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PRODUCTION OF PHTHALOCYANINE VAT DYES

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This invention relates to the production of phthalocyanine coloring matters and more particularly to dye-stuff mixtures containing cobalt phthalocyanines modified in such manner as to adapt them for the dyeing of textile fibers by vatting.

Metallized and metal-free phthalocyanine coloring matters, which are distinguished by their strong, clear shades and excellent fastness properties, have been used for the most part for pigmenting and as dyestuffs for lake-making. As early as 1929 (British Patent 322,169) it was shown that certain phthalocyanine compounds have the property of being vatted. For example, it was stated that both the unsulfonated and sulfonated copper, nickel and iron phthalocyanines could be vatted. These products never were used as vat dyes chiefly because of their poor affinity to the fiber, the dull shades they produced, and their lack of light fastness. The first mention of the use of cobalt phthalocyanine as a vat dye is found in the work of Bienert [P.B. No. 70,339, Frame 11206 (1948)]. Practically speaking, however, cobalt phthalocyanine per se has poor solubility in the vat, producing as a result weak blue dyeings.

It is an object of this invention to provide a cobalt phthalocyanine composition which may be employed for dyeing textile fibers from the vat. Another object of this invention is the provision of a vat dyeing composition containing a cobalt phthalocyanine dyestuff. A further object of this invention is the provision of a process for dyeing textile fibers with a cobalt phthalocyanine from the vat. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention which is based upon the discovery that the solubility of a cobalt phthalocyanine in the vat and consequently the strength of dyeing obtained therewith can be immensely improved by reacting at least part of the color with formaldehyde or a substance yielding same such as para-formaldehyde, trioxane or the like, in the presence of a strong acid having a concentration of at least about 90% by weight, and if desired, also in the presence of an amide. The dyeings obtained from the products of the aforementioned process have been found to be surprisingly superior to dyeings produced in a similar manner with unreacted cobalt phthalocyanine, or with similar compositions having a basis of copper phthalocyanine instead of cobalt phthalocyanine.

The reaction may be carried out at temperatures ranging from about 40 to 150° C., the upper temperatures being determined by the boiling point of the mixture and the solubility of the cobalt phthalocyanine therein. Temperatures of from about 70 to 100° C. are preferred. While sulfuric acid is preferred as the acid medium, other acids may be employed such as phosphoric acid and methyl sulfuric acid. These acids are employed in concentrations of at least 90% and up to 100% or more. Thus, 5% or more oleum may be employed providing the proper temperature is chosen so as to prevent sulfona-

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tion from taking place. It will of course be understood that the temperature to be used is inter-related with the concentration of acid, and the like, the more concentrated the acid, the lower the temperature that should be used.

While there are sixteen positions available for substitution in cobalt phthalocyanine, it has been found that the most useful range of proportions of reactants in general varies from about 0.1 to 5 equivalents of formaldehyde per cobalt phthalocyanine molecule. Within this range, proportions of about 0.3 to 1 equivalent of formaldehyde per molecule of cobalt phthalocyanine are preferred. It will thus be understood that there will be produced as a result of the reaction, compositions containing unreacted cobalt phthalocyanine molecules admixed with cobalt phthalocyanine molecules having varying numbers of substituents depending upon the proportions of reactants employed, the reaction conditions, and the like. If desired, the cobalt phthalocyanine to be reacted with the formaldehyde in accordance with this invention may be more or less substituted with other substituents such as chlorine. While the mechanism of the reaction is not clearly understood, it is obvious that the cobalt phthalocyanine reacted in accordance with this invention assists the reacted cobalt phthalocyanine as well as any unreacted cobalt phthalocyanine included therewith to dye from the vat. It has been found that even small amounts of the cobalt phthalocyanine derivatives of this invention will convert larger amounts of unreacted cobalt phthalocyanine with poor vatting properties into a state in which they exhibit excellent vatting properties. Accordingly, it will be understood that the proportion of unreacted cobalt phthalocyanine to reacted cobalt phthalocyanine in such mixtures may be adjusted as desired by controlling the proportions of reactants or by mixing predetermined amounts of unreacted cobalt phthalocyanine with the cobalt phthalocyanine derivatives produced in accordance with the process of this invention.

As stated above, the reaction may be carried out in the presence of an amide, it having been found that the use of the amide yields products dyeing a strong bright blue shade in comparison with products obtained in the absence of the amide which are generally greener. As amides which may be employed in the process of this invention, there may be mentioned simple aliphatic and aromatic amides such as propionamide, butyramide, benzamide, urea, biuret, and the like, and especially formamide and acetamide. These amides may be employed in proportions of about 5 to 40 percent by weight of the formaldehyde.

The cobalt phthalocyanine derivatives of this invention may be vatted in known manner with caustic and hydro-sulfite, and the vats employed for dyeing textile fibers in strong, bright blue shades of excellent light fastness. Subsequent oxidation may be achieved in known manner by exposing the dyed fiber to the air or by dipping it in an oxidizing bath, for instance a solution of sodium perborate or aqueous acetic acid solutions of sodium dichromate. The dyestuff mixtures of this invention are capable of being vatted even in a weakly alkaline medium, for instance in the presence of ammonia, and therefore may also be employed for dyeing animal fibers from the vat in addition to fibers having a basis of synthetic polymeric materials.

The following examples, in which parts are by weight unless otherwise indicated, are illustrative of the instant invention and are not to be regarded as limitative. Parts by weight are in grams and parts by volume are in cc. Examples 1 through 15 illustrate the preparation of dye-stuff mixtures in accordance with this invention, and Examples 16 through 18 illustrate representative dyeing procedures employing such dyestuff mixtures.

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Example 1

5 parts of cobalt phthalocyanine is dissolved in 70 parts of 100% sulfuric acid. The temperature rises to 39° C. Without cooling there is added 0.6 part acetamide, 2.6 parts paraformaldehyde. The temperature rises to 44° C. The solution is heated to 70–75° C. in a half hour and held at 70–75° C. for one hour. The solution is drowned in 1500 parts water. The product is filtered, washed neutral with water and filter cake made into homogeneous paste. The product dyes cotton from a greenish-yellow vat in a full, clear blue shade which is distinguished by excellent fastness to light.

If the acetamide and paraformaldehyde are omitted from the above example, the mere solution of the cobalt phthalocyanine in 100% sulfuric acid at 70–75° C. for one hour does not yield a product possessing acceptable vatting properties and affinity to the fiber. On the contrary, the product, although partly vatted, does not dye the fiber from the vat to any extent.

Example 2

10 parts of cobalt phthalocyanine is dissolved in 140 parts 100% sulfuric acid at 25–30° C. 2.4 parts acetamide and 8.0 parts paraformaldehyde are added and the temperature is allowed to rise exothermally.

The solution is then heated to 70–75° C. in a half hour and the temperature is maintained at 70–75° C. for one hour. The solution is drowned in 3000 parts water. The product is filtered, washed neutral with water and the filter cake made into a homogeneous paste. The product dyes cotton a strong, blue shade from a yellowish-green vat. The dyeings exhibit excellent light fastness.

Example 3

5 parts cobalt phthalocyanine is dissolved in 70 parts 100% sulfuric acid. 4 parts paraformaldehyde are added and the temperature of the solution is raised to 70–75° C. in a half hour. The temperature is maintained at 70–75° C. for one hour.

The solution is drowned and the dark blue product is isolated as described in Example 1. The product dyes cotton in a strong, blue shade somewhat greener than the dyeings obtained in Examples 1 and 2.

Example 4

6 parts cobalt phthalocyanine is dissolved in 84 parts 100% sulfuric acid. The temperature is allowed to rise to 39° C. during the addition. Without cooling, 1.45 parts acetamide and 4.8 parts paraformaldehyde are added and the temperature is allowed to rise to 43.5° C. The reaction is heated to 80–82° C. and maintained at 80–82° C. for one hour.

The isolation of the product is performed as described in Example 1. The dyestuff dyes cotton from a yellow-olive vat in a full, bright blue shade whose fastness to light properties is excellent.

Example 5

10 parts cobalt phthalocyanine is dissolved in 140 parts 100% sulfuric acid. The temperature rises to 44° C. Without cooling, there are added 2.4 parts acetamide and 8 parts paraformaldehyde and the temperature is allowed to rise to 51° C.

The solution is heated to 85–87° C. in a half hour and this temperature is maintained for another hour. The solution is drowned in water, filtered, washed neutral and made into a homogeneous paste. The product dyes cotton in a strong, blue shade from a yellowish-green vat. The dyeings exhibit excellent light fastness.

Example 6

10 parts cobalt phthalocyanine is dissolved in 140 parts 100% sulfuric acid. The temperature rises to 43° C. There is added then 8 parts paraformaldehyde.

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The reaction is heated to 85–87° C. and this temperature is maintained for one hour. The solution is drowned in water and the product isolated according to the method described in Example 1.

The product dyes cotton from a greenish-yellow vat in a full, bright blue shade somewhat greener than the shade exhibited by the product of Example 5. The dyeings possess superior light fastness properties.

If the paraformaldehyde is omitted from the above reaction, the mere solution of the cobalt phthalocyanine in 100% sulfuric acid at 70–75° C. for one hour does not yield a product possessing acceptable vatting properties and affinity to the fiber. On the contrary, the product does not dye the fiber from the vat.

Example 7

10 parts cobalt phthalocyanine, 2.4 parts acetamide and 8.0 parts paraformaldehyde are dissolved in 140 parts 100% sulfuric acid.

The solution is heated to 90–92° C. and this temperature is maintained for one hour. The product obtained dyes from the vat in a strong blue shade of good light fastness.

Example 8

10 parts cobalt phthalocyanine and 8 parts paraformaldehyde are dissolved in 140 parts 100% sulfuric acid. The solution is heated to 95–97° C. and maintained at 95–97° C. for one hour. The product is isolated as in Example 1. The product dyes cotton from a greenish-yellow vat in a full, clear blue shade which is distinguished by excellent fastness to light.

If the paraformaldehyde is omitted in the above reaction, the mere solution of the cobalt phthalocyanine in acid does not yield a tinctorially strong product upon vatting.

Example 9

10 parts cobalt phthalocyanine are dissolved in 140 parts 100% sulfuric acid. There are then added 2.4 parts formamide and 8.0 parts paraformaldehyde.

The reaction is heated to 90–92° C. and held at this temperature for one hour. The solution is drowned in water, filtered and washed neutral. The product thus isolated dyes cotton from a yellow-olive vat in a fully bright blue shade of excellent light fastness.

Example 10

10 parts cobalt phthalocyanine, 2.4 parts urea and 8.0 parts paraformaldehyde are dissolved in 140 parts 100% sulfuric acid. The temperature of the reaction solution is raised to 90–92° C. and the reaction is maintained at 90–92° C. for one hour longer.

The product obtained as described in the instant example dyes cotton in a strong blue shade greener than the shade obtained in Example 9. Its light fastness is excellent. When urea and paraformaldehyde are omitted in the above example, the mere solution of the cobalt phthalocyanine in 100% sulfuric acid does not yield a strong dye.

Example 11

Example 9 was repeated but the reaction temperature was raised to 95–97° C. and maintained at 95–97° C. for one hour. The product obtained after the usual drowning and filtration dyed approximately the same as the product isolated in Example 9.

Example 10 was repeated but the reaction temperature was raised to 95–97° C. and maintained at 95–97° C. for one hour.

Example 12

The product obtained after the usual work-up dyed

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from the vat a shade that was much greener, although just as strong, as the shade of the dyeing obtained in Example 10. A mere solution of cobalt phthalocyanine in 100% sulfuric acid at 95-97° C. yields a product which has no tinctorial strength.

Example 13

10 parts cobalt phthalocyanine and 8 parts paraformaldehyde are dissolved in 150 parts 90% sulfuric acid. The reaction is heated to 99-100° C. and the temperature is maintained at 99-100° C. for two hours. The product when vatted dyes a full blue shade of excellent light fastness properties.

Example 14

7.1 parts of cobalt phthalocyanine are added to 100 parts methylsulfuric acid. The temperature is raised to 39° C. Without cooling there is added 5.7 parts paraformaldehyde. The temperature rises to 42° C. The solution is heated to 95-97° C. in a ½ hour and held at 95-97° C. for two hours. The solution is drowned in 1000 parts water. The product is filtered, washed neutral with water and the filter cake made into a homogeneous paste.

The product dyes cotton from a greenish-yellow vat full, clear blue shade which is distinguished by excellent fastness to light. If the paraformaldehyde is omitted from the above example, the mere solution of the cobalt phthalocyanine in methylsulfuric acid does not produce a vatable product.

Example 15

10 parts cobalt phthalocyanine are dissolved in 200 parts 96% sulfuric acid. The temperature rises to 35° C. Without cooling there is added 8 parts paraformaldehyde. The temperature of the reaction is raised to 95-97° C. in a ½ hour and maintained at 95-97° C. for two hours. The solution is drowned in 3000 parts water.

The product is filtered, washed neutral with water. The filter cake is now placed in 1000 parts 5% caustic soda solution. The temperature is raised to 80° C. and maintained at 80° C. for ½ hour. The product is filtered and washed neutral. The filter cake is made into a homogeneous cake. A dried sample contains less than 0.2% sulfur. The product dyes cotton a full clear blue shade of excellent light fastness when applied to cotton from its hydrosulfite-caustic vat.

Example 16

1.60 parts of a cobalt phthalocyanine paste derivative of any of Examples 1-15 (corresponding to 0.2 parts of the 100% dyestuff) are added to enough water to make a total of 300 parts by volume of dye solution. 6 parts by volume of concentrated caustic solution (30° Bé.) and 1.5 parts of sodium hydrosulfite are added and the dye mixture is reduced by heating at 130° F. for ten minutes. The vat is used to dye 10 parts of cotton in the usual manner at 130° F. for 45 minutes. The cotton is squeezed off and hung in the air for ten minutes to oxidize. The cotton dyeing is rinsed in cold water, treated with dilute acetic acid solution and it is rinsed with water.

The dyeing is then washed at the boil with soap for twenty minutes, rinsed and dried. Full blue to greenish-blue shades are obtained.

Example 17

The following process describes the dyeing of wool with the cobalt phthalocyanine derivatives prepared in Examples 1-15:

0.18 part of a cobalt phthalocyanine derivative prepared as in the subject invention is vatted by adding 2 parts by volume of concentrated ammonia (25%) and 0.8 part sodium hydrosulfite in a total volume of 125 parts by volume of water. The vating is accomplished by heating at 75° C. The final volume of the vat is brought to 500 parts by volume by adding water. 10

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parts of wool are dyed in this liquor by the usual technique at 51-52° C. for 50 minutes.

After wringing out the wool, it was hung in the air for 30 minutes, rinsed with water and then treated with dilute acetic acid (5 parts by volume of glacial acetic acid per 1000 parts by volume of water), rinsed and dried.

Blue to greenish-blue dyeings of good light fastness properties are obtained.

Example 18

2.90 parts of a cobalt phthalocyanine paste made in accordance with this invention (corresponding to 0.2 part of the 100% dyestuff) are added to 3.5 parts by volume of concentrated caustic solution (34° Bé.) and 1.5 parts sodium hydrosulfite and enough water to make a total volume of 50 parts of dye solution. The dye solution is heated at 110° F. for ten minutes. The volume of the dye solution is brought to 300 parts by the addition of cold water. The temperature is adjusted to 80° F. and 10 parts of cotton are dyed in the vat in the usual manner at 80° F. for 45 minutes. After 20 minutes of dyeing, 10 parts of Glauber's salts are added, the dyeing is completed for the remaining 25 minutes.

The cotton is squeezed off and hung in the air for 10 minutes. The cotton dyeing is rinsed in cold water, treated with dilute acetic acid solution, rinsed once more with water, and boiled for 20 minutes with soap, rinsed and dried. Full blue to greenish-blue shades are obtained.

This invention has been disclosed with respect to certain preferred embodiments, and various modifications and variations thereof will become obvious to the person skilled in the art. It is to be understood that such modifications and variations are to be included within the spirit and purview of this application and the scope of the appended claims.

We claim:

1. A process for converting a cobalt phthalocyanine into a vat dye of improved solubility in the vat which comprises reacting same with a substance consisting of formaldehyde in the presence of a strong acid selected from the group consisting of sulfuric, phosphoric and methyl sulfuric acids and having a concentration of at least about 90% by weight.

2. A process as defined in claim 1 wherein the acid is sulfuric acid.

3. A process as defined in claim 1 wherein the acid is methyl sulfuric acid.

4. A process as defined in claim 1 wherein the acid is phosphoric acid.

5. A process for converting a cobalt phthalocyanine into a vat dye of improved solubility in the vat which comprises reacting same with formaldehyde in the presence of about 5 to 40%, based on the weight of the formaldehyde, of an amide selected from the group consisting of formamide, acetamide, propionamide, butyramide, benzamide, urea and biuret and a strong acid selected from the group consisting of sulfuric, phosphoric and methyl sulfuric acids and having a concentration of at least about 90% by weight.

6. A process as defined in claim 5 wherein the acid is sulfuric acid.

7. A process as defined in claim 5 wherein the acid is methyl sulfuric acid.

8. A process as defined in claim 5 wherein the acid is phosphoric acid.

9. A process as defined in claim 5 wherein the amide is acetamide.

10. A process as defined in claim 5 wherein the amide is formamide.

11. A process as defined in claim 5 wherein the amide is urea.

12. A coloring composition produced in accordance with the process of claim 1.
13. A coloring composition produced in accordance with the process of claim 5.
14. A coloring composition produced in accordance with the process of claim 9.
15. A coloring composition produced in accordance with the process of claim 10.
16. A coloring composition produced in accordance with the process of claim 11.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

October 13, 1959

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David I. Randall et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 70, 71, and 72, strike out "Example 10 was repeated but the reaction temperature was raised to 95-97° C. and maintained at 95-97° C. for one hour." and insert the same between lines 74 and 75 as the beginning paragraph of Example 12".

Signed and sealed this 30th day of May 1961.

(SEAL)
Attest:

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