United States Patent Office 3,419,343 Patented Dec. 31, 1968

3,419,343

METHOD FOR COLORING CELLULOSE TEXTILE FIBERS WITH DYESTUFFS CONTAINING PENDANT THIOSULFATE GROUPS

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No Drawing. Filed May 28, 1965, Ser. No. 459,933
2 Claims. (Cl. 8—54.2)

ABSTRACT OF THE DISCLOSURE

A method for coloring textile fibers comprising the steps of applying an aqueous composition comprising water and dye having per dye molecule at least one pendant thiosulfate group selected from the group consisting of —SSO_3Na, —SSO_3K and —SSO_3NH_4 to textile fibers selected from the group consisting of cotton, regenerated cellulose, polyamide and polyacrylic; applying to the fibers an aqueous solution comprising Na_2S_{2-4}; and washing the fibers with water.

The present invention relates to a method for coloring textile fibers.

The method of the present invention is particularly characterized in being a method for coloring textile fibers comprising the steps of applying an aqueous composition comprising water and dye having per dye molecule at least one pendant thiosulfate group selected from the group consisting of —SSO_3Na, —SSO_3K and —SSO_3NH_4 to textile fibers selected from the group consisting of cotton, regenerated cellulose, polyamide and polyacrylic; applying to the fibers an aqueous solution comprising Na_2S_{2-4}; and washing the fibers with water.

At the time of initial contact of the dye with the Na_2S_{2-4} solution, the unfixed dye will be on the fiber and in the thiosulfate form, e.g. each dye molecule will have at least one pendant —SSO_3Na, —SSO_3K or —SSO_3NH_4 group per molecule of dye.

It has been suggested in the prior art that sodium sulfide or sodium cyanide may be used for fixing azo, anthraquinone, vat, dioxazine and metal phthalocyanine dyes having thiosulfuric acid groups onto cellulosic fibers.

These prior art processes have a number of disadvantages and limitations, some of which follow.

Handling sodium cyanide and the resulting effluent involves problems of extreme toxicity to humans and fish. Accordingly, it is altogether too dangerous a chemical for practical commercial use in a textile finishing plant.

Sodium sulfide presents a number of problems when used according to the above prior art method. For example, it must be used in combination with heat to effect fixation; or, when used at room temperature it must either be used in high concentrations or remain in contact with the dye for 10–60 minutes to effect fixation. Sodium sulfide affects unfavorably the softness and feel (hand) of cellulosic fibers and especially that of regenerated cellulose, and particularly so when used in combination with heat, or in high concentration, or when permitted to remain in contact with the cellulosics over a relatively long period of time. Regenerated cellulose swells on contact with strong Na_2S solutions, thereby requiring repeated after-washing, and also causing stickness in the unwinding of yarn from bobbins. Moreover, sodium sulfide is strongly alkaline and precipitates insolubles from water, especially from hard water, and these insolubles interfere with dyeing procedures and require additional soap for their removal in washing processes.

Some azo dyes are particularly sensitive to sodium sulfide, in that the color value of the azo groups is destroyed and color yield is correspondingly lowered when sodium sulfide is used, and particularly so when the sodium sulfide is at high concentration, or in the presence of heat, and the longer the azo dye remains in contact with sodium sulfide the more color value is lost.

There are two distinct types of azo dyes having pendant thiosulfate groups, i.e. (1) those in which the thiosulfate group is attached directly to an aryl nucleus of the dye molecule, and (2) those in which a bridge member, such as an aliphatic or hydrocarbon radical which may be substituted and interrupted by hetero groups, is interposed between the thiosulfate group and an aryl nucleus of the dye.

Sodium sulfide presents additional and special problems when used as a fixing agent for those azo dyes having a pendant thiosulfate group attached directly to an aryl nucleus of the dye molecule. The primary problem is color yield.

With many of the azo dyes having at least one pendant thiosulfate group attached directly to an aryl nucleus of the dye molecule, it is impossible to obtain high color yield using sodium sulfide as the fixing agent under any conditions, as an inadequate amount of the dye is fixed on the fibers. Moreover, in the fixation of azo dyes having at least one pendant thiosulfate group attached directly to an aryl nucleus of the dye molecule, a narrow and specific amount of sodium sulfide must be employed for each individual dyestuff, otherwise color yield will be reduced. Slight increases or decreases in the amount of sodium sulfide used for fixing any given azo dye of the type in which a pendant thiosulfate group is attached directly to an aryl nucleus of the dye molecule can influence color yield markedly. This problem is made even more difficult because of very great differences in the amounts of sodium sulfide required to fix different azo dyes having at least one pendant thiosulfate group attached directly to an aryl group of the dye molecule; for example, one such azo dye may require 12 times as much sodium sulfide as another such dye to achieve commercially acceptable color yield. Obviously, searching for optimum sodium sulfide concentrations of fixing baths and changing these concentrations for individual dyes is a time consuming and expensive burden that few dyers dyeing many different colors would care to assume. To obtain a desired shade it is frequently necessary to mix two or more azo dyes, each having at least one pendant thiosulfate per dye molecule attached to an aryl nucleus of the dye, and in which the amount of sodium sulfide required for fixing each dye is markedly different; in such cases, it is impossible to obtain full color fixation of both dyes with sodium sulfide.

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

Na_2S_{2-4} is much less hazardous and toxic than sodium cyanide.

In contrast to sodium sulfide, there is no necessity for using Na_2S_{2-4} in combination with heat to achieve dye fixation, and excellent dye fixation is obtained at room temperature; neither is there any necessity for using the Na_2S_{2-4} in high concentration nor for the Na_2S_{2-4} to remain in contact with the dye for any appreciable length of time to achieve fixation.

One surprising feature of the present invention is that fixation of the dyestuff may be achieved at room temperature, and at very low Na_2S_{2-4} concentration, and without having the dye and Na_2S_{2-4} in contact for more than 1–30 seconds. Thus, the process of the present invention is particularly valuable for use with modern high

speed dyeing equipment, such as continuous padding ranges. Also, with Na_2S_{2-4} the fixation is achieved at a lower degree of alkalinity than with sodium sulfide, which results in a softer and improved hand of cellulosic fibers, as well as less precipitation of insolubles from water.

Surprisingly, azo dyes having a pendant thiosulfate group attached directly to an aryl group of the dye molecule may be fixed with about two-thirds less weight of Na_2S_{2-4} than Na_2S.

The fact that fixation may be achieved at room temperature without any necessity for high Na_2S_{2-4} concentration or prolonged contact between the polysulfide and azo dyes results in less loss of color value of the sensitive azo groups and improved color yield, and in some cases in improved brightness of shade, in comparison with sodium sulfide.

Improvement in color yield is particularly noticeable in the dyeing of azo dyes having at least one pendant thiosulfate group attached directly to an aryl group of the dye molecule. With many of these dyes, color yield is 20%–100% higher when Na_2S_{2-4} is used than when the optimum sodium sulfide concentration is used.

Another surprising and very advantageous feature of the present invention is that the optimum concentration of Na_2S_{2-4} for fixing azo dyes having at least one pendant thiosulfate group attached directly to an aryl nucleus of the dyestuff and obtaining high color yield extends over a very much wider range than does sodium sulfide, and thus color yield is not adversely affected by slight variations in Na_2S_{2-4} concentration, as contrasted to sodium sulfide. Moreover, there is only a small difference between optimum Na_2S_{2-4} concentration for fixing one azo dye of the foregoing type and another, quite unlike sodium sulfide. Thus, standard fixing solutions of Na_2S_{2-4} may be utilized in textile finishing plants without the necessity for changing concentrations every time a different dye is utilized. Also, better color yield can be obtained in dyeing mixtures of certain azo dyes with Na_2S_{2-4} than with Na_2S.

Finally, the system is very economical as Na_2S_{2-4} costs less than Na_2S, and less Na_2S_{2-4} is required than Na_2S; and soap, time and heat are saved.

A more detailed description of the process of the present invention follows:

The present process may be used in dyeing or printing textile fibers selected from the group consisting of cotton, regenerated cellulose, polyamide and polyacrylic. The textile fibers may be in any desired form, such as fabric, yarn, ball warps, non-woven fabric, raw stock, etc.

Examples of dyes which may be fixed according to the method of the present invention include azo, sulfur, phthalocyanine, metal phthalocyanine, perylene, dioxazine, anthraquinone, vat and dibenzanthrone dyes, said dyes being further characterized in having at least one pendant thiosulfate group selected from the group consisting of $—SSO_3Na$, $—SSO_3K$ and SSO_3NH_4 per molecule of dye.

The dye stuff may be applied to the fibers in any desired manner, such as by jig, pad, beck, printing roller, etc. The amount of dye employed will depend upon the depth of shade desired.

In addition to dye and water, the dye composition may optionally contain conventional additives, such as inorganic electrolytes to increase adsorption of the dye onto the fiber, leveling agents such as sodium alginate, penetrating assistants such as anionic and non-ionic surface active agents, alkalies, urea, thiourea, etc., and in the case of printing pastes conventional gums, thickeners, emulsifiers, etc.

Following application of the dyestuff, the fibers may optionally be batched for a period of time at ambient temperature or in a closed chamber controlled for humidity and temperature, steamed or dried to facilitate penetration of the dyestuff into the fibers. However, the fibers may be taken directly from the dye application to the Na_2S_{2-4} solution.

As used herein, the term Na_2S_{2-4} refers to a sodium polysulfide or to mixtures of sodium polysulfides, e.g. to disodium disulfide, or disodium trisulfide, or disodium tetrasulfide, or to mixtures of any two or three of these polysulfides. In the case of mixtures, the 2–4 subscript of the S atom would not necessarily be a whole number. Sodium polysulfides are well known, and are prepared by adding flowers of sulfur to a hot aqueous solution of sodium sulfide.

Sulfur is precipitated from highly concentrated stock solutions of sodium tetrasulfide on extended exposure to the air, and this may be prevented by adding 5% by weight of Carbitol to the concentrated stock solutions, which stock solutions may be used subsequently in preparing the fixing solutions.

The fibers, having thereon the unfixed dyestuff in thiosulfate salt form, are then contacted with the aqueous Na_2S_{2-4} fixing solution, such as by immersing the fibers in the fixing solution. The fibers may be wet or dry at the time of contact with the fixing solution.

The fixing solution comprises an aqueous solution of Na_2S_{2-4}. The amount of Na_2S_{2-4} utilized is based upon the amount of dye which is to be fixed; about 0.07–0.64 gm. Na_2S_{2-4}, and preferably about 0.214 gm. Na_2S_4, may be applied to the fibers for each gram of dye to be fixed. The fixing solution may also optionally comprise a simple water soluble inorganic electrolyte, such as NaCl, to deter those dyes which tend to bleed into the fixing solution from so doing. About 25–300 gm. NaCl per liter of fixing solution is suitable for this purpose. The Na_2S_{2-4} is applied as an aqueous solution to the fibers, and may be applied by the pad-nip method, spraying, immersing the fibers in the solution, or any other convenient method. A convenient and illustrative method is to pass the fibers having the unfixed dye thereon through a pad box containing about 1–10 gm. Na_2S_{2-4} per liter of fixing solution for each percent by weight of the dye upon the fibers, and squeezing the fibers between rubber coated pressure rollers to permit 60% wet pick up of fixing solution based on fabric weight. Fixation of the dye is very rapid, and in many cases may be regarded as instantaneous. In most cases, fixation will be complete when the dye and Na_2S_{2-4} have been in contact about 1–30 seconds.

After contact with the Na_2S_{2-4} the fibers are washed with water, which may be at room temperature. The water serves to remove polysulfide salt residues and other water soluble residues from the fibers. If desired, the fibers may optionally be passed through air, steam or brine prior to washing.

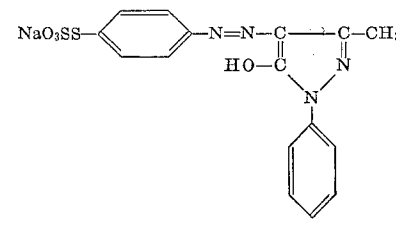
Following washing, the fibers may be scoured and dried in conventional manner.

Dyeings and prints having excellent color yield and wash fastness properties result from the above process.

The following examples are illustrative of the process of the present invention. All parts are by weight unless otherwise specified.

Example 1

Onto mercerized cotton fabric weighing 112 gms. per square yard is padded a dye composition consisting of 25 gms.



per liter of water at 120° F.; the fabric is squeezed to permit 60% wet pick up based on fabric weight (whereby the fabric has thereon 0.015 gm. of dye calculated as solids for each gm. of fabric). The fabric is dried and padded through an aqueous fixing solution consist-

ing of 6.05 gm. Na_2S_4 and 200 gm. NaCl per liter at room temperature; the fabric is squeezed to permit 60% wet pick up based on fabric weight (whereby the fabric has thereon 0.214 gm. Na_2S_4 for each gm. of dye. The fabric is washed with water at room temperature and dried.

A bright yellow dyeing with excellent wash fastness results.

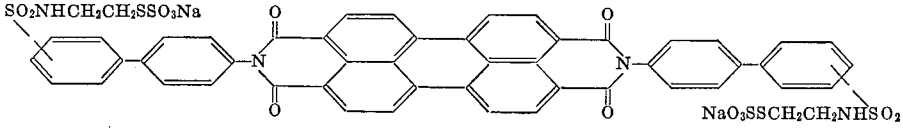
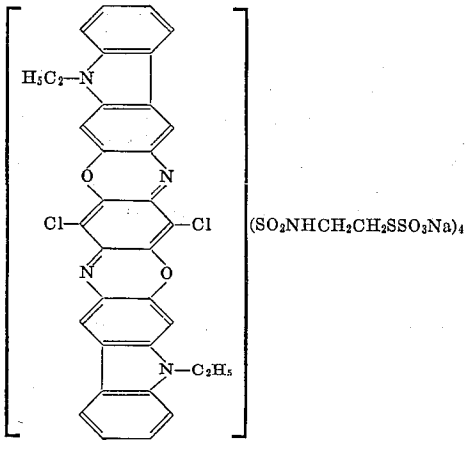
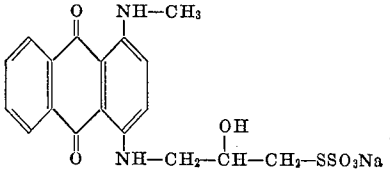
If desired, the NH_4 or K salt of the above dye may be substituted for the dye used in this example.

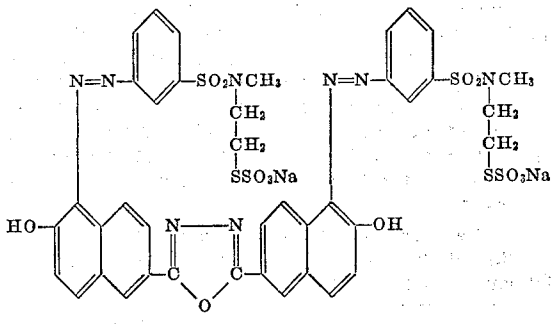
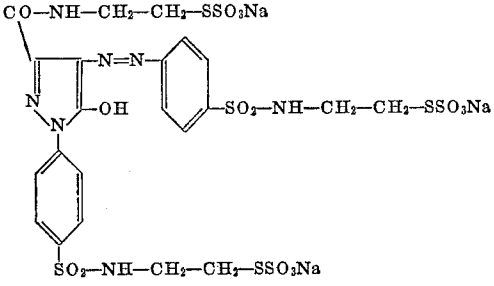
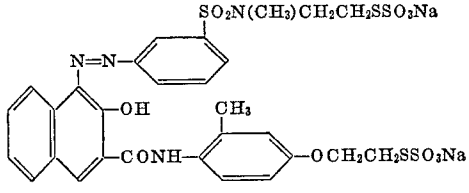
The color yield in the above dyeing is at least twice as great as obtainable by using Na_2S as the fixing agent.

Examples 2–46

In the examples given in the following table, there is padded onto cotton, viscose rayon, polyamide or polyacrylic fabric an aqueous dye composition consisting of 25 gm. of the dye indicated in the second column per liter of water at 140° F., whereafter the fabric is squeezed so as to have picked up 0.015 gm. dye (calculated as dry solids) per gm. of fabric; the fabric is pre-dried in open width with infra-red units to about 10% moisture content and then dried to substantial dryness in open width on a housed tenter frame heated to 350° F.; the fabric is steamed for 2 minutes at 230° F. in an air-free steamer; padded through a solution consisting of 4.537 gm. of the polysulfide shown in column 3 and 200 gm. NaCl per liter of water at room temperature; squeezed so as to have picked up the number of gm. shown in the fourth column of the polysulfide shown in the third column (calculated as dry solids) for each gm. of dye on the fibers, passed through pad boxes equipped with exit nip rollers and containing water at room temperature for 15 seconds, and then soaped, rinsed with water, and dried. Wash fast dyeings of the color shown in the fifth column and having good color yield result.

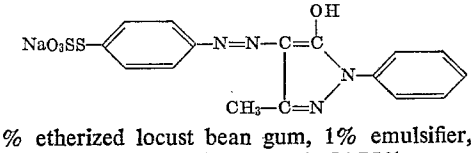
It will be understood that the Na atoms of the pendant thiosulfate groups of the dyes shown in the second column may be substituted by K or NH_4.

Ex. No.	Dye	Polysulfide	Gms.	Color
2	Dye of Example 1	Na_2S_2	0.20	Yellow.
3	do	Na_2S_3	0.27	Do.
4	do	$Na_2S_{3.5}$	0.15	Do.
5	Sodium salt of dye obtained by coupling equimolar amounts of diazotized 3-amino-benzylthiosulfuric acid and 3-(2',3'-hydroxynaphthoylamino)benzylthiosulfuric acid.	Na_2S_2	0.30	Scarlet.
6	do	Na_2S_3	0.21	Do.
7	do	Na_2S_4	0.15	Do.
8	Sodium salt of dye obtained by coupling mole of diazotized sodium S-4-aminophenylthiosulfate and mole of 8-amino-2-naphthol, and coupling equimolar amounts of result and diazotized sodium S-4-aminophenylthiosulfate.	Na_2S_2	0.30	Black.
9	do	Na_2S_3	0.25	Do.
10	do	Na_2S_4	0.15	Do.
11	Sodium salt of C.I. Solubilized Sulphur Green 2 (C.I. No. 53572)	Na_2S_2	0.20	Green.
12	do	Na_2S_3	0.15	Do.
13	do	Na_2S_4	0.30	Do.
14	Sodium salt of dye obtained by condensing mole of phthalocyanine disulfonylchloride and 2 moles sodium S-4-aminophenylthiosulfate.	Na_2S_2	0.17	Turquoise.
15	do	Na_2S_3	0.22	Do.
16	do	Na_2S_4	0.30	Do.
17	Sodium salt of dye obtained by condensing mole of copper phthalocyanine trisulfonyl chloride and 3 moles sodium S-4-aminophenylthiosulfate.	Na_2S_2	0.15	Do.
18	do	Na_2S_3	0.23	Do.
19	do	Na_2S_4	0.28	Do.
20	Sodium salt of dye obtained by condensing 1 mole of nickel phthalocyanine trisulfonyl chloride with 3 moles sodium S-(2-aminoethyl)thiosulfate.	Na_2S_2	0.24	Do.
21	do	Na_2S_3	0.30	Do.
22	do	Na_2S_4	0.15	Do.
23		Na_2S_2	0.15	Red.
24	Same as Ex. 23 above	Na_2S_3	0.26	Red.
25	do	Na_2S_4	0.22	Red.
26		Na_2S_2	0.29	Blue.
27	Same as Ex. 26 above	Na_2S_3	0.24	Do.
28	do	Na_2S_4	0.15	Do.
29		Na_2S_2	0.21	Do.

Ex. No.	Dye	Poly-sulfide	Gms.	Color
30	Same as Ex. 29 above	Na_2S_3	0.30	Do.
31	do	Na_2S_4	0.15	Do.
32	Sodium salt of dye obtained by reacting mole of disulfonyl chloride of isodibenzanthrone and 2 moles sodium S-(2-aminoethyl)thiosulfate.	Na_2S_2	0.16	Do.
33	do	Na_2S_3	0.19	Do.
34	do	Na_2S_4	0.30	Do.
35		Na_2S_2	0.22	Orange.
36	Same as Ex. 35 above	$Na_2S_{2.5}$	0.20	Do.
37	do	Na_2S_4	0.18	Do.
38		Na_2S_2	0.15	Yellow.
39	Same as Ex. 38 above	$Na_2S_{3.5}$	0.30	Do.
40	do	Na_2S_4	0.20	Do.
41		Na_2S_2	0.17	Red.
42	Same as Ex. 41 above	Na_2S_3	0.19	Red.
43	do	Na_2S_4	0.26	Red.
44	Sodium salt of dye resulting from condensing mole of copper phthalocyanine trisulfonyl chloride with 3 moles sodium S-(4-amino-benzyl)thiosulfate.	Na_2S_2	0.30	Blue.
45	do	Na_2S_3	0.24	Do.
46	do	Na_2S_4	0.15	Do.

Example 47

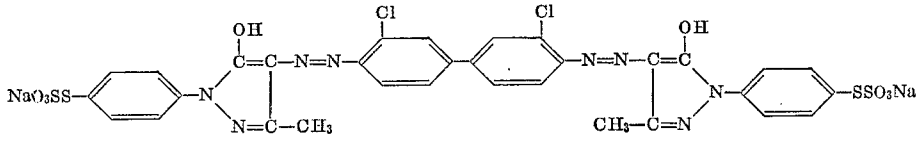
Onto cotton fabric is printed a paste consisting of, by weight, 2.5%



1.75% etherized locust bean gum, 1% emulsifier, 40% "Varsol" petroleum solvent, and 54.75% water; the fabric is dried, steamed at 214° F. for 30 seconds, padded through 1% Na_2S_3 and 20% NaCl in aqueous solution at room temperature, squeezed, rinsed with water, soaped, rinsed with water and dried. A yellow print with excellent wash fastness and color value is obtained.

Example 48

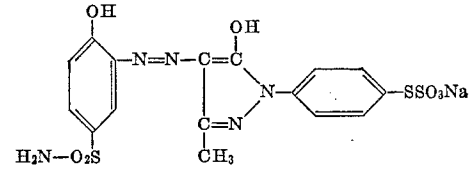
Onto cotton fabric weighing 112 gm./sq. yd. is padded a dye composition consisting of 12.5 gm.



per liter of water at 120° F.; the fabric is squeezed to 60% wet pick up so as to retain 0.0075 gm. dye, calculated as solids, per gm. of fabric. The fabric is immersed for 30 seconds in a solution consisting of 0.375 gm. Na_2S_4 per liter of water at a liquor to goods ratio of 10:1, rinsed with water at room temperature for 5 minutes, soaped, rinsed with water and dried, resulting in a bright orange dyeing.

Example 49

An aqueous composition containing the 1:1 chromium complex of

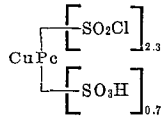


is padded onto cotton fabric and squeezed so as to deposit 1.5 gm. dye/100 gm. cotton. The fabric is dried and padded through a solution consisting of 7.86 gm. Na_2S_4 and 200 gm. NaCl per liter of water at room temperature, squeezed to permit 60% wet pick up, rinsed with water, scoured and dried. A bright orange dyeing results.

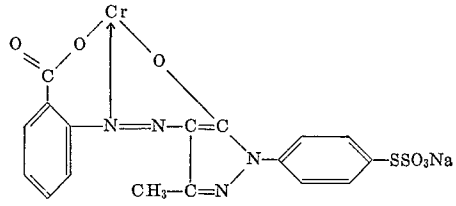
Nearly twice as much Na_2S as Na_2S_4 is required to give somewhat less color yield and less brightness.

Example 50

Onto cotton corduroy fabric is padded a dye composition consisting of 10 gm. of the sodium salt of the dye resulting from condensing a mole of



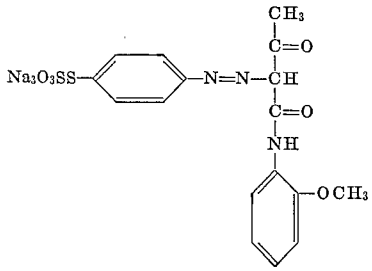
and 2.3 moles sodium S-4-aminophenylthiosulfate, 7 gm. of the sodium salt of C.I. Solubilized Sulphur Green 2 (C. I. No. 53572), and 15 gm.



per liter of water at 130° F. The fabric is dried, padded through an aqueous solution consisting of 6 gm. Na_2S_4 and 200 gm. NaCl per liter of water at room temperature, squeezed to permit 60% wet pick up, rinsed with water, soaped, rinsed and dried. A green dyeing results.

Example 51

An aqueous composition containing 25 gm.



per liter of water at 120° F. is padded onto cotton fabric and squeezed so that the fabric retains 0.015 gm. dye per gm. of fabric, and the fabric is dried. The fabric is then padded through a solution containing 1.9 gm. Na_2S_4 and 200 gm. NaCl per liter of water at room temperature and squeezed so as to have picked up 0.07 gm. Na_2S_4 per gm. of dye. The fabric is rinsed with water, soaped, rinsed and dried. A bright yellow dyeing with excellent color yield and wash fastness results.

Example 52

This example is the same as Example 51 above, except that the amount of the Na_2S_4 per liter is increased from 1.9 to 10 gm., and except that the amount of Na_2S_4 picked up per gm. of dye is increased from 0.07 to 0.64 gm.

What is claimed is:

1. A method for coloring textile fibers consisting essentially of the steps of applying an aqueous composition comprising water and dye having per dye molecule at least one pendant thiosulfate group selected from the group consisting of —SSO_3Na, —SSO_3K and —SSO_3NH_4 to textile fibers selected from the group consisting of cotton and regenerated cellulose; applying to the fibers an aqueous solution comprising Na_2S_{2-4} so that about 0.07–0.64 gm. Na_2S_{2-4} are applied to the fibers for each gram of dye on the fibers; and washing the fibers with water.

2. A method for coloring textile fibers consisting essentially of the steps of applying to textile fibers selected from the group consisting of cotton and regenerated cellulose, an aqueous composition comprising water and dye, said dye being selected from the group consisting of azo, sulfur, phthalocyanine, metal phthalocyanine, perylene, dioxazine, anthraquinone, vat and dibenzanthrone dyes having per dye molecule at least one pendant thiosulfate group selected from the group consisting of —SSO_3Na, —SSO_3K and —SSO_3NH_4; applying to the fibers an aqueous solution comprising Na_2S_{2-4} so that about 0.07–0.64 gm. Na_2S_{2-4} are applied to the fibers for each gram of dye on the fibers; and washing the fibers with water.

References Cited

UNITED STATES PATENTS

3,088,790	5/1963	Schultheis et al.	8—54.2
3,225,025	12/1965	Jeremias et al.	8—37 X
3,264,053	8/1966	Holtzclaw et al.	8—37 X

OTHER REFERENCES

G. Kaufman: Melliand Textilberichte, November 1963, pp. 1245 and 1246, 8/1.213.

K. Venkatataman: The Chemistry of Synthetic Dyes, volume 2, 1952, p. 1093, TP913 V4C.3.

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U.S. Cl. X.R.

8—34, 39, 41

UNITED STATES PATENT OFFICE

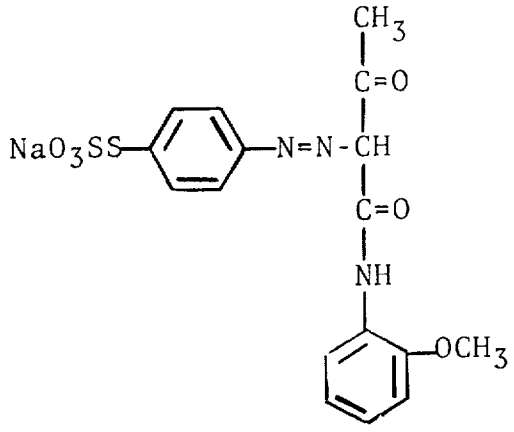
CERTIFICATE OF CORRECTION

Patent No. 3,419,343 December 31, 19(

Charles D. Weston 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 1, line 66, "stickness" should read -- stickiness --. Column 3, line 54, "SSO_3NH_4" should read -- SSO_3NH_4 --; line 56, "dye stuff" should read -- dyestuff --. Column 9, lines 38 to 50, the formula should appear as shown below:



Signed and sealed this 10th day of March 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents