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COMPOSITIONS COMPRISING VAT DYES SENSITIVE TO OVERREDUCTION AND METHODS OF DYEING

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18 Claims. (Cl. 8—34)

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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 high 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 dyebath 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 the present invention, it has been found that if there is present in the dye bath a nitrogen compound in which a nitrogen is attached by at least one covalence bond to oxygen and by at least one covalence bond to an element other than oxygen or nitrogen, the deleterious results of high temperature dyeing are not noted, or are greatly minimized.

The amount of the nitrogen compound is not

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critical. There is, of course, a lower limit below which no practically useful increases in strength and brightness are obtained when high temperature dyeing is used. In general, this lower limit is about 1 part of nitrogen compound to 4 parts of actual dyestuff. When larger amounts of the nitrogen compound are used, improved results are obtained; but a practical result, closely approaching maximum improvement, is quickly reached. With many dyestuffs, this is about 1.5–2 parts of the nitrogen compound per 1 part of real dye. Still larger amounts of nitrogen compound do not result in an improvement which warrents the additional cost. There is, however, no real upper limit; 16 and more times the weight of the dyestuff showing no adverse result. However, since there is no improvement in using such enormous quantities of the nitrogen compound, it is practically unattractive because of excessive costs.

The nitrogen compounds are, for the most part, organic in nature, including such compounds as nitroparaffins, aromatic nitro compounds, nitroso compounds, and the like. There are also some compounds, such as the hydroxylamine, and, particularly, hydroxylamine disulfonate, which, while containing no carbon, are often considered in the realm of organic chemistry. These compounds are also useful. The various nitrogen compounds all exert some beneficial effect. There is, however, a variation in the effectiveness of the individual compounds. Among the most powerful are notropropane and hydroxylamine, and as these compounds are readily obtainable at a moderate cost, they present a definite economical advantage. Nitrobenzene is almost as effective, and its even lower cost also makes it a desirable material to use.

It is not known just how the nitrogen compound 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 nitrogen compounds 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 continuous or semicontinuous dyeing processes, and the like.

Another advantage of the present invention is that when nitrogen compounds 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 dying 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 anthraquinonyl-amino pyranthrone, 3,4,8,9-dibenzpyrene-5,10-quinone, 1,1',4,1''-trianthrimide carbazole. Other dyestuffs are those having the Color Index Nos.: 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 nitrogen compounds, 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 nitrogen compounds 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

Ten 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 nitro propane 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 bright blue and the yarn was dyed a full shade.

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

EXAMPLE 2

The procedure of the preceding example was repeated except the 1.5 parts of nitropropane were replaced with 1.5 parts of para chloro ortho nitraniline. 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 3

The procedure of the preceding example was repeated except the 1.5 parts of para chloro ortho nitraniline were replaced with 1.5 parts of hydroxylamine hydrochloride. Again the dyeing was a bright blue with a good strong shade showing that the presence of the hydroxylamine hydrochloride prevented the decomposition of the dye when dyed at 200° F.

EXAMPLE 4

The procedure of the preceding example was repeated except the 1.5 parts of hydroxylamine hydrochloride were replaced with 1.5 parts of nitrobenzene potassium sulfonate and after 15 minutes one part additional sodium hydroxide and 3 parts additional sodium hydrosulfite were added. The presence of the nitrobenzene potassium sulfonate caused a bright blue dyeing to be obtained with excellent color value, showing that this material prevented decomposition of the dyestuff.

EXAMPLE 5

The procedure of Example 3 was repeated except the 1.5 parts of hydroxylamine hydrochloride were replaced with 1.5 parts of nitrobenzene and after 15 minutes 1.5 parts sodium hydrosulfite were added. The shade of this dyeing was a blue, showing that decomposition had not occurred as in the control sample.

EXAMPLE 6

The procedure of the preceding example was repeated except 1.5 parts of nitrobenzene were replaced by 1.5 parts of N-nitrosodiphenylamine and a strong bright blue dyeing was obtained.

EXAMPLE 7

The procedure of Example 1 was repeated except the dye has Color Index No. 1102. The yarn dyed in the bath containing the nitropropane is stronger than that dyed in the control bath, especially when after-treated.

EXAMPLE 8

The procedure of the preceding example is repeated except that oxy nitro dibenzanthrone was used. The color of the yarn dyed in this bath is stronger than that of the yarn dyed in the control bath.

EXAMPLE 9

The procedure of Example 8 was repeated except that the dye having Color Index No. 1112 was used. The yarn dyed in this bath is excellent in shade and strength compared to the yarn dyed in the bath in which no nitropropane was used.

EXAMPLE 10

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

EXAMPLE 11

The procedure of the preceding example was repeated except that dye having Color Index No. 1112 was used and 3 parts additional sodium hydrosulfite were added after 5 minutes and another 3 parts after 20 minutes. The yarn dyed in the bath containing the nitropropane was much stronger and brighter than that dyed in the control bath. If desired, the dye having Color Index No. 1114 may be used with good results.

EXAMPLE 12

The procedure of Example 1 was repeated except that dye having Color Index No. 1106 was used. The yarn dyed in the bath containing the nitropropane was much stronger and brighter than that dyed in the control bath.

EXAMPLE 13

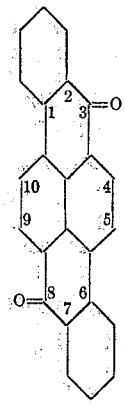
The procedure of Example 1 was repeated except the dye having Color Index No. 1151 was used. The yarn dyed in the bath containing the nitropropane was superior to that dyed in the control bath.

EXAMPLE 14

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

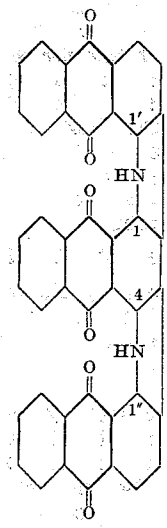
EXAMPLE 15

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



EXAMPLE 16

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



EXAMPLE 17

The procedure of Example 1 was repeated except that only 0.025 part nitropropane was added. The improvement in blue shade, when compared to the control dyeing in which no nitropropane was present, was evident.

EXAMPLE 18

The procedure of Example 1 is repeated except the nitropropane is replaced with 1.5 parts of dinitrobenzene. The resulting dyeing is blue and not the dirty gray shade obtained in the control sample in which no dinitrobenzene was present.

EXAMPLE 19

The procedure of the preceding experiment was repeated except that the dinitrobenzene was replaced with para-nitro acetanilide. The results were very similar to those obtained in Example 18.

EXAMPLE 20

The procedure of the preceding experiment was repeated except the para-nitro acetanilide was replaced with ortho-nitroso metacresol, and the results were similar to those obtained in the preceding example.

EXAMPLE 21

A dye bath prepared as in Example 1 was boiled for four hours, after which ten parts of cotton were dyed at the boil for 45 minutes. The yarn was dyed a bright blue shade having excellent strength, whereas yarn dyed in a control bath in which no nitropropane was present was dyed a weak dirty gray shade.

EXAMPLE 22

The procedure of Example 1 was repeated except the compound $HON(SO_3K)_2 \cdot 2H_2O$ was used in place of the nitropropane of Example 1. This compound was prepared as follows:

Preparation of $HON(SO_3K)_2 \cdot 2H_2O$

42.5 parts of KNO_2 (0.5 mole) and 50 parts of $KC_2H_3O_2$ were dissolved in 100 parts ice water. This was placed in a 3-neck flask fitted with a stirrer. 750 parts finely chipped ice were added and the stirrer started. SO_2 gas was passed into this mixture until an excess was added, as indicated by the effluent gas discoloring a dilute $KMnO_4$ solution. The temperature was kept around 0° C. during the reaction. The crystals of $HON(SO_3K)_2 \cdot 2H_2O$ were filtered with a Büchner funnel and the precipitate washed with four portions of ice water, each amounting to 25 parts, to remove sulfites and acetates. The precipitate was not dried, but stored damp in a refrigerator. Reference: Rollefson and Oldershaw, J. Am. Chem. Soc., 54, 977 (1932).

The yarn dyed in the presence of the $HON(SO_3K)_2 \cdot 2H_2O$ was a brilliant blue of excellent strength as compared to the dull dirty gray of the control dyeing.

EXAMPLE 23

Five parts of the dye paste having C. I. No. 1113 and containing about 0.9 part of real dye were blended with five parts of nitropropane 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 nitropropane 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 nitropropane were a bright blue shade of good strength, while prints made from the control paste were a dull dirty gray.

EXAMPLE 24

Three parts of the dye having Color Index No. 1113 and containing about 13.5% real dye were mixed with 3.0 parts of N(2-nitro-2-methyl-

propyl) sulfanilic acid. This mixture was then dissolved in 1170 parts of water at 120° F. To this was added 35 parts of 30° Bé. sodium hydroxide, after which the temperature was again adjusted to 120° F., nine parts of sodium hydrosulfite added and dissolved. The temperature was maintained at 120° F. for fifteen 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.

Twenty parts of natural cotton yarn were prewet with approximately ½% solution of pine oil soap. The excess was removed by squeezing and the yarn then entered into the 400 parts of reduced vat dye and dyed at 120° F. for 45 minutes. The dyed yarn was then removed and the excess dye liquor was extracted from the yarn. The remaining dye on the yarn was then oxidized for 5 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.

The control dye bath was prepared exactly like the above except the N(2-nitro-2-methyl-propyl) sulfanilic acid was omitted. This was used to make a control dye using the same procedure as above. The yarn dyed in the bath containing the N(2-nitro-2-methyl-propyl) sulfanilic acid was approximately 10% stronger, slightly redder and slightly brighter than the control dyeing.

EXAMPLE 25

The procedure of Example 24 was repeated except the dyeing time was one hour and forty-five minutes. The yarn dyed in the bath containing N(2-nitro - 2 - methyl-propyl) sulfanilic acid was about 15% stronger, slightly redder and slightly brighter than the control dyeing.

EXAMPLE 26

The procedure of Example 24 was repeated except the dye was reduced and dyed at 140° F. The yarn dyed in the bath containing the N(2-nitro-2-methyl-propyl) sulfaniiic acid was approximately 20% stronger, redder and brighter than the yarn dyed in the control bath.

EXAMPLE 27

The procedure of Example 1 was repeated except rayon was used and the results were substantially the same as for cotton.

EXAMPLE 28

The procedure of the preceding example was repeated except linen was used. The dyeing made in the bath containing the nitro propane was a strong, bright blue shade.

EXAMPLE 29

The procedure of Example 1 was repeated except the cotton was replaced with a nylon piece and dyed at the boil. Under these dyeing conditions this fiber, which is so difficult to dye with vat dyes, is dyed a commercially satisfactory bright blue shade.

EXAMPLE 30

The procedure of Example 1 was repeated except the nitropropane was replaced with the com-

pound N-(2-nitro - 2 - methyl-propyl) sulfanilic acid. The dyeing made from the bath containing the sulfanilic acid compound was a bright, strong, blue shade as compared to a dirty gray shade for the control dyeing.

EXAMPLE 31

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 of 300 parts liquor containing 0.09 part of real dye having Color Index No. 1113, one part of the agent used in the preceding example, 5.0 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 N-(2-nitro-2-methyl-propyl) sulfaniiic acid was used, but otherwise made as above, had a dull gray shade.

EXAMPLE 32

The procedure of the preceding example was repeated using nylon instead of cotton. The piece dyed in the presence of the N-(2-nitro-2-methyl-propyl) sulfanilic acid had a brilliant blue shade. The piece dyed in the control test had a brown shade.

EXAMPLE 33

Five hundred parts of No. 20's, 2-ply, natural cotton yarn in package form were wet out with 7000 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 N-(2-nitro-2-methyl-propyl) sulfaniiic acid 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 nitropropane was omitted from the dye bath. The package dyed in the control bath was an uneven, dull greenish-blue shade with no commercial value.

Other nitrogen compounds which can be used to prevent the decomposition of the vat dye are 3-(2-ethoxy phenyl)-5-amino isoxazole, azoxy benzene, n-nitroso diphenylamine, 1-carbethoxy-4-nitroso piperazine, nitromethane, N-(3-phenyl-5-isoxazoyl)-phenol-4-sulfonamide, 3-(2-ethoxy phenol)-5-(-4)-isoxazolone, 3-phenyl-5-hydroxy isoxazole.

EXAMPLE 34

900 parts of the real dye, having Color Index No. 1106, were ground and dry blended with 250 parts of N-(2-nitro-2-methyl-propyl) sulfanilic acid. 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 1. 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 N-(2-nitro-2-methyl-propyl) sulfanilic acid.

EXAMPLE 35

450 parts of the real dye used in Example 16 were ground and dry blended with 7,500 parts of p-nitro-acetanilide. 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 p-nitro-acetanilide was present.

EXAMPLE 36

960 parts of the dye having Color Index No. 1113 and 2,400 parts of $HON(SO_3K)_2 \cdot 2H_2O$ 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 1, and the results were similar to those obtained in Example 1.

EXAMPLE 37

460 parts of a 20% wet press cake containing 92 parts of the real dye used in Example 15, and 25 parts of hydroxylamine hydrochloride 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 hydroxylamine hydrochloride was stronger and brighter than that made from a control dye bath in which no hydroxylamine hydrochloride was present.

EXAMPLE 38

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 N-(2-nitro-2-methyl-propyl) sulfanilic acid 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 39

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 40

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 41

The procedure of the preceding example was repeated except the wet press cake was dispersed

with 10 parts of the sodium salt of di-sulfodinaphthyl 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 38 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 a nitrogen compound in which a nitrogen is attached by at least one covalence to oxygen and by at least one covalence to an element other than oxygen or nitrogen equal to at least one-quarter 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 nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

4. A method according to claim 1 in which the nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

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 nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

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 nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

9. As a new article of manufacture a blend of a vat dyestuff sensitive to over-reduction at elevated temperatures and an amount of a nitrogen compound, in which a nitrogen is attached by at least one covalence bond to oxygen and by at least one covalence bond to an element other than oxygen or nitrogen, equal to 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 nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

12. An article of manufacture according to claim 9 in which the nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

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 nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

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 nitrogen compound is N-(2-nitro-2-methyl-propyl) sulfanilic acid.

17. A method according to claim 1 in which the nitrogen compound is a nitroalkane.

18. A method according to claim 17 in which the nitroalkane is a nitropropane.

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