United States Patent Office 3,112,982 Patented Dec. 3, 1963

3,112,982

DYEING WITH ACID LEUCO VAT DYES

Alfred A. Hinckley, Beverly, Mass., assignor to Metal Hydrides Incorporated, Beverly, Mass., a company of Massachusetts

No Drawing. Filed July 24, 1961, Ser. No. 125,971
27 Claims. (Cl. 8—34)

The present invention relates to dyeing textile materials, such as wool, silk and synthetic fibers, with vat dyes.

Textile materials, such as cotton fabrics, usually are dyed by padding a dispersion of the vat dye on to the fabric, squeezing out the excess, and then passing the dye impregnated fabric through an aqueous bath containing sodium hydroxide, sodium hydrosulfite and sodium chloride having a pH between about 9.5 to 13. The reducing liquor reduces the dye and converts it to the water soluble sodium leuco form, the presence of the salt shifting the equilibrium of the reduced dye from the solution to the fabric. The cloth then is removed from the bath and the dye oxidized to give a level dyeing of desired shade. This procedure requires the use of as much as a 5 to 40 fold excess of hydrosulfite over the stoichiometric requirement since the hydrosulfite is very unstable under the conditions of air oxidation present in dyeing and the high temperatures used in the dyeing operation.

The above procedure is not satisfactory for dyeing certain fibers, such as wool, silk and synthetic fibers, with vat dyes either because the dye does not have satisfactory affinity for the fiber or because of fiber degradation due to the presence of the alkali metal hydroxide in the reducing solution. Some attempts have been made to dye such fibers with a vat dye in its acid leuco form. The acid leuco form of the dye has been obtained by first preparing the water soluble sodium leuco form of the dye by reducing the dye in an aqueous medium containing sodium hydroxide and sodium hydrosulfite and then adding acetic acid and a dispersing agent with agitation to convert the sodium leuco form of the dye to the water insoluble acid leuco form of the dye. The fabric to be dyed then is contacted with the aqueous dispersion of the acid leuco dye, removed and subjected to an oxidizing operation. These attempts to dye with the vat dye in its acid leuco form have not been commercially practical due to the inherent instability of the acid leuco vat dyes even in the presence of excessively large amounts of sodium hydrosulfite and the great instability of the hydrosulfite at the low pH required in such acid leuco dyeing operations.

The present invention is based upon the discovery that vat dyes may be reduced to their acid leuco form and maintained in such reduced form for surprisingly long periods of time in an aqueous solution of an alkali metal hydrosulfite, such as sodium hydrosulfite or potassium hydrosulfite, and an amine borane, said solution containing a dispersing agent. Silk and wool fabrics may be dyed with excellent results by contacting them with such a bath for a desired period of time followed by subjecting the fabric to a conventional oxidizing operation. For dyeing synthetic fibers, such as nylon, Dacron, zefran, acrilan, rayon, etc., it is preferable to add a carrier or swelling agent to the dye bath. A carrier may also be added to the baths used for dyeing other fibers, such as wool and silk, in instances where it is desired to increase the life of the bath. The concentration of hydrosulfite used in preparing the dye bath of the invention should be sufficient to reduce the vat dye to its acid leuco form and the concentration of amine borane used should be sufficient to maintain the dye in such reduced form.

The amine boranes which may be used in preparing the dye bath of the invention are adducts of a primary, secondary, or tertiary amine, and borane (BH_3). Because

of their greater thermal stability, I prefer to employ the tertiary amine boranes, such as trimethyl, triethyl, pyridine, picoline, lutidine, N-methyl morpholine boranes, etc. As illustrative of other amine boranes which may be used, I may mention secondary amine boranes, such as dimethyl, diethyl, and piperidine amine boranes, and primary amine boranes, such as isopropyl, methyl and ethyl amine boranes.

As illustrative of conventional inert wetting agents which may be used, I may mention Triton X–100 and Igepal CO–630. As inert carriers or swelling agents which may be used, I may mention benzyl alcohol, monochlorobenzene, tributylphosphate, methyl salicylate, and polyvinylpyrrolidene.

I have successfully used in the practice of the invention many vat dyes selected from the various types commonly used in vat dyeing. As illustrative I may mention anthraquinone type dyes, such as Mayvat Jade Green (C.I. #59105), Carbanthrene Blue BCS (C.I. #69825), Ponsul Brilliant Violet 4RN (C.I. #60010), Ponsul Golden Orange 3G (C.I. #69025), Indanthrene Golden Yellow RK (Vat Orange 1, C.I. #59105/6), Indanthrene Brilliant Orange RK (Vat Orange 3, C.I. #59300), Amanthrene Golden Orange F (Vat Orange 9, C.I. #59700), Indanthrene Orange RRT (Vat Orange 1, C.I. #59705), and Indanthrene Dark Blue BO (Vat Blue 20, C.I. #59800), Tinan Navy Blue RAF (Vat Blue 18, C.I. #59815), Ahcovat Jade Green B (Vat Green 1, C.I. #59825), Indanthrene Brilliant Violet 3B (Vat Violet 9, C.I. #60005), Cibanone Violet 4R (Vat Violet 1, C.I. #60010); anthraquinone type dyes containing amino groups, such as Cibanone Black DRB (Vat Black 9, C.I. #65230); dyes containing a heterocyclic nucleus fixed to a central vatting system, such as Indanthrene Red FBB (Vat Red 10, C.I. #67000), Tinon Yellow GC (Vat Yellow 2, C.I. #67300), Carbanthrene Red BN (Vat Red 35, C.I. #68000), Cibanone Violet BNA (Vat Violet 13, C.I. #68700), Indanthrene Brown RN (Vat Brown 3, C.I. #69015), Indanthrene Red Brown 5 RF (Vat Brown 25, C.I. #69020), Tinon Olive BF (Vat Green 3, C.I. #69500), Tinon Olive SF (Vat Black 25, C.I. #69525), Cibanone Blue GCDN (Vat Blue 14, C.I. #68810), Ponsul Blue BF (Vat Blue 6, C.I. #69825), Indanthrene Khaki GG (Vat Green 8, C.I. #71050); Indigo and its derivatives and homologues, such as Cibanone Blue 2BGD (Vat Blue 5, C.I. #73065); thioindigo and its derivatives and homologues, such as Hostavat Brilliant Pink R (Vat Red 1, C.I. #73360), Indanthrene Printing Violet 6R (Vat Violet 3, C.I. #73395); phthalocyanine dyes, such as Algol Brilliant Blue 4G (Vat Blue 29, C.I. #74140).

The results indicated in the following tables are illustrative of the stability of the acid leuco dye baths prepared in accordance with the invention. Unless otherwise indicated in the tables, the dye bath of the invention was prepared by dissolving 0.5 gram of 2,6-lutidine borane and 0.2 gram of sodium hydrosulfite in an aqueous liquor containing 700 cc. of water, 1 gram of vat dye, and 2.5 grams of Triton X–100 (isooctyl phenoxy polyethoxy ethanol). The baths using hydrosulfite alone were prepared by dissolving 7.5 grams of sodium hydrosulfite in an aqueous liquor containing 700 cc. of water, 1 gram of vat dye, and 2.5 grams of Triton X–100 (isooctyl phenoxy polyethoxy ethanol). Where a carrier is indicated it was 25 cc. of benzyl alcohol added to the bath. The results indicated in Table I are illustrative of the stability of baths prepared in accordance with the invention as compared to baths in which hydrosulfite is the sole reducing agent. Table II indicates the results where all the components were added to the dye baths at 40° C. and then the temperature was slowly raised to 90° C. at which temperature 4 to 5 grams of wool was immersed in the bath for 15 minutes. Table III indicates the results where

all the components of the baths were mixed together and the baths were heated to the boil and 3 grams of silk was immersed for 15 minutes. Table IV indicates the results where all the components of the baths were mixed and the baths were heated to 80–85° C., with occasional stirring, at which temperature 7 grams of nylon were immersed for 15 minutes.

TABLE I

Stability of Vat Acid Leuco at 85°–90° C. in Minutes

Dye Used	Hydrosulfite		Borane and Hydrosulfite	
	Carrier	No Carrier	Carrier	No Carrier
Vat Red 1 (C.I. #73360)	18		38	
Vat Yellow 2 (C.I. #67300)		26		43
Vat Green 1 (C.I. #50825)	29	4	137	50
Vat Green 3 (C.I. #69500)	6		114	
Vat Blue 5 (C.I. #73065)	18	4	115	23
Vat Black 25 (C.I. #69525)	3		115	

The above table illustrates the marked synergistic stability effect of using a combination of benzyl alcohol and lutidine borane with hydrosulfite. A dye bath composed of hydrosulfite alone has a life of 4 min. in the case of Vat Green 1. When benzyl alcohol is present the bath has a life of 29 min. When lutidine borane is used the bath life is 50 min. When a combination of lutidine borane and benzyl alcohol is used the bath life is 137 min. which is significantly longer than would be predicted from the stabilizing effect of lutidine borane and benzyl alcohol when used separately. It also will be noted that when 0.5 gram of borane replaces 7.3 grams of hydrosulfite the bath stability is increased by 46 min.

The benzyl alcohol may be replaced by other compounds such as m-cresol, propylene carbonate, β-napthol, methyl salicylate, benzoic acid, monochlorobenzene, o-phenyl phenol, p-phenyl phenol, methylphenyl carbinol, butyl carbitol, tributyl phosphate, polyvinylpyrrolidene, isopropanol, etc.

TABLE II

Wool Dyeing With Vat Acid Leuco

Dye Used	Reducing System, Weight in grams		Stability in Minutes	pH Before and After Dyeing	
	Hydrosulfite	Borane		Before	After
Vat Yellow 2 (C.I. #67300)	7.5		26	6.4(40)	5.3(85)
Do	0.2	0.5	42	5.5(40)	5.1(70)
Vat Green 1 (C.I. #59825)	1.5		11		
Do	7.5		4	6.4(42)	5.3(88)
Do	0.2	0.5	50	6.8(45)	6.2(80)
Vat Blue 5 (C.I. #73065)	7.5		4	6.0(44)	5.3(80)
Do	0.2	0.5	23	7.3(44)	5.8(85)

The figures in parentheses indicate the temperature at which the pH was determined.

TABLE III

Silk Dyeing With Vat Acid Leuco

Dye Used	Reducing System, Weight in grams		Stability in Minutes	pH Before and After Dyeing	
	Hydrosulfite	Borane		Before	After
Vat Yellow 2 (C.I #67300)	0.2	0.5	75	6.9(95)	
Vat Blue 5 (C.I. #73065)	7.5		8		
Do	0.2	0.5	>15		

The figures in parentheses indicate the temperature at which the pH was determined.

TABLE IV

Nylon Dyeing With Vat Acid Leuco

Dye Used	Reducing System, Weight in grams		Stability in Minutes	pH Before and After Dyeing	
	Hydrosulfite	Borane		Before	After
Vat Red 1 (C.I. #73360)	7.5		18	5.5(80)	5.7(75)
Do	0.2	0.5	38	6.7(80)	5.8(70)
Vat Red 10 (C.I.#67000)	0.2	0.5	108	6.8(83)	6.2(80)
Vat Green 1 (C.I. #59825)	7.5		28	5.5(80)	5.5(70)
Do	0.2	0.5	137	6.6(80)	5.8(75)
Do	0.2	0.1	105	6.6(85)	5.2(80)
Vat Green 3 (C.I. #69500)	7.5		5	5.6(78)	5.6(75)
Do	0.2	0.5	114	6.8(80)	6.6(75)

The figures in parentheses indicate the temperature at which the pH was determined.

I claim:

1. A bath for use in dyeing textile materials with vat dyes consisting of an aqueous solution of an amine borane and an alkali metal hydrosulfite containing a vat dye in acid leuco form.

2. A bath as claimed by claim 1 wherein the alkali metal hydrosufite is sodium hydrosulfite.

3. A bath as claimed by claim 1 which also contains a swelling agent.

4. A bath as claimed by claim 2 which also contains a swelling agent.

5. A bath as claimed by claim 2 wherein the amine borane is a primary amine borane.

6. A bath as claimed by claim 2 wherein the amine borane is a secondary amine borane.

7. A bath as claimed by claim 2 wherein the amine borane is a tertiary amine borane.

8. A bath as claimed by claim 3 wherein the swelling agent is benzyl alcohol.

9. A bath as claimed by claim 4 wherein the amine borane is a primary amine borane.

10. A bath as claimed by claim 4 wherein the amine borane is a secondary amine borane.

11. A bath as claimed by claim 4 wherein the amine borane is a tertiary amine borane.

12. A bath as claimed by claim 4 wherein the swelling agent is benzyl alcohol.

13. A bath as claimed by claim 7 wherein the amine borane is lutidine borane.

14. A bath as claimed by claim 7 wherein the amine borane is N-methyl morpholine borane.

15. A bath as claimed by claim 11 wherein the amine borane is lutidine borane.

16. A bath as claimed by claim 11 wherein the amine borane is N-methyl morpholine borane.

17. A stable composition consisting essentially of an amine borane, an alkali metal hydrosulfite and water.

18. A stable composition consisting essentially of an amine borane, an alkali metal hydrosulfite, a carrier and water.

19. In a method of dyeing animal fibers, such as wool and silk, with vat dyes, the step which comprises bringing the animal fiber in contact with a bath consisting of an aqueous solution of an amine borane and an alkali metal hydrosulfite containing a vat dye in acid leuco form and a dispersing agent.

20. In a method of dyeing synthetic fibers, such as nylon, with vat dyes, the step which comprises bringing the synthetic fiber in contact with a bath consisting of an aqueous solution of an amine borane and an alkali metal hydrosulfite containing a vat dye in acid leuco form and a dispersing agent, said bath also containing a swelling agent.

21. A stable composition as claimed by claim 17 wherein the amine borane is lutidine borane.

22. A stable composition as claimed by claim 17 wherein the amine borane is N-methyl morpholine borane.

23. A stable composition as claimed by claim 18 wherein the carrier is benzyl alcohol.

24. A stable composition as claimed by claim 18 wherein the amine borane is lutidine borane.

25. A stable composition as claimed by claim 18 wherein the amine borane is N-methyl morpholine borane.

26. An aqueous acid leuco vat dye composition stabilized with an amine borane.

27. An aqueous acid leuco vat dye composition stabilized with an amine borane selected from the group consisting of primary, secondary, and tertiary amine boranes.

References Cited in the file of this patent

UNITED STATES PATENTS

2,745,788	Frohnsdorff et al.	May 15, 1956
2,890,093	Mautner	June 9, 1959
2,992,061	Fleming	July 11, 1961
3,000,688	Schubert et al.	Sept. 19, 1961

OTHER REFERENCES

Rathjens et al.: Journal of the Amer. Chem. Soc., vol. 71, pp. 2783–2785.