 minutes. A wash and wear fabric with good fastness properties results.

Example 24

Fabric printed according to Example 2 above, without any further wet processing or drying subsequent to dye fixation and prior to resin padding, is resinated in the manner described in Example 23.

What is claimed is:

1. A method for producing dyeings and prints on fibers selected from the group consisting of cellulosic, polyester and polyamide which consists essentially of applying to said fibers a composition comprising water, thio-sulfuric acid derivative of sulfur dye, and a fixing agent selected from the group consisting of thiourea, ammonium thiocyanate, urea, acetyl thioureas, hexamethylenetetramine, 2-mercapto-benzothiazole, formic acid and trisodium thiocyanurate; and fixing the dyestuff at an elevated temperature.

2. The method according to claim 1, and further characterized in that the fibers are pre-dried subsequent to application of the dye composition and prior to fixation.

3. The method according to claim 1, and further characterized in that the dyestuff is fixed by subjecting it to a temperature of 360°-450° F. for 5-0.1 minutes.

4. The method according to claim 1, and further characterized in that the fibers are resinated subsequent to

fixation of the dye without wet processing intervening between the fixing and resinating steps.

References Cited

UNITED STATES PATENTS

3,088,790 5/1963 Schultheis et al. ----- 8-54.2
3,113,824 12/1963 Kohl et al. ----- 8-37

FOREIGN PATENTS

657,314 2/1963 Canada.

OTHER REFERENCES

G. Kaufmann: Melliand Textilberichte, November 1963, pp. 1245-1247, 8-1.213 Lit.

5 K. VenKataraman: The Chemistry of Synthetic Dyes, vol. 2, 1952, page 1093, publ. by Academic Press, Inc., N.Y. City TP913 V4 C. 3.

NORMAN G. TORCHIN, *Primary Examiner.*

10 J. H. HERBERT, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,387,913

June 11, 1968

Leon Tigler et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, after line 39 insert the following paragraph:

One important feature of the present invention is that fibers dyed or printed with thiosulfuric acid derivatives of sulfur dyes according to the present method may be taken directly from the dye fixing step into a resin bath, without the necessity of any wet processing and drying steps intervening after dye fixation and prior to resination. This is in marked contrast to the prior art, in which it is necessary to wash and dry fibers that had been dyed or printed with sulfur dyes or thiosulfuric acid derivatives of sulfur dyes after the dye fixing step and prior to resination to remove unfixed dye and/or chemical oxidizing agents. This result obtains because there is such a high degree of dye fixation by the present process.

Signed and sealed this 18th day of November 1969.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents