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SINGLE BATH PROCESS FOR PRUSSIAN BLUE-PIGMENTING OF CELLULOSIC WEBBING TO RENDER IT ALKALI- AND ALGAE-RESISTANT

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ABSTRACT OF THE DISCLOSURE

Prussian blue is solubilized in aqueous oxalic acid solutions to which zirconyl acetate is added to produce a single applicational bath to treat cellulosic webbing. The webbing is thoroughly wetted with the bath solution, followed by squeezing out excess liquid. The wet cellulosic webbing is then dried followed by curing. A cured Prussian blue-zirconium basic acetate pigment is deposited in the webbing and the colored webbing is then washed removed loose pigment and excess oxalic acid. The pigmented webbing is then dried by conventional means. The pigmented webbing demonstrates alkali and algaecidal properties. The use of zirconyl acetate in the process in some manner counteracts the usual degrading action of oxalic acid on the cellulosic webbing while inhibiting alkaline hydrolysis of the Prussian blue.

A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all government purposes, throughout the world, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This application is related to copending application, Ser. No. 422,462, filed of even date.

This invention relates to an improved, one-step process for coloring cellulosic fibrous materials with Prussian blue pigments. Further, it relates to a one-step process for coloring cellulosic webbing with an aqueous, oxalic acid solution of Prussian blue containing zirconyl acetate. The pigmented cellulose is not physically damaged and is resistant to attack by algae and alkali.

As used herein, the term "cellulosic fibrous material" relates to the individual components of cellulose such as cotton, rayon staple, flax, hemp, ramie, partially substituted cellulose, wood, etc. It may be in the form of fibers, yarn, fabric, webbing, paper, and the like. Because of its wide use, cotton fabric or webbing will frequently be referred to below as the "cellulosic fibrous material." It is to be understood that this usage is illustrative only.

The term Prussian blue, as used herein, relates to various iron cyanide blue pigments but more specifically to the ferric ferrocyanide. Because of its wide use, Prussian blue will frequently be referred to below as the "iron blue" or the "blue pigment."

The term "zirconyl acetate" relates to the compound $H_2ZrO_2(C_2H_3O_2)_2$ which is a normal zirconyl acetate. (Blumenthal, Ind. and Eng. Chem. 46,537 (1954.) The zirconyl acetate-13% ZrO_2, is a commercially available aqueous solution of normal zirconyl acetate, water, and acetic acid, and contains 13% ZrO_2. This is the product used herein, and will be referred to as "normal" zirconyl acetate or "zirconyl acetate (13% ZrO_2)."

Because of its low cost, excellent fastness, deep bright shade, high color, strength, and its resistance to the action of water and of acids, Prussian blue has been widely used in coloring heavy webbing such as awings, tent-canvas, and the like.

In the past, two methods have been used for applying Prussian blue:

(A) The fabric is first padded with a solution of a ferrocyanide after which it is dried. It is then padded with a solution of ferric chloride and again dried. The two iron salts react to form an iron cyanide compound having a blue color. According to Lange (Handbook of Chemistry, 1961, McGraw-Hill, New York) the pigment has a composition $Fe_4^{+++}[Fe^{++}(CN)_6]_3$.

This method has several disadvantages:

(1) In the first place, it is a two-step process, requiring one pass through each of two different solutions, with a drying step after each pass.

(2) In the second place, much of the colored pigment is deposited on the surface of the webbing and the yarns. This causes possible serious crocking when the webbing is folded or rubbed against a solid surface and results in streaks on the colored webbing.

(3) In the third place, ferric chloride is a very corrosive chemical and is avoided in textile finishing plants, if possible.

(4) In the fourth place, the uniformity of shade of the colored webbing is determined in part by the particle size of the pigment. Control of the size of these pigment particles is difficult as they may vary with changes in the temperature of the pad bath, the presence of impurities, and the pH of the water used in preparation of the solution of the iron salts.

(B) In the second method the Prussian blue is first prepared and then dissolved in an oxalic acid solution. The cotton webbing is then passed into and through this acid solution of Prussian blue, the excess is removed by a pair of squeeze rolls, and the fabric is then dried. This method has one serious disadvantage. In order that the pigment on the webbing be secured, or locked, so that it will not be removed during subsequent washing, the oxalic solution of Prussian blue must be completely dried, preferably at a high temperature. During this drying step the gradual loss of water causes the concentration of oxalic acid to increase. As a result, the high concentration of the aqueous solution of oxalic acid, and the high temperature effect a degrading action of the cellulose, the latter being quite sensitive to oxalic acid. Simultaneously, the reducing action of the oxalic acid may affect the Prussion blue resulting in a change in shade. The pigmented webbing is then washed to remove the oxalic acid. Best removal is obtained when a slightly alkaline aqueous bath is employed. However, as is well known, Prussian blue is unstable in the presence of alkali, even weak alkali such as calcium carbonate, and a brown deposit of iron oxide results with a consequent deterioration of shade.

Therefore, prior to the present invention there still remained a need for a commercially suitable process for coloring cellulosic webbing with Prussian blue pigments to produce products having high color strength with excellent fastness and having good resistance to water, algae, and improved stability to alkali. Such a process should be economical. It should be simple and easily carried out in presently available commercial equipment. Such a process should preferably be carried out with commercially available Prussian blue pigments thereby eliminating the need for additional operations in the dye house. Last, but not least important, the process should not degrade the cotton webbing.

In accordance with this invention, the disadvantages outlined above are avoided by a procedure which basically involves the following steps:

(1) An aqueous oxalic acid solution is prepared containing from about 4 to 15 weight percent of the acid.

(2) Prussian blue from about 1 to 4 weight percent is then dissolved in the oxalic acid solution.

(3) There is then added to the oxalic acid solution of Prussian blue from about 2 to 25 parts, by weight, normal zirconyl acetate (13% ZrO_2) per part oxalic acid.

(4) The aqueous solution comprising Prussian blue pigment, oxalic acid, and normal zirconyl acetate is then applied to the cellulosic webbing by passing the webbing into, and through, the aqueous solution of pigment to cause the pigment solution to completely permeate the webbing.

(5) The excess solution is then removed from the pigmented cellulosic webbing by means of squeeze (padder) rolls.

(6) The pigmented, wet cellulosic webbing is then dried.

(7) The dry webbing is then cured to convert the aqueous-soluble normal zirconyl acetate (13% ZrO_2) to an aqueous-insoluble basic zirconyl acetate. During this curing step one molecule of acetic acid is driven from the normal zirconyl acetate as will be discussed more fully below.

(8) The cured, pigmented cellulosic fabric is then washed with water to remove any excess oxalic acid, and

(9) The acid-free, pigmented cellulosic webbing is again dried, after which it is ready for packaging.

As so described, the process of the present invention appears deceptively simple; however, each of the several steps is critical. Each involves certain criteria which, within certain ranges, must be observed. Therefore, each will be more fully discussed in relation to the problem solved thereby, as well as its place in the overall treatment.

Oxalic acid solution

This solution may be prepared from either technical or reagent grade oxalic acid. Because of its good solubility, no solubilizing assistants are required. Concentrations ranging from about 4–15 weight percent may be used although about 4–10% effects good solubility of the Prussian blue. The temperature of the aqueous medium for dissolving the oxalic acid is not critical. Because of its reactivity with iron oxides, we prefer to use commercially available wooden kettles equipped with mechanical wooden stirrers.

Prussian blue solution

Some dyers may prefer to use commercially available Prussian blue since it eliminates the necessity of preparing the pigment. However, when large quantities of Prussian blue are required, it may be more economical to prepare the product at the place of use since the freshly prepared product does not require a drying step. Drying may cause the pigment to become "gritty" and, consequently, make it more difficult to use. Regardless of which type of pigment is used, the amounts indicated herein are based on dry weight and any water present in a freshly prepared press cake must be considered in determining the precentage of dry pigment employed.

The amount of Prussian blue added to the oxalic acid may vary from about 1 to 4%, to weight percent being a good practice. However, as will be discussed more fully below, the amount of pigment added will be that amount necessary to match the customer's sample.

It is a critical feature of this invention that all the Prussian blue be dissolved in order to avoid carrying through the pad rolls any gritty material which may cause damage to the pad rolls, or specks upon the dyed fabric. Complete solution may be easily determined by filtering a portion of the soluble Prussian blue through a filter paper and noting what type of residue, if any, is retained.

Addition of zirconyl acetate

The zirconyl acetate is a water-soluble liquid comprising acetic acid, water, and normal zirconyl acetate having a concentration equivalent to 13% ZrO_2. As noted above, such a product is commercially available and it may be added directly to the oxalic acid solution of the Prussian blue pigment. A clear, colored solution results which may be filtered without evidence of suspended solids. The amount of normal zirconyl acetate (13% ZrO_2) used may range from about 2 to 25 parts per part oxalic acid, parts being by weight. At ambient room temperature, 4 to 6 parts normal zirconyl acetate per part oxalic acid is a good practice.

Application of the pigment to the webbing

Two methods of coloring may be employed.

(a) Where overall coverage is required, the Prussian blue is applied from an aqueous bath (pigment bath). This bath should contain the amount of soluble Prussian blue pigment needed to produce the required shade on the webbing. Usually, amounts ranging from about 0.5 to 4.0 weight percent of the pigment causes satisfactory results to be obtained. We prefer to omit wetting or penetrating agents from the baths and pass the webbing into and through the coloring bath at least twice, removing the excess pigment liquor after each pass by means of a pair of squeeze rolls. The pigmented wet fabric is then ready to be dried.

It is within the scope of our invention to "sky" the wet fabric after each pass through the squeeze rolls to permit more time for the soluble pigment solution to penetrate or permeate into the interior of the webbing. It is a critical feature of our invention that the webbing be fully and uniformly impregnated or penetrated. The particular procedure used will depend largely upon the type of fabric and the type of equipment available, and will be known to those skilled in the art.

(b) Where the coverage is to be in the form of stripes (or other pattern) the solubilized Prussian blue may be applied by printing. We prefer roller printing although screen- or block-printing methods may be employed. It is a critical feature that the thickener should not contain starch or partially solubilized carbohydrates which are hydrolyzed by the acid. We prefer an oil-in-water emulsion as a thickener for the Prussian blue liquor. This emulsion usually contains no solids and permits better penetration of the solution into the webbing. Methods for the preparation of oil-in-water printing emulsions are known to those skilled in the printing art. Since the webbing may be passed through the print machine only once, the concentration of the pigment in the thickener should be somewhat higher, 1 to 6 weight percent being a good practice. However, as is well known in the art, the concentration of the pigment should be sufficiently high to produce a colored webbing matching the customer's sample, and the amount used is judged accordingly. The wet, printed fabric is then ready to be dried.

Drying and curing the colored cellulosic webbing

The next step in the application of Prussian blue pigment to cellulosic webbing is the drying and curing operation. These steps are necessary regardless of the particular method employed in applying the Prussian blue solutions to the webbing, i.e., dyeing or printing.

The purpose of the drying step is, of course, to remove the aqueous solution comprising water and acetic acid from the webbing. The purpose of the curing it to remove one molecule of acetic acid from the aqueous-soluble normal zirconyl acetate and convert it to the aqueous-insoluble basic zirconyl acetate. The reaction is

$$\underset{\text{normal}}{H_2ZrO_2(C_2H_3O_2)_2} \xrightarrow[80°\text{–}145°\text{ C.}]{\Delta} \underset{\text{basic}}{HZrO_2(C_2H_3O_2)} + CH_3COOH$$

The drying and curing may be carried out in two consecutive steps using different pieces of commercially available equipment or the two steps may be carried out continuously. We prefer the continuous method.

Since the molecule of acetic acid is somewhat more

difficult to remove from the normal zirconyl acetate than removing the aqueous solution from the webbing, either higher curing temperatures or longer periods of curing at the lower temperatures are required. Best results are obtained when the drying and curing operations are conducted with hot air, thereby avoiding the surfaces of hot cans although the latter may be used when wrapped with a protective coating of webbing. We prefer a preliminary drying at the lower temperature to prevent migration of the pigment to the surface of the impregnated webbing, and thereafter curing at a higher temperature. Drying temperatures may range from about 80–85° C. to about 120° C., while curing temperatures may range from about 80–85° C. to about 145° C. In the examples below, both drying and curing have been carried out at about 145° C. It is an advantage of this process that at these higher temperatures, the evaporation of the aqueous solution from the webbing has a cooling effect and maintains a temperature of about 85° C. during the drying step. Of course, as the amount of aqueous solution in the webbing is reduced, the rate of evaporation decreases and the temperature of the webbing gradually increases. However, it is critical that preliminary drying be carried out at the lower temperatures in order to avoid migration of the pigment to the surface of the fabric. We have found that satisfactory drying, curing, and freedom from migration of the pigment to the surface of the webbing may be obtained in about five to six minutes at 80° to 85° C. At 145° C., the time may be reduced to about two to three minutes, but the migration is more pronounced. Satisfactory curing may readily be determined by washing a portion of the dried and cured pigmented webbing in water. When the curing is incomplete, some of the pigment is removed whereas, when the curing is complete, no pigment is removed.

Washing the colored webbing

The cured, pigmented cellulosic webbing is then washed to remove loose pigment and excess oxalic acid. Because of the high acid content of the colored webbing passing through squeeze rolls after each wash box. boxes, as in a commercial range, are employed, the webbing passing through squeeze rolls after each wash box. For those cotton finishers who do not have commercial ranges, a dye-jig may be used with an overflow wash. Although not a critical requirement, it is an advantage that the webbing is passed between squeeze rolls after each end-through the dye-jig during the later stages of washing to remove the last traces of the oxalic acid. Regardless of the method of washing employed, the webbing is passed through squeeze rolls prior to drying.

Finishing the pigmented webbing

When the free oxalic acid has been removed, the pigmented webbing is dried. The use of hot air on a pin frame, tenter frame, or a loop drier is preferred. A drier in which hot air is impinged on both sides of the fabric helps to prevent possible migration of the colored pigment. The dry product is then packaged, thus completing the operation.

It is an advantage in the above process that incorporating the normal zirconyl acetate in the oxalic acid solution of Prussian blue does not cause the soluble pigment to come out of the solution.

It is a further advantage that the presence of the zirconyl acetate in the pigmented solution sorbed by the webbing in some manner counteracts the usual degrading action of oxalic acid on the cotton or other celluosic material. Such a protective action was unexpected.

It is a still further advantage that the presence of the zirconyl acetate on the Prussian blue pigmented fabric renders the fabric resistant to attack by algae.

It is a still further advantage of our invention that the presence of the zirconyl acetate in the oxalic acid solution of Prussian blue sorbed by the webbing in some manner imparts alkali stability to the colored pigment after drying and curing.

The following examples will further illustrate the embodiment of our invention and are given for illustrative purposes only. Temperatures are in degrees centigrade. Percents are in weight percents and based on the total weight of the solution unless otherwise indicated:

Example 1

In the following example the protective or stabilizing action of the zirconyl acetate on canvas colored with Prussian blue pigment is demonstrated.

One hundred ml. of 10% oxalic acid solution in water are prepared and divided into two equal volumes (50 ml.). One (1.0) gram of ferric ferrocyanide (Prussian blue) is dissolved in each of the two 50-ml. portions of oxalic acid. To one solution is then added 15 ml. of normal zirconyl acetate, (13% ZrO_2) while 15 ml. of distilled water are added to the other, making the volumes and percent Prussian blue the same in each solution.

A piece of duck (10 oz.), 8" x 4", is padded with the Prussian blue in oxalic acid (without zirconyl acetate) and used as a control. A similar piece of duck is padded with the Prussian blue in oxalic acid containing the zirconyl acetate. The paddings consist of two dips and two nips, followed by a conventional oven drying and curing at 145° C. for 5 minutes.

When both cured samples are removed from the oven, they are typically Prussian blue colored. The samples are cooled to room temperature and then subjected to a 30-minute hot (alkaline) tap-water wash (55° C.), the water having a pH of 10.0. At the end of the wash, the sample containing zirconyl acetate retains its Prussian blue color, while the sample containing no zirconyl acetate acquired a brown color due to alkali sensitivity, resulting in decomposition of the Prussian blue with probable formation of ferric hydroxide. "Tear tests" on the above two pieces of canvas show:

(a) The piece of canvas colored with the oxalic acid solution of Prussian blue has been degraded, and is very weak.

(b) The piece of canvas colored with the oxalic acid solution of Prussian blue to which normal zirconyl acetate is added has not been degraded noticeably and has retained its strength.

"Break tests" on the above two pieces using the Scott Tensile Tester (using 1" x 6" strips of fabric) show:

Untreated control	134.2 lbs. (100%)
Pigmented (contains zirconyl acetate	145.7 lbs. (>100%)
Pigmented — no zirconyl acetate present	42.5 lbs. (31.6%)

Example 2

In the following example, the Prussian blue is prepared as follows:

16.9 grams $Na_4Fe(CN)_6$ + 12.88 grams $FeCl_3$ →
10.0 gm. $Fe_4^{+++}[Fe^{++}(CN)_6]_3$ + NaCl (byproduct)

The pigment is washed free of salt and dried, after which it is used for coloring 10-oz. cotton duck as follows:

(a) 10 grams oxalic acid are dissolved in 250 ml. water.

(b) The Prussian blue prepared above is dissolved in the oxalic acid solution of step (a).

(c) 20 ml. of the Prussian blue solution of step (b) is then poured into each of two 250-ml. beakers labeled X and Y.

(d) 20 ml. of normal zirconyl acetate (13% ZrO_2) is added to beaker X.

(e) 20 ml. distilled water is added to beaker Y.

(f) A five-gram piece of cotton duck (10-oz.) which has previously been scoured and dried is padded in the solution in beaker X, and a second five-gram piece of cotton duck from the same lot is padded in beaker Y. Each padding consists of two dips and two nips.

(g) Each sample is then dried at 145° C. for 5 minutes.

(h) Each sample is then washed, in separate beakers in tap water having a pH of about 10. The cotton duck treated with the zirconyl acetate solution of Prussian blue is dyed a good strong shade. The piece of cotton duck which is dyed in the oxalic acid solution of Prussian blue but without the zirconyl acetate lost its blue color and became brown, again showing sensitivity to alkali.

Example 3

The procedure of Example 1 is repeated using a commercial Prussian blue pigment, and generally similar results are obtained.

Example 4

The procedure of Example 2 is repeated using, however, the following amounts of normal zirconyl acetate (13% ZrO_2):

(a) 10 ml. zirconyl acetate (13% ZrO_2)
(b) 20 ml. zirconyl acetate (13% ZrO_2)

In each instance, a pigmented blue fabric is obtained, and the tearing strength is not noticeably impaired.

Example 5

Pieces of duck (10-oz. scoured) are treated in each of the aqueous solutions of Examples 1 through 4 and evaluated for resistance to algae. In every instance, the Prussian blue pigmented webbing containing zirconyl acetate showed resistance to algae.

We claim:

1. A single-bath process for pigmenting cellulosic webbing with Prussian blue and simultaneously rendering it resistant to attack by algae and alkali, which process comprises the following steps:

(a) preparing an aqueous oxalic acid solution comprising about 4 to 15 weight percent oxalic acid,
(b) dissolving in the oxalic acid solution from about one to four weight percent Prussian blue,
(c) adding to the oxalic acid solution of Prussian blue from about 2 to 25 parts normal zirconyl acetate (13% ZrO_2) per part oxalic acid, parts being by weight,
(d) passing the cellulosic webbing into and through the aqueous solution comprising Prussian blue pigment, oxalic acid, and normal zirconyl acetate to cause the pigment solution to completely permeate the webbing,
(e) passing the wet, pigmented webbing through a pair of squeeze rolls to remove the excess solution,
(f) drying the wet, cellulosic webbing,
(g) curing the dry cellulosic webbing to convert the aqueous-soluble, normal zirconyl acetate to an aqueous-insoluble, basic zirconyl acetate,
(h) washing the cured cellulosic webbing to remove any excess oxalic acid, and
(i) drying the acid-free, pigmented cellulosic webbing.

2. The process according to claim **1** wherein the cellulosic webbing is cotton.

3. The process according to claim **1** wherein the webbing padded with the soluble Prussian blue solution is dried and cured with hot air.

4. The process according to claim **3** wherein the temperature of the hot air is from about 80° to 145° C.

5. A pigmented webbing which is resistant to attack by alkali and algae comprising cellulosic webbing impregnated with Prussian blue and aqueous-insoluble basic zirconyl acetate.

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