Patented Apr. 10, 1951

2,548,543

UNITED STATES PATENT OFFICE

2,548,543

COMPOSITIONS AND METHODS USING REDUCTION-SENSITIVE VAT DYES AND INORGANIC NITRITES

Jerry M. Mecco, Somerville, N. J., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application November 30, 1949, Serial No. 130,356

16 Claims. (Cl. 8—35)

1

This invention relates to an improved method of vat dyeing with dyes which show a tendency to over-reduce at high temperatures.

In the past, there has arisen a considerable problem with respect to a large number of vat dyes. These dyes are sensitive to high temperature vats. The sensitivity appears to be due primarily to over-reduction caused by the hydrosulfite, or other strong reducing agent which is an essential part of any vat dye bath. It is possible and, in case of some dyes even probable that other reactions take place and result in decomposition which is not, strictly speaking, an over-reduction. The net effect is that these sensitive dyes, of which the anthraquinone dihydroazines are typical, have required low temperature dyeing conditions which preclude the rapid dyeing which is possible at higher temperatures and which has made various continuous and semi-continuous processes possible. High temperature dyeing usually improves dye penetration and/or levelness, particularly with such fabrics as nylon. In referring to a "dye bath," it should be understood that we are considering the situation at the time the dye is affixed to the fiber. In many processes, the dyestuff is present in a dye bath or vat in solution in the form of its reduced leuco compound and the goods are introduced into this bath. In other processes, such as, for example, pigment dyeing processes, which lend themselves to continuous and semi-continuous processes of the package dyeing variety, the dyestuff may be originally incorporated loosely in the fiber in the form of a pigment and then reduced by the dye bath which contains only the reducing constituents and the caustic alkali which is necessary. In such a case, the dye bath at the fiber includes the dyestuff, but includes it actually in position in the fiber. Throughout this case, the term "dye bath" will be used to cover both types of situation.

Acsording to this invention, it has been found that the sensitivity of the dyes to over-reduction at elevated temperatures can be avoided and dyeings of greater strength and brightness obtained if the dye bath contains a soluble inorganic nitrite. The ordinary soluble nitrites, such as alkali and alkaline earth metal nitrites, may be used. Because of its cheapness and excellent results obtained, sodium nitrite is the preferred member.

The amount of nitrite to be used is not critical; but there is, of course, a minimum below which useful improvement does not result. This practical minimum is about one-quarter the weight

2

of the dyestuff. When more nitrite is added, results improve; but soon a practical optimum is reached at from 1.5–2 parts of nitrite per part of dye, beyond which additional nitrite usually does not give results which warrant the additional cost. However, as much as 16 or more parts of nitrite per part of dyestuff may be used with no deleterious results. The additional cost, however, is not warranted, and such procedures are economically unattractive.

It is not known just how the nitrite acts. It seems probable that one factor may be a kind of reduction-buffer action preventing over-reduction in this type of reaction. There is, however, strong evidence to show that this is not the only factor, because other oxidizing agents, such as inorganic nitrates or organic nitrites and nitrates, will not give the improved results of the inorganic nitrites of the present invention. It would seem logical, therefore, that there is at least one and maybe a number of other factors involved in the operation of the present invention. Accordingly, it is not intended to limit the invention to any particular theory of action, the above discussion being given purely as the best partial explanation of certain possible factors, as far as present knowledge goes.

The various dyestuffs which are sensitive to overreduction at high temperature do not all show the same sensitivity. Some are much more sensitive than others, or rather, show bad results at much lower temperatures. The anthraquinone dihydroazines are among the most sensitive, and some of them give bad results at dyeing temperatures as low as 120° F. Others do not show deleterious results until temperatures of 140–160° F. are reached; and some do not give trouble until the temperature approaches much closer to the boiling point of water.

The optimum dyeing temperature with each dye will be somewhat different; and it is not possible, therefore, to give any single temperature, which is equally effective with all dyes. However, it is an important factor of the present invention that, in most cases, dyeing can be effected at temperatures approaching the boiling point of water without material loss of strength or brilliance; and many sensitive dyestuffs can, therefore, be used at high temperatures, which makes the present invention of particular significance where such high temperature dyeing is important from the standpoint of savings in time, use of continuous or semi-continuous dyeing processes, and the like.

Another advantage of the present invention is

that when inorganic nitrites are present in the dye bath, the dyeing process becomes relatively insensitive to temperature changes within reasonaable operating limits, and small accidental temperature fluctuations are completely immaterial. It is therefore unnecessary when using the present invention to control the dye temperature with extreme accuracy, a drawback which was a factor in making high temperature dyeing with sensitive dyes practically unattractive before the present invention, even though the dyes were not seriously over-reduced if a certain definite temperature limit were not exceeded. Extremely critical supervision of any chemical process adds cost and is a disadvantage. It is particularly unfortunate in dyeing operations where exact temperature control, at all times, is often a difficult thing to achieve. When the present invention is used only reasonable care need be exercised to prevent very great temperature changes.

In addition to the anthraquinone dihydroazines referred to above, a large number of other vat dyestuffs show sensitivity to high temperature dyeing. Typical dyestuffs are the following: Dinitro dibenzanthrone, oxy nitro dibenzanthrone, 1:4 di-benzoylamino-anthraquinone, 4,4'-dihydroxy indanthrene, 2(1-amino-anthraquinonyl-2)-4,5,beta anthraquinone-oxazole, di-dibenzanthronylamino-di-alpha anthraquinonylamino pyranthrone, 3,4,8,9 - dibenzpyrene - 5,10 - quinone, 1,1',4,1''-trianthrimide carbazole. Other dyestuffs are those having the Color Index Numbers: 1135, 1106, 1112, 1113, 1114, 1151, 1162, 1102, 1099, 1173, 1150, 1163 and 1109.

It is an advantage of the present invention that it may be applied in several ways. For example, vat dye baths can be made up by adding all of the ingredients, that is dye, alkali, reducing agent and nitrite, to produce a finished bath. Another method which has the practical advantage of making it unnecessary for the dyer to control closely the proportion of all ingredients going into the dye bath, is to blend with the dyestuff a suitable amount of nitrite to form a powder or a paste. This blend, which constitutes a new article of manufacture included within the scope of the present invention, may be sold. The dyer may then prepare his bath with the dyestuff blend, the alkali and the reducing agent in any convenient order.

The invention will be illustrated in greater detail in conjunction with the following specific examples. Parts are by weight.

Example 1

Three parts of the dye having Color Index No. 1113 and containing about 18.5% real dye were mixed with 3 parts of sodium nitrite. This mixture was then added to 1170 parts of water at 160° F. To this was added 35 parts of 30° Bé. sodium hydroxide, after which the temperature was again adjusted to 160° F., and nine parts of sodium hydrosulfite added and dissolved. The temperature was maintained at 160° F. for 15 minutes, after which time the color was reduced. This will be referred to as the standard leuco solution. 400 parts of this reduced dye solution was then transferred to a separate dye beaker.

20 parts of natural cotton yarn were pre-wet with approximately ½% solution of a pine oil soap, the excess removed by squeezing, and the yarn then entered into the 400 parts of reduced vat dye and dyed at 160° F. for 15 minutes. The dyed yarn was then removed and the excess dye liquor extracted from the yarn. The remaining dye on the yarn was then oxidized for five minutes in the air at room temperature, after which it was immersed in an oxidizing solution consisting of 0.1% sodium peroxide (100 volumes) and 0.1% glacial acetic acid solution for 10 minutes at 140° F. The dyed yarn was then rinsed in warm water to remove the excess glacial acetic, soaped at the boil for 10 minutes in 0.1% soap and 0.1% soda ash solution, rinsed and dried.

A control dye bath was prepared exactly like the above except the sodium nitrite was omitted. This was used to make a control dyeing using the same procedure as above. The yarn dyed in the bath containing the sodium nitrite was approximately 80% stronger, redder, and brighter than the control dyeing.

Example 2

The standard leuco solution prepared in Example 1 was maintained at a temperature of 160° F. for an additional 20 minutes, after which 6 parts of 30° Bé. sodium hydroxide and 2 parts of sodium hydrosulfite were added and the temperature maintained at 160° F. for an additional 40 minutes, making a total standing time of 75 minutes. 400 parts of this standard leuco solution was then removed and transferred to a dye beaker.

20 parts of cotton yarn, pre-wet as in Example 1, was then entered into the dye bath and dyed as in Example 1. The same procedure was used with the control dye bath, again having a standing time of 75 minutes, after which 20 parts of cotton yarn, pre-wet as above, was entered and dyed as above.

The yarn dyed from the bath containing the sodium nitrite after the dye bath had stood for 75 minutes was similar in strength and shade to the yarn dyed in the bath containing the sodium nitrite in Example 1. However, the yarn dyed in the control bath in Example 2 was now a dirty gray and not a bright red-blue. This indicates a chemical change of the dye in the control bath in which no sodium nitrite was present when the dyeing was made after the bath had stood at 160° F. for 75 minutes.

Example 3

The procedure of the preceding two examples was repeated except the temperature was raised from 160° F. to 190° F. Again the yarn dyed in the bath containing the sodium nitrite was blue, bright and strong, whereas the yarn dyed in the control bath was a dirty gray and unfit for practical use.

Example 4

The procedure of the preceding example was repeated except that the temperature was raised to about 212° F. Again the dyeing made in the dye bath containing the sodium nitrite was a commercially satisfactory blue whereas the yarn dyed in the control dye bath was dyed a dirty gray.

Example 5

10 parts of cotton yarn were dyed in a bath containing about 0.09 part of the real dye having Color Index 1113, three parts of sodium hydroxide, three parts of sodium hydrosulfite, 1.5 parts of sodium nitrite in 400 parts of water. The bath was heated for five minutes at about 200° F. during which time the vat dye was reduced, after which the cotton yarn was entered and dyed for

60 minutes at about 200° F. The dyed yarn was then removed, and the excess dye liquor extracted from the yarn. The remaining dye on the yarn was then oxidized for five minutes in the air at room temperature, after which it was immersed in an oxidizing solution consisting of 0.1% sodium peroxide (100 volumes) and 0.1% glacial acetic acid solution for ten minutes at 140° F. The dyed yarn was then rinsed in warm water to remove the excess acid, soaped at the boil for ten minutes in 0.1% soap and 0.1% soda ash solution, rinsed and dried. The color was a bright blue and the yarn was dyed a full shade.

A second dyeing was made like the above except the 1.5 parts of sodium nitrite were omitted from the dye bath. The material dyed in this bath was a dull, dirty gray.

Example 6

The procedure of the preceding example was repeated except 1.5 parts of the sodium nitrite were used and the dye had Color Index No. 1102. The yarn dyed in the bath containing the sodium nitrite was stronger than that dyed in the control bath.

Example 7

The procedure of the preceding example was repeated except the dye oxy-nitro-dibenzanthrone was used. The color of the yarn dyed in this bath was stronger than that of the yarn dyed in the control bath, especially when aftertreated.

Example 8

The procedure of the preceding example was repeated except that the dye having Color Index No. 1135 was used. The yarn dyed in the bath containing the sodium nitrite was stronger and brighter than the yarn dyed in the control bath.

Example 9

The procedure of the preceding example was repeated except that the dye having Color Index No. 1112 was used and three parts additional sodium hydrosulfite were added after five minutes and another three parts after twenty minutes. The yarn dyed in the bath containing the sodium nitrite was much stronger and brighter than that dyed in the control bath. The dye having Color Index No. 1114 gave generally similar results.

Example 10

The procedure of Example 5 was repeated except that the dye having Color Index No. 1106 was used. The yarn dyed in the bath containing the sodium nitrite was much stronger and brighter than that dyed in the control bath.

Example 11

The procedure of Example 5 was repeated except that the dye having Color Index No. 1151 was used. The yarn dyed in the bath containing the sodium nitrite was superior to that dyed in the control bath.

Example 12

The procedure of the preceding example was repeated except that the dye having Color Index No. 1162 was used. The results were satisfactory.

Example 13

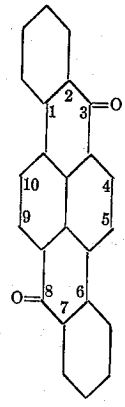
The procedure of Example 5 was repeated except 1.5 parts of KNO_2 were substituted for the 1.5 parts of $NaNO_2$. Cotton yarn dyed in this bath was a bright blue, whereas the yarn dyed in the control bath was a weak gray.

Example 14

The procedure of Example 5 was repeated except 1.5 parts of $LiNO_2$ were substituted for the 1.5 parts of $NaNO_2$.

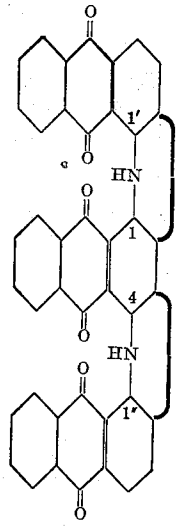
Example 15

The procedure of Example 5 was repeated except that the dye 1,2,6,7-dibenzpyrene-3,8-quinone was used.



Example 16

The procedure of the preceding example was repeated except the dye 1,1',4,1''-trianthrimide carbazole was used.



Example 17

The procedure of Example 5 was repeated except that only 0.025 part $NaNO_2$ was added. Cotton yarn dyed in this bath showed some loss in blue shade but was superior to the control sample.

Example 18

The procedure of Example 5 was repeated except that frequent additions of nitrite and hydrosulfite, totaling ½ part nitrite and 1½ parts hydrosulfite, were made to the dye bath at a temperature of 200° F. over a period of 3 hours. Finally 10 parts cotton yarn were entered and dyed at 200° F. for 15 minutes and the resulting dyeing showed that little if any loss in blue shade had occurred.

Example 19

The procedure of Example 5 was repeated using the dye 6,6'-dichloro-4,4'-dimethyl-2,2'-bis thionaphthene indigo and the resulting dyeing was commercially satisfactory.

Example 20

Five parts of the dye paste having Color Index No. 1113 and containing about 0.9 part of real dye were blended with five parts of sodium nitrite and 90 parts of a standard vat printing paste prepared as follows:

A paste was prepared by slurrying 2,000 parts of 177 British gum (Stein Hall) in 5,000 parts of water and the mixture was heated with continuous stirring until the temperature reached about 185° F. Heating was continued for about 1½ hours after which 450 parts of powdered potassium carbonate and 450 parts of powdered sodium carbonate were added and the mixture stirred until the carbonates dissolved. Heating was discontinued but stirring was continued until the temperature reached approximately 150° F. at which time 700 parts of sodium sulphoxylate were dissolved therein, 600 parts of glycerine were added, and the paste bulked to 10,000 parts. Stirring was continued until the paste cooled to room temperature.

A control printing color paste was prepared as the above except the sodium nitrite was omitted.

Pieces of 80 x 80 bleached, unmercerized cotton fabric were printed, air-dried, aged in a steam ager, oxidized, rinsed, soaped at the boil in a 0.1% soap solution for five minutes, rinsed again, and ironed dry.

Prints made from the color paste which contained the sodium nitrite were a bright blue shade of good strength, while prints made from the control paste were a dull dirty gray.

Example 21

The procedure of Example 5 was repeated except the dye was reduced for 15 minutes and dyed for 45 minutes at 120° F. instead of 200° F. as in Example 5. The yarn dyed in the bath containing the sodium nitrite was approximately 10% stronger, slightly redder and slightly brighter than the control dyeing.

Example 22

The procedure of the preceding example was repeated except the dyeing time was one hour and 45 minutes. The yarn dyed in the bath containing the sodium nitrite was approximately 15% stronger, slightly redder and slightly brighter when dyed for this longer period.

Example 23

The procedure of Example 21 was repeated except the dye was reduced and dyed at 140° F. The yarn dyed in the bath containing the sodium nitrite was about 25% stronger, brighter and redder than the control dyeing.

Example 24

The procedure of Example 5 was repeated except that rayon was used and the results were substantially the same as for cotton.

Example 25

The procedure of the preceding example was repeated except linen was used. The dyeing made in the bath containing the nitrite was bright blue while the dyeing made in the control bath was a dirty gray.

Example 26

The procedure of Example 5 was repeated except a nylon piece was used and the dye bath temperature was 212° F. The piece dyed in the bath containing the sodium nitrite was commercially satisfactory.

Example 27

A dyeing was made at a temperature of about 250° F. (approximately 50 pounds' pressure) on 2.5 parts of bleached unmercerized cotton in the apparatus described in U. S. P. 2,405,167, using a dye bath of 300 parts liquor containing 0.09 part of real dye having Color Index 1113, one part of sodium nitrite, five parts of sodium hydroxide and six parts of sodium hydrosulfite. The piece was dyed for two minutes. The bath was then flushed with water to the sewer, the dyeing removed, oxidized and finished as in Example 1. A good, strong, bright blue shade was obtained even at this high temperature.

A control dyeing, in which no sodium nitrite was present, but otherwise made as above, was dyed a dull gray shade.

Example 28

The procedure of the preceding example was repeated using nylon instead of cotton. The nylon dyed in the presence of the sodium nitrite had a bright blue shade, whereas the nylon dyed in the bath in which no sodium nitrite was present was dyed a brown shade.

Example 29

500 parts of No. 20's, 2-ply, natural cotton yarn in package form were wet out with 7,000 parts of a ¼% solution of a surface-active anionic material, which had been preheated to 190% F. The package was then dyed in a dye bath containing nine parts of real dye having Color Index 1113, 15 parts of a surface-active anionic material and 22.5 parts of sodium nitrite in 1,000 parts of water, making a total dye bath volume of 8,000 parts.

The dye dispersion was first heated to 190° F., and then circulated through the wet-out package for ten minutes, after which 200 parts of 30° Bé. sodium hydroxide, which had been preheated to 190° F., were added to the dye bath and circulated for five minutes, after which 50 parts of solid sodium hydrosulfite were added and circulated for 25 minutes. The spent dye bath was then flushed with water from the machine, the dye was oxidized with 2% of 100-volume hydrogen peroxide for 10 minutes at 140° F., after which the package was soaped, rinsed and dried. A bright blue dyeing having excellent levelness was obtained.

A control dyeing was made in the same manner except the sodium nitrite was omitted from the dye bath. The package dyed in the control bath was an uneven, dull, greenish-blue shade with no commercial value.

Example 30

900 parts of the real dye, having Color Index No. 1106, were ground and dry blended with 250 parts of potassium nitrite. Ten parts of cotton were dyed in a bath containing 0.115 part of this blend, 3 parts of sodium hydroxide, and 3 parts of sodium hydrosulfite in 400 parts of water using the general method of Example 5. The resultant dyeing was bluer and brighter than a control dyeing made from a bath containing the same amount of real dye, alkali and hydrosulfite but omitting the potassium nitrite.

Example 31

450 parts of the real dye used in Example 16 were ground and dry blended with 7,500 parts of sodium nitrite. Ten parts of cotton yarn were dyed in a bath containing 1.6 parts of this blend,

3 parts of sodium hydroxide and 3 parts of sodium hydrosulfite in 400 parts of water using the general method of the preceding example. The dyeing obtained from this dye bath was stronger and brighter than that obtained from a control dye bath in which no sodium nitrite was present.

Example 32

960 parts of the dye having Color Index No. 1113 and 2,400 parts of sodium nitrite were ground and dry blended to give a homogeneous mixture. Ten parts of rayon yarn were dyed in a bath containing 0.35 part of this blend, 3 parts of sodium hydroxide, and 3 parts of sodium hydrosulfite in 400 parts of water by the general method used in Example 5, and the results were similar to those obtained in Example 5.

Example 33

460 parts of a 20% wet press cake containing 92 parts of the real dye used in Example 15 and 25 parts of lithium nitrite were stired together and made up to 1,000 parts with water. One part of this aqueous paste was substituted for the 0.35 part of dry blended material of the preceding example, the dyeing being made as in the preceding example. The dyeing made from the bath containing the lithium nitrite was stronger and brighter than that made from a control dye bath in which no lithium nitrite was present.

Example 34

462.5 parts of the 20% wet press cake containing about 92.5 parts of the dye having Color Index No. 1113 and 400 parts of sodium nitrite were stirred together and then made up to 1,000 parts with water. One part of this paste was substituted for the one part of the paste of the preceding example, the dyeings were made as in the preceding example, and the results were satisfactory.

Example 35

The procedure of the preceding example was repeated except part of the water needed to bring the paste to 1,000 parts was replaced with glycerine to give a glycerine content of 5%–10% on the final weight. Dyeings made with pastes containing glycerine were quite satisfactory.

Example 36

The proceudre of the preceding example was repeated except the glycerine was replaced by ethyleen glycol. Cotton yarn dyed with this paste is commercially satisfactory.

Example 37

The procedure of the preceding example was repeated except the wet press cake was dispersed with 10 parts of the sodium salt of disulfo-dinaphthyl methane, the humectant then added and the paste made up to 1,000 parts. Cotton yarn dyed in a bath containing one part of this paste but otherwise dyed as in Example 34 gave satisfactory results.

I claim:

1. A method of vat dyeing fibrous material to which alkali metal salts of leuco vat dyestuffs are substantive with a vat dye which is sensitive to overreduction at the boiling point of water in an ordinary vat containing strong alkali and sufficient reducing agent to maintain reduction of the vat dyestuff, which comprises effecting the dyeing in the presence of such a bath containing, in addition to the strong alkali and reducing agent for the vat dyestuff, an amount of an inorganic nitrite at least one-fourth the weight of the real dyestuff.

2. A method according to claim 1 in which the dyestuff is an anthraquinone dihydroazine.

3. A method according to claim 2 in which the nitrite is sodium nitrite.

4. A method according to claim 1 in which the nitrite is sodium nitrite.

5. A method according to claim 1 in which the dyestuff is an anthrimide carbazole.

6. A method according to claim 5 in which the nitrite is sodium nitrite.

7. A method according to claim 1 in which the dyestuff is a cyanuric chloride derivative of an aminoanthraquinone.

8. A method according to claim 7 in which the nitrite is sodium nitrite.

9. As a new article of manufacture a blend of a vat dyestuff sensitive to over-reduction at the boiling point of water in a vat dye bath containing strong alkali and sufficient reducing agent for the vat dyestuff to maintain reduction and an amount of an inorganic nitrite at least one-quarter the weight of the real dyestuff.

10. An article of manufacture according to claim 9 in which the dyestuff is an anthraquinone dihydroazine.

11. An article of manufacture according to claim 10 in which the nitrite is sodium nitrite.

12. An article of manufacture according to claim 9 in which the nitrite is sodium nitrite.

13. An article of manufacture according to claim 9 in which the dyestuff is an anthrimide carbazole.

14. An article of manufacture according to claim 13 in which the nitrite is sodium nitrite.

15. An article of manufacture according to claim 9 in which the dyestuff is a cyanuric chloride derivative of an aminoanthraquinone.

16. An article of manufacture according to claim 15 in which the nitrite is sodium nitrite.

JERRY M. MECCO.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,029,999	Grieshaber	Feb. 4, 1936
2,146,646	Nusslein	Feb. 7, 1939
2,383,393	Kienle	Aug. 21, 1945