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PYRANTHRONE DYE COMPOSITION COMPRISING AN INORGANIC NITRITE AND PROCESS FOR DYEING

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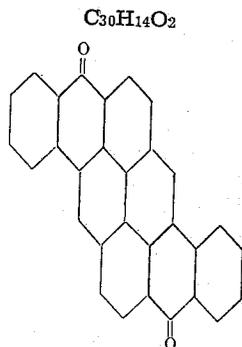
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This invention relates to an improved process of dyeing with pyranthrone and its halogenated derivatives.

Pyranthrone (C. I. 1096), has the following formula



and it, and its dibromo derivative (C. I. 1098), are well known vat dyes of golden-orange color. When these dyes are dyed by ordinary vat dyeing processes, which involve a strong alkali, such as sodium hydroxide and a reducing agent, such as sodium hydrosulfite, there is a loss in strength and brilliance, when the dyeing operation is carried out at high temperatures. On the other hand, high temperature dyeing presents such large practical economic advantages, that the properties of these two dyes, for dyeing at high temperatures, approaching that of boiling water, has hampered their economic exploitation.

High temperature dyeing usually improves dye penetration and/or levelness, particularly with such fabrics as nylon. The fast-dyeing which is possible at high temperatures also makes various continuous and semi-continuous processes possible.

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 fabric. In many processes the dyestuff is present in a dye bath or vat in solution in the form of the 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 dye-

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stuff, 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.

We have found that the addition of an inorganic nitrite, such as an alkali metal nitrite, removes the disadvantage noted in ordinary high temperature dyeing with pyranthrone, and its halogenated derivatives. As all of the alkali metal nitrites behave in the same manner, sodium nitrite is, ordinarily, used because of its low cost. The particular metal cation, however, does not appear to enter into the mechanism, by which the nitrites achieve their improved results. Therefore, practically, sodium nitrite is preferred.

It is not known how the nitrite operates in preventing loss of strength and brilliance in high temperature dyeing with a pyranthrone; and, accordingly, the present invention is not intended to be limited to any theory of action. In particular, the phenomena which underlie the present invention are all the more mysterious, because, as is described and claimed in my co-pending application Serial No. 130,356, filed November 30, 1949, inorganic nitrites exert a similar action with vat dyestuffs which are sensitive to over reduction or decomposition at high temperatures. In the case of these dyes, which are easily decomposed or over reduced, it is possible that the nitrite may act as some kind of a reduction buffer. In the case of pyranthrone and its halogenated derivatives, however, such an explanation is not tenable, because it is a known characteristic of these dyes that they do not show any appearance of decomposition or over reduction in baths up to the boiling point of water. In spite of this well known stability of the dyestuffs, the nitrites exert their beneficial action to a marked degree. It is obvious that factors other than prevention of over reduction or decomposition at high temperatures must be involved. What these other factors are, however, has still not been determined.

The advantages of the present invention are obtained both with pyranthrone and its halogenated derivatives. The degree of improvement, however, is considerably greater with dibromopyranthrone than with pyranthrone itself.

It is an advantage of the present invention that the amount of inorganic nitrite to be used is not critical. There is, of course, a lower limit, and it has been found that when the amount of nitrite is less than one-quarter by weight of the content of actual dyestuff in the bath, the improvements are not sufficiently marked to be

of practical value. Above this minimum, results improve for a while, with increasing amount of nitrite, but soon reach the point at which greater amounts of nitrite do not give any improvement. This point is approximately 16 parts by weight of nitrite to 1 of dye. However, for practical operation, the improvement obtained with much smaller amounts (for example, from 1 to 3 parts of nitrite per part of dye), so closely approach the maximum improvement obtainable, that larger amounts of nitrite do not produce sufficient improvement to justify the additional cost. Even the upper limit of 16 parts of nitrite does not represent the maximum amount which can be used, without destroying the improvement in strength and brilliance, which is the purpose of the present invention. Even when 50 parts of nitrite to 1 part of dye are used, the improvements are still to be noted; but, of course, such enormous amounts of nitrite are only of theoretical interest.

Another advantage of the present invention is that the manipulative techniques of high temperature dyeing are not, in any way, changed by its use. Dyeing conditions remain the same, as do dyeing times; and the only change is that the shades obtained are stronger and brighter.

The optimum amount of inorganic nitrite to be used depends, to some extent, on the temperature of the dye bath and on the time during which dyeing takes place. In general, the faster the dyeing, the smaller the amount of nitrite which can be used to give results so closely approximating the optimum results, as to make larger amounts of nitrite practically unnecessary. When dyeing time is longer, as is customary, additional amounts of hydrosulfite are added to make up for hydrosulfite oxidized by the air, or by other factors.

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

10 parts of cotton yarn were dyed in a bath containing about 0.09 part of the real dye having Color Index 1098, 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 a 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 acid, soaped at the boil for 10 minutes in 0.1% soap and 0.1% soda ash solution, rinsed and dried. The color was a bright orange 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 dull, weak, and yellow.

Example 2

The procedure of the preceding example was repeated except the dye having Color Index No. 1096, and 1.5 parts of sodium hydrosulfite were added after 5 minutes and another 1.5 parts were added after 20 minutes. The color value of the yarn dyed in this dye bath is a stronger and brighter orange than that of the yarn dyed in the control sample in which no sodium nitrite is present.

Example 3

10 parts of cotton yarn were dyed in a bath containing 0.09 parts of the real dye having Color Index No. 1096, 3 parts of sodium hydroxide, 3 parts of sodium hydrosulfite, 1.5 parts of potassium nitrite in 400 parts of water. The bath was reduced for 5 minutes at 200° F., after which the cotton yarn was entered and dyed for 60 minutes at 200 F. The dyeing was bright orange and the yarn was dyed a full shade.

A second dyeing was made exactly as above except the 1.5 parts of potassium nitrite were omitted from the dye bath. The cotton yarn dyed in this bath was a weaker and yellower shade of orange.

Example 4

The procedure of the preceding example was repeated except the dye having Color Index No. 1098, and 1.5 parts of sodium hydrosulfite were added after 5 minutes and another 1.5 parts were added after 20 minutes. The color value of the yarn dyed in this dye bath is a much stronger and brighter orange than that of the yarn dyed in the control sample in which no potassium nitrite is present.

Example 5

10 parts of cotton yarn were dyed in a bath containing 0.09 parts of the real dye having Color Index No. 1096, 3 parts of sodium hydroxide, 3 parts of sodium hydrosulfite, 1.5 parts of lithium nitrite in 400 parts of water. The bath was reduced for 5 minutes at 200° F., after which the cotton yarn was entered and dyed for 60 minutes at 200° F. The dyeing was bright orange and the yarn was dyed a full shade.

A second dyeing was made exactly as above except the 1.5 parts of lithium nitrite were omitted from the dye bath. The cotton yarn dyed in this bath was a weaker shade of orange.

Example 6

The procedure of the preceding example was repeated except the dye having Color Index No. 1098, and 1.5 parts of sodium hydrosulfite were added after 5 minutes and another 1.5 parts were added after 20 minutes. The color value of the yarn dyed in this dye bath is a much stronger and brighter orange than that of the yarn dyed in the control sample in which no lithium nitrite is present.

Example 7

Three parts of the dye having Color Index No. 1098 and containing about 19% 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 were added 35 parts of 30° Bé. sodium hydroxide, after which the temperature was again adjusted to 160° F. and 9 parts of sodium hydrosulfite added and dissolved. The temperature was maintained at 120° F. for 15 minutes, after which time the color was reduced. This dye solution will be referred to as the standard solution. 400 parts of this reduced dye solution were then transferred to a separate dye beaker.

20 parts of natural cotton yarn were pre-wet with approximately one-half percent solution of 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 45 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 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 acid, 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 10% stronger and somewhat redder and brighter than the control dyeing. When this dye decomposes due to over-reduction at high temperatures in an alkaline reducing solution, it loses its bright red shade and becomes yellow and dull.

Example 8

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 nitrite was much stronger, redder and brighter than the yarn which was dyed in the control bath.

Example 9

The procedure of Example 1 was repeated except rayon was used in place of cotton. The yarn dyed in the bath containing the sodium nitrite was approximately 50% stronger, redder and brighter in shade than the yarn dyed in the control bath.

Example 10

The procedure of the preceding example was repeated except the yarn was made of nylon and the temperature was 212° F. The dyed yarn was a good, strong, level, commercially satisfactory orange shade as compared to the weak yellow shade of the yarn dyed in the bath in which no nitrite was present.

Example 11

The procedure of Example 1 was repeated except only 25 parts of the sodium nitrite were added. The yarn dyed in the bath containing the nitrite was superior in shade and brightness to that dyed in the control bath but the difference was not as pronounced as when the larger amount

of sodium nitrite such as was used in Example 1 was present.

Example 12

A dyeing was made at a temperature of about 250° F. (approximately 50 pounds of pressure) 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. 1098 on 80 x 80 bleached, unmercerized cotton fabric weighing about 2.5 parts, one part of sodium nitrite, 5.0 parts of sodium hydroxide and 6 parts of sodium hydrosulfite, the dyeing being carried out for about two minutes. The bath was then flushed with water to the sewer, the dyeing removed, oxidized and finished as in Example 7. A good, strong reddish shade of orange was obtained.

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

Example 13

The procedure of the preceding example was repeated except the dyeing was made on a piece of nylon fabric, and the dyeing made in the presence of the nitrite was commercially satisfactory.

Example 14

500 parts of No. 20's, 2-ply, natural cotton yarn in package form was wet out with 7,000 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 9 parts of real dye having Color Index No. 1098, 15 parts of a surface-active anionic material and 22.5 parts sodium nitrite in 1,000 parts water, the entire dye bath volume being 8,000 parts.

The dye dispersion was first heated to 190° F. and then circulated through the wet-out package for 10 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 5 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 orange dyeing having excellent levelness and a reddish shade 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 uneven, dull and yellow in shade.

Example 15

900 parts of the real dye, having Color Index No. 1098, 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 1. The resultant dyeing was stronger, redder 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 16

450 parts of the real dye of the preceding example 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

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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 17

960 parts of the dye having Color Index No. 1096 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 1. The yarn dyed in the bath containing the sodium nitrite was redder and brighter than the control dyeing.

Example 18

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 stirred together and made up to 1,000 parts with water. One part of this aqueous paste was substituted for the 0.115 part of dry blended material of Example 15, the dyeing being made as in Example 15. 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 19

462.5 parts of the 20% wet press cake containing about 92.5 parts of the dye having Color Index No. 1098 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 20

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 21

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

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Example 22

The procedure of the preceding example was repeated except the wet press cake was dispersed with 10 parts of the sodium salt of di-sulfo-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 19 gave satisfactory results.

I claim:

1. A method of vat dyeing fibrous material to which alkali metal salts of the leuco vat pyranthrone dye are substantive with a pyranthrone dye, which comprises dyeing the material at high temperature approaching the boiling point of water in a bath containing the dyestuff, strong alkali, reducing agent, and an amount of an inorganic nitrite at least one-quarter the weight of the real dyestuff.

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

3. A method according to claim 2 in which the dyestuff is pyranthrone.

4. A method according to claim 2 in which the dyestuff is dibromopyranthrone.

5. A method according to claim 1 in which the dyestuff is pyranthrone.

6. A method according to claim 1 in which the dyestuff is dibromopyranthrone.

7. As a new article of manufacture a blend of a pyranthrone vat dyestuff with an amount of an inorganic nitrite at least one-quarter the weight of the real dyestuff.

8. An article of manufacture according to claim 7 in which the nitrite is sodium nitrite.

9. An article of manufacture according to claim 8 in which the dyestuff is pyranthrone.

10. An article of manufacture according to claim 8 in which the dyestuff is dibromopyranthrone.

11. An article of manufacture according to claim 7 in which the dyestuff is pyranthrone.

12. An article of manufacture according to claim 7 in which the dyestuff is dibromopyranthrone.

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

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