

UNITED STATES PATENT OFFICE

2,548,544

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

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. 130,357

16 Claims. (Cl. 8—34)

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.

According 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 halogenate. The ordinary soluble halogenates, such as alkali and alkaline earth metal halogenates, such as chlorates, bromates and iodates, may be used. Because of its cheapness and excellent results obtained, sodium chlorate is the preferred member.

The amount of halogenate to be used is not critical; but there is, of course, a minimum below which useful improvement does not result. This

2

practical minimum is about one-quarter the weight of the dyestuff. When more halogenate is added, results improve; but soon a practical optimum is reached at from 1.5-2 parts of halogenate per part of dye, beyond which additional halogenate usually does not give results which warrant the additional cost. However, as much as 16 or more parts of halogenate 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 halogenate 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 halogenates 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 over-reduction 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 contin-

uous or semi-continuous dyeing processes, and the like.

Another advantage of the present invention is that when inorganic halogenates are present in the dye bath, the dyeing process becomes relatively insensitive to temperature changes within reasonable operating limits, and small accidental temperature fluctuations are completely immaterial. It is therefore unnecessary when using the present invention to control the dyeing 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 dibenzoylamino - anthraquinone, 4,4'-dihydroxy indanthrene, 2(1-amino anthraquinonyl-2)-4,5 beta anthraquinone-oxazole, di-dibenzanthronyl-amino-di-alpha anthraquinonylamino pyranthrone, 3,4,8,9-dibenzpyrene-5,10-quinone, 1,1',4,1''-trianthrimide carbazole. Other dyes are those having the Color Index Nos.: 1135, 1106, 1112, 1113, 1114, 1151, 1162, 1102, 1099, 1109, 1173, 1150 and 1163.

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 halogenate, 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 halogenate 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 three parts of sodium chlorate. 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 ¼% 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. 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 dye yarn was then rinsed in warm water to remove the excess glacial acetic, soaped at the boil for ten 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 chlorate 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 chlorate 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 twenty minutes, after which 6 parts of 30° Bé. sodium hydroxide and two parts of sodium hydrosulfite were added and the temperature maintained at 160° F. for an additional forty minutes, making a total standing time of 60 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 the standard leuco solution having a standing time of 60 minutes, after which 20 parts of cotton yarn, pre-wet as above, were entered and dyed as above.

The yarn dyed from the bath containing the sodium chlorate after the dye bath had stood for 60 minutes was similar in shade to the yarn dyed in the bath containing the sodium chlorate 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 chlorate was present when the dyeing was made after the bath had stood at 160° F. for one hour.

Example 3

The above two examples were repeated using the dye having Color Index No. 1106. Again the yarn dyed in the bath containing the sodium chlorate retained its blue shade whereas the yarn dyed in the control bath was a dirty gray.

Example 4

The procedure of Examples 1 and 2 was repeated except the dye having Color Index No. 1112 was used. Again, the yarn dyed in the bath containing the sodium chlorate retained its bright reddish blue shade whereas the yarn dyed in the control bath was a dirty gray.

Example 5

The procedure of Examples 1 and 2 was repeated except that dye having Color Index No. 1114 was used, and the results were substantially the same as those obtained in Example 1.

Example 6

10 parts cotton yarn were dyed in a bath containing about 0.18 part of the real dye having Color Index 1113, three parts of sodium hy-

5

dioxide, three parts of sodium hydrosulfite, 1.5 parts of sodium chlorate 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 chlorate were omitted from the dye bath. The material dyed in this bath was a dull, dirty gray.

Example 7

The procedure of the preceding example was repeated except the amount of dye and chemicals in the dye bath was reduced to half, the volume remaining at 400 parts. The results were excellent.

Example 8

The procedure of Example 6 was repeated except the 1.5 parts of sodium chlorate were replaced with 1.5 parts of sodium bromate. The presence of this compound in the dye bath caused a bright blue dyeing to be obtained which had excellent color value. The dyeing made in the control bath, as in the preceding example, was a dull, dirty gray, showing that the dye had decomposed.

Example 9

The procedure of the preceding example was repeated except the 1.5 parts of sodium bromate were replaced with 1.5 parts of potassium iodate. Again the dyeing was a bright blue with a good strong shade showing that the presence of the potassium iodate prevented the decomposition of the dye when dyed at 200° F.

Example 10

The procedure of the preceding example was repeated except the 1.5 parts of potassium iodate were replaced with 1.5 parts of sodium chlorate and after 15 minutes one part additional sodium hydroxide and three parts additional sodium hydrosulfite were added. The presence of the sodium chlorate caused a bright blue dyeing to be obtained with excellent color value, showing that this material prevented decomposition of the dyestuff.

Example 11

The procedure of Example 6 was repeated except the dye had Color Index No. 1102. The yarn dyed in the bath containing the sodium chlorate was stronger than that dyed in the control bath. The after-treated shade is even better than the regular shade.

Example 12

The procedure of the preceding example was repeated exactly except that dye having Color Index No. 1151 was used. The yarn dyed in the bath containing the sodium chlorate was much

6

stronger and brighter than that dyed in the control bath.

Example 13

The procedure of the preceding example was repeated except that dye having Color Index No. 1112 was used and three parts additional sodium hydrosulfite were added after five minutes and another three parts after 20 minutes. The yarn dyed in the bath containing the sodium chlorate was much stronger and brighter than that dyed in the control bath.

Example 14

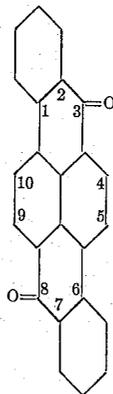
The procedure of Example 6 was repeated except the dye having Color Index No. 1162 was used. The yarn dyed in the bath containing the sodium chlorate was superior to that dyed in the control bath.

Example 15

The procedure of Example 6 was repeated except 1.5 parts of potassium iodate were substituted for the 1.5 parts of sodium chlorate. A cotton yarn dyed in this bath was a bright blue, whereas the yarn dyed in the control bath was a weak gray.

Example 16

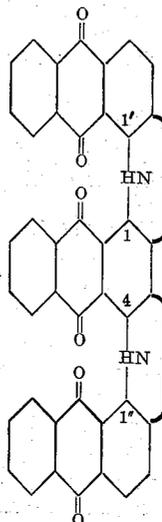
The procedure of Example 6 was repeated except the dye 1,2,6,7 dibenzpyrene-3,8-quinone was used.



A cotton yarn dyed in this bath gave a good bright shade.

Example 17

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



Example 18

Five parts of the dye paste having Color Index 1113 and containing about 0.9 part of real dye were blended with five parts of potassium chlorate and 90 parts of a standard vat printing paste prepared as follows:

A paste was prepared by slurring 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 were dissolved. Heating was discontinued but stirring was continued until the temperature reached approximately 150° F. at which time 700 parts of sodium sulfoxylate formaldehyde were dissolved therein, 600 parts of glycerine were added and the paste brought 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 that the potassium chlorate 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, again rinsed and ironed dry.

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

Example 19

The procedure of Example 1 was repeated except the dye was reduced and dyed at 120° F. instead of 160° F. The yarn dyed in the bath containing the sodium chlorate was approximately 10% stronger, slightly redder and slightly brighter than the control dyeing.

Example 20

The procedure of the preceding example was repeated except the dyeing time was 1 hour and 45 minutes. The yarn dyed in the bath containing the sodium chlorate was approximately 15% stronger, slightly redder and slightly brighter than the control dyeing.

Example 21

The procedure of the preceding example was repeated except the dye was reduced and dyed at 140° F. The yarn dyed in this bath was approximately 25% stronger, redder and brighter than that dyed in the control bath.

Example 22

The procedure of Example 6 was repeated except a rayon was used instead of the cotton and the results were substantially the same as for the cotton.

Example 23

The procedure of the preceding example was repeated except linen was used. The dyeing made in the bath containing the potassium chlorate was a nice, strong, bright blue as compared to the dirty gray color of the dyeing made in the control bath.

Example 24

The procedure for Example 23 was repeated except a nylon piece was dyed at the boil and the result was a nice, bright blue shade.

Example 25

A dyeing was made at a temperature of about 250° F. (approximately 50 pounds pressure) using 2.5 parts of bleached, unmercerized cotton in the apparatus described in U. S. P. 2,405,167 using a dye bath containing about 300 parts liquor, 0.09 part of real dye having Color Index No. 1113, one part of potassium chlorate, five parts of sodium hydroxide and six parts of sodium hydrosulfite, the dyeing time being 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.

A control dyeing in which no potassium chlorate was present, but otherwise made as above, had a dull gray shade.

Example 26

500 parts of No. 20's, 2-ply, natural cotton yarn in package form were wet out with seven thousand parts of a ¼% solution of a surface-active anionic material which had been preheated to 190° F. This was then dyed in a dye bath containing nine parts of real dye having Color Index No. 1113, 15 parts of a surface-active anionic material and 22.5 parts of sodium chlorate in 1000 parts of water, making a total dye bath volume of 8000 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 ten 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 chlorate 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 27

The procedure of Example 6 was repeated except that only 0.025 part of sodium chlorate was added. Cotton yarn dyed in this bath showed some loss in blue shade but was superior to the control sample.

Example 28

900 parts of the real dye, having Color Index 1106, were ground and dry blended with 250 parts of potassium chlorate. Ten parts of cotton were dyed in a bath containing 0.115 part of this blend, three parts of sodium hydroxide, and three parts of sodium hydrosulfite in 400 parts of water using the general method of Example 6. 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 chlorate.

Example 29

450 parts of the real dye used in Example 17 were ground and dry blended with 7,500 parts of sodium iodate. 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

9

water using the general method of the preceding example. The dyeing obtained from this dyebath was stronger and brighter than that obtained from a control dyebath in which no sodium iodate was present.

Example 30

960 parts of the dye having Color Index No. 1113 and 2,400 parts of sodium bromate 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 6, and the results were similar to those obtained in Example 6.

Example 31

460 parts of a 20% wet press cake containing 92 parts of the real dye used in Example 16 and 25 parts of lithium chlorate were stirred 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 chlorate was stronger and brighter than that made from a control dyebath in which no lithium chlorate was present.

Example 32

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 chlorate were stirred together and then made up to 1,000 parts with water. One part of this paste was substituted for one part of the paste of the preceding example, the dyeings were made as in the preceding example, and the results were satisfactory.

Example 33

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 34

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

Example 35

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 32 gave satisfactory results.

I claim:

1. A method of dyeing fibrous material to

10

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 dyestuffs, an amount of an inorganic halogenate of 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 halogenate is sodium chlorate.

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

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 halogenate is sodium chlorate.

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 halogenate is sodium chlorate.

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 halogenate 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 halogenate is sodium chlorate.

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

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 halogenate is sodium chlorate.

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 halogenate is sodium chlorate.

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