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PROCESS OF DYEING WITH VAT DYES

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This invention relates to a process of dyeing with vat dyes and more particularly to an improved process for applying vat dyes to fabrics by continuous dyeing processes which will be suitable for the application of colors of the vat dye class not only to cotton but to fabrics comprising fibers which are deleteriously affected by strong alkalis such as wool, silk, mohair, acetate rayon, etc.

In the normal application of vat dyes, which are water insoluble colors, the dye is rendered soluble in caustic alkali solutions by being reduced in such solution with reducing agents, such as with sodium hydrosulfite, to the leuco form, which as the alkali metal salt is quite soluble in relatively strong alkali solutions but is much less soluble in solutions of low alkalinity. The process of dissolving vat colors in alkaline hydrosulfite solutions is usually referred to as "vatting."

While certain of the vat colors when in the form of the alkali metal salts of the leuco are soluble in sodium carbonate solutions in sufficient amount to permit dyeing fibers from such a solution in weak shades, the class as a whole and particularly those of the anthraquinone series are not sufficiently soluble in such alkaline solution to permit the preparation of commercially satisfactory dyeings therefrom.

Because it is necessary to use the vat dyes in caustic alkali solutions their use has been limited almost exclusively to the dyeing of cotton or other cellulose fibers, for silk, wool and cellulose acetate are deleteriously affected by caustic alkali solutions of the strength normally used in vat dyeing.

With the development of the newer fibers such as cellulose rayons, cellulose acetate, nylon, etc., great advances have been made in fabric design by mixing these fibers with wool, silk and cotton. For instance, viscose rayon in filament or staple form, cellulose acetate, wool, silk or nylon may be woven as effect threads with cotton or with each other or they may be mixed in staple form to give threads from which many novel and valuable fabrics may be produced, and many such fabrics are on the market today.

The advance of these new fabrics, however, has been retarded somewhat because of the difficulties encountered in dyeing them in fast shades for the fast colors of the vat dye class could not be commercially applied to the alkali sensitive fibers or to goods containing such fibers by the usual methods of dyeing, or by any previously

known method of vat dyeing where even mediumly strong shades were required.

Modified derivatives of the vat colors have been produced with the hope of finding a method of applying the vat colors to the alkali sensitive fibers by methods that would not require strong alkalis. As illustrative of this type are the dyes known in the trade as "Indigosols" which are leuco sulphuric acid esters of certain vat colors which are dyed from an aqueous solution and developed by means of dilute acids and suitable oxidizing agents which are not as harmful to wool, silk and cellulose acetate as are the strong alkalis. These colors, however, are very expensive to manufacture and are difficult to apply to fibers in even mediumly strong shades because of their limited solubility in the water and their lack of substantivity for most fibers.

While attempts have been made to dye mixed fabrics and wool with vat dyestuffs in mild alkaline solutions such as in solutions of sodium carbonate, ammonia, etc., these processes have not been satisfactory for they are applicable only to those colors that show extreme solubility in the vat and in the main the fast anthraquinone vat dyestuffs are not sufficiently soluble in such mild alkalis to dye in the required depth of shade.

Today a large amount of the dyeing of fabrics is done in the piece, particularly by what is known as the "continuous piece goods dyeing process" wherein the fabric is passed through the padder, developing bath, oxidizing bath, soaper, etc., in a continuous piece. Such continuous dyeing processes introduce difficulties that are not experienced in the ordinary "batch" dyeing processes, although in certain cases the continuous process permits the application of vat dyestuffs to fabrics that could not ordinarily be dyed with vat dyes by the batch process. Because of the speed with which the fiber passes through the caustic alkali solution certain fabrics containing caustic alkali sensitive fibers such as wool and cellulose acetate could be dyed without harmfully affecting such sensitive fibers where the temperature and time of treatment were held at a minimum. Such process, however, can be used only for dyeing in very light shades, because the restricted conditions do not permit sufficient absorption of the dye to give heavier shades.

In the dyeing of cotton piece goods by the continuous dyeing process it was found, as disclosed by Tice, U. S. 1,652,649, that better penetration and absorption of the vat dye is obtained by passing the material, after being padded with

the vat color, through a second reducing bath containing a less concentration of dye. It has been found, however, that in this process it is impossible to obtain uniform dyeings over the continuous piece because of the fluctuation that normally takes place in the alkalinity of the re-reduction bath.

Hebden, U. S. 1,148,966, describes a process for dyeing with vat colors by the batch process in which the color is forced on the goods by progressively diminishing the solvent capacity of the bath for the leuco compound during the dyeing operation. It is also alleged that this method can be employed in the dyeing of animal fibers with vat dyes, although the process has never been commercially successful for such fibers. This process, however, can not be applied to continuous piece goods dyeing processes.

In the continuous piece goods dyeing of cotton fabrics by a process such as described, for instance, in the Tice patent above mentioned, the re-reduction bath is originally charged with the same color that is used in the padding bath, caustic soda and sodium hydrosulfite but in reduced concentrations. However, the chemical reaction which normally occurs, due to the reduction of the vat dye and to exposure of the sodium hydrosulfite on the goods and in the open vat as it comes in contact with air, forms sodium bisulfite and sodium bisulfate which react with the caustic soda in the re-reduction bath to form sodium sulfite and sulfate. These salts exert a salting out action in the dye bath, tending to change the strength of dyeing as the goods passes there-through as the concentration of salt increases in the bath. The reaction as more particularly described by Hebden. Because the caustic soda in the re-reducing bath is used up due to the oxidation of the hydrosulfite it was found that the re-reduction bath finally became acid causing precipitation of the dye from the solution unless additional caustic is added. In the continuous piece goods dyeing of cotton by the Tice process, the loose improperly fixed color, together with some of the color that is actually fixed but which can be stripped off with alkaline sodium hydrosulfite is capable of being dissolved in the re-reduction bath and bleeds off until an equilibrium is reached where the amount of color in the solution that is being absorbed by the fabric is equal to that being stripped off. Since the affinity of these vat colors for fabrics varies with the alkalinity of the dye bath any change in the alkalinity in the re-reduction bath shifts the equilibrium to cause a greater or less amount of dye to be absorbed by the fiber or to go into solution in the dye bath. As long as there are fluctuations in the alkalinity of the re-reduction bath material variations in the resulting dyeings are noted. It was therefore found necessary to continually add caustic soda to the re-reduction bath to maintain as near as possible uniform conditions but due to the chemical reactions as above pointed out it was found to be necessary to add considerable quantities of caustic soda to maintain the original dyeing conditions and that due to the rapid accumulation of the salts in the bath some means had to be devised for preventing their accumulation. This was done by the addition of water with continuous draining off of part of the solution. Any water drained off also carries some valuable dye which must be continually replaced either by addition or by bleeding from the goods being dyed. This process, because of the use of

caustic alkali in the re-reduction bath, is not of general practicability for dyeing fabrics containing wool, silk or cellulose acetate fibers because of the time required for treating the dyed goods in the developing bath.

It is therefore an object of this invention to provide a method for dyeing fabrics comprising cellulose fibers, particularly by continuous piece goods dyeing processes, in uniform shades and with a minimum consumption of dyestuffs and other chemicals necessary for the dyeing operation.

It is a further object of the invention to provide a commercial method for dyeing animal fibers or mixed goods containing animal fibers and/or hydrolyzable cellulose esters or ethers with vat dyestuffs without harmful effect to such alkali sensitive fibers.

I have found that in continuous processes for dyeing piece goods with vat colors uniform dyeings can be obtained with a minimum consumption of color and other chemicals by padding the goods with the usual caustic alkaline solution of the reduced color and then subjecting the goods while the color is still in a substantially reduced state to a development with an alkaline hydrosulfite or similar reducing agent solution in which the alkalinity is maintained sufficiently high to retain the color in solution at all times, but which has a pH value materially less than that of a caustic alkaline hydrosulfite solution, and which can be maintained at a predetermined alkalinity without difficulty because of the reserve of alkali carbonate that may be maintained without having too high an alkalinity. By passing the piece goods which have been padded with the usual caustic alkaline hydrosulfite solution of a vat dye or dyes into a developing bath comprising an alkali metal carbonate, an alkali metal hydrosulfite and a small amount of the color employed in the original vat, the color is fixed in the fiber and uniform shades are obtained as long as the development solution is maintained within relatively narrow limits of alkalinity. By the use of sodium carbonate in the development bath the reaction products of the dyeing process involved in the oxidation of the alkali hydrosulfite are such that they are in part employed over and over again in maintaining constant alkalinity of the developing solution. The sodium bisulfite formed during the reaction is converted with sodium carbonate to sodium bicarbonate and sodium sulfite, while the sodium bisulfate reacts with sodium carbonate to give sodium bicarbonate and sodium sulfate. The accumulation of the undesirable salts in the solution is therefore at a very much reduced rate as compared with the process in which caustic soda is employed as the alkali in the developing bath. The sodium bicarbonate formed in the reaction reacts with the sodium hydroxide being brought in on the fiber from the original pad liquor to form more sodium carbonate in the developing bath. This obviates the addition of further alkali as long as undue oxidation of the hydrosulfite is not experienced such as when there is too long a contact with air or when working with pile fabrics or other very loosely woven fabrics which carry larger quantities of adsorbed air into the development bath, or when the run is of such a length that the sodium carbonate reserve falls below the ascertained limits for any particular set of conditions. When dyeing such goods larger amounts of caustic are usually employed in the padding liquor, although if desired, additional

caustic may be added in small amounts to the development bath to neutralize the sodium bicarbonate that is formed. Because of the rapid reduction of the alkalinity of the liquor padded on the goods by the acidic oxidation products of the hydrosulfite and the carbon dioxide picked up from the air this process is particularly suitable for the dyeing of wool, or fabrics which contain animal fibers or hydrolyzable cellulose esters or ethers, for it has been found that such goods can be dyed in the same manner as cotton goods without harming the alkali sensitive materials or fibers to any noticeable extent. In the dyeing of ordinary flat piece goods of cotton and cellulose rayons it has been found that the alkalinity of the development bath, where sodium carbonate is employed, remains very constant and little or no additions of alkali or bicarbonate need be made provided the alkalinity of the original padding solution for any set of conditions has been evaluated and adjusted. It has been found that in the dyeing of vat dyestuffs with caustic soda considerable amounts of sodium carbonate are formed due to the absorption of material quantities of carbon dioxide from the air by the caustic soda solution in the padding liquor both on the goods and in the vat. This sodium carbonate is detrimental where caustic soda alkalinity is desired but is a necessary and desired reagent in the present process. The ever present amount of sodium carbonate contained in commercial caustic soda used in the padding solution is also employed to advantage by this process.

While in the main, vat dyestuffs in the form of the alkali metal salt of the leuco are not sufficiently soluble in an alkali metal carbonate-hydrosulfite vat to permit satisfactory dyeing on cotton or other fabrics, it has been found that they are sufficiently soluble in alkaline hydrosulfite solutions having a pH value of from 8 to 12 to permit the use of these weaker alkalies in the developing bath. While some of the colors particularly of the indigoid class in the leuco form are readily soluble in alkali hydrosulfite solutions having a pH of as low as 8, others, particularly those of the anthraquinone class usually require an alkaline hydrosulfite solution of a pH of 10 or above.

The entire range of vat colors when applied to the cloth from the ordinary caustic alkaline hydrosulfite vat are sufficiently soluble in the sodium carbonate alkaline hydrosulfite solution (provided no undue oxidation has occurred) to permit complete development of the color on the fiber when it is treated in such a solution. In most cases, even where there is some pre-oxidation of the color on the fabric as the padded material leaves the padding solution, sodium carbonate-hydrosulfite is sufficiently strong to reduce the oxidized color and cause fixation. However, with a few of the anthraquinone vat colors, such as the chlorinated indanthrones, care should be taken to prevent undue oxidation on the fiber in the interval of time between the padding and development operation because of the difficulty experienced in re-reducing such colors. With many vat colors, mild alkalies having a pH lower than 10 may be employed. The limits of alkalinity within which a particular color is sufficiently soluble can be readily determined by a simple experimentation. As long as the color is slightly soluble in the development bath the alkalinity of that solution may be maintained at any predetermined point, above that at which the color is precipitated for while, as above stated,

the equilibrium between the amount of color coming off of the padded material and that going on from the development bath changes with a change in the alkalinity, when once the equilibrium is established and that set of conditions is maintained, the depth of shade of the resulting dyeings is uniform, irrespective of whether it is at the lower or higher alkalinity but during the change and until equilibrium is established the goods will vary in depth of shade. To obtain uniform dyeing it is therefore necessary to see that the development bath is maintained within relatively narrow limits within the operable range of alkalinity which practice has shown will not cause any shade variations. To be sure that the alkalinity of the development bath is maintained constant, continual sampling and testing of this solution is advisable, particularly until proper running conditions are established after which periodic checks are made to detect any trend away from the starting conditions. Where sodium carbonate is employed auxiliary feeds of caustic soda, sodium carbonate, and sodium bicarbonate are made readily available in case unforeseen conditions arise which cause a variation in the alkalinity beyond the tolerances allowable. Where proper running conditions are established originally with many fabrics only minor and sometimes no additions need be made to the development bath for runs of several thousand yards of cloth. In this process, due to the lower alkalinity employed in the development bath, the equilibrium with regard to the color is quickly established, because of the small amount of color in solution as compared with the amount in solution when caustic soda is used, thus effecting a material saving particularly in short runs of cloth where the color or colors employed are quite soluble and relatively large amounts are required for establishing equilibrium in the developing bath. While the amounts of the colors necessary to establish the equilibrium are added to the development bath at the start, it is not always possible to completely anticipate the exact amount required, however, where sodium carbonate is employed equilibrium with regard to the color is quickly established in passing the padded goods through this solution, whereas when sodium hydroxide is employed larger amounts of color are required and many more yards of cloth pass through before equilibrium is established. Since this cloth is not dyed in the same strength as that obtained after equilibrium is established, this means a material loss to the dyer in yardage.

The padding solution of the vat color is made up in the usual manner with caustic alkalies and alkali metal hydrosulfite or other reducing agent for the color and preferably with the addition of suitable penetrating and foam control agents such as now employed in the art. The alkali concentration of the padding liquor will depend upon the nature of the particular vat color involved in the depth of shade and the type of fabric being dyed. Free caustic alkalinity and an excess of the reducing agent are always maintained.

After the dyed goods is removed from the developing bath it is oxidized, rinsed, soaped, rinsed, dried and finished by the methods usually employed for the particular type of dyed goods involved. By the continuous dyeing process we refer more particularly to those processes in which the goods is passed directly from the pad solution through the development bath. We also include those continuous piece goods dyeing processes.

wherein the goods is transferred from one machine to another between the padding and developing operations. In such cases where the goods must be batched off the padder and cannot be readily transferred to another machine, such as the jig or reel machine for developing, it is necessary to arrest the dyeing or oxidation process, which if permitted to continue result in uneven dyeings throughout the batched goods. In cases where the fabrics contain alkali sensitive fibers it is also necessary to reduce the temperature and caustic alkalinity to a point where such fibers will not be injuriously effected during this transfer operation.

I have found that satisfactory results can be obtained if the goods to be batched off is passed through a solution containing approximately 1% of sodium carbonate between the padding and batching operation. It is of course understood that in the padding, developing and in the batching-off steps the goods is passed through the squeeze or nip rolls usually employed in the dyeing processes whereby the amount of liquid remaining in the fabric can be controlled.

In the dyeing of cellulose rayons and other fabrics containing alkali sensitive fibers it is often impossible, due to their low tensile strength when wet, to dye this type of goods in the usual continuous piece goods dyeing equipment because of the tension required on the goods. This tension also stretches the goods and imparts undesirable effects which cannot be corrected in subsequent operations. By using sodium carbonate or other weak alkali in the development bath such goods can be dyed by padding in the continuous dye machine and then developed on machines which handle the goods in a slack manner such as the various types of reel dyeing machines and dye becks. The time required to load this type of machine and complete the development is too long to permit the use of caustic alkali alkalinity in the development bath. The padding may be carried out adjacent these machines so that the batching off and treatment with sodium carbonate is not necessary except in cases where the dye employed is extremely sensitive to air oxidation. It is therefore to be understood that the use of mild alkalies in the developing bath according to this invention is not limited to continuous dyeing processes.

Where sodium carbonate is employed the amount may vary within wide limits for its alkalinity is such that alkali sensitive fibers are not detrimentally affected by it. A sufficient quantity should be used to maintain the color in the developing bath in solution and a reserve to prevent the solution from becoming too low in alkalinity before the proper adjustments can be made. From 0.5 to 2.5 ounces per gallon will usually be found to be sufficient for proper operation.

The amount of alkali metal hydrosulfite in the developing bath should be sufficient to keep the color in the reduced state. A substantial excess of hydrosulfite is desirable. Limits of from 0.15 to 0.5 ounce per gallon are adequate for proper operation and control.

While in determining what mild alkalies may be employed in the developing bath and the concentrations in which they may be used the pH values may be determined by the usual colorimetric or electrometric methods in water solutions, it has been found that the alkalinity of the developing bath which contains oxidizing and reducing agents can best be determined for

control purposes by titration with certain indicators. The following practical methods have been developed for determining the alkalinity in terms of sodium bicarbonate or caustic soda content, and for determining the total alkalinity of the developing solution in terms of sodium carbonate.

50 cc. of the solution from the development bath are placed in a small beaker or Erlenmeyer flask and 15 cc. of 10% barium chloride solution are added. After the addition of phenolphthalein the solution is titrated with N/10 NaOH if the solution is acid or with 10/N HCl if the solution is alkaline. While the end-point is somewhat obscure it may be readily estimated within 0.5 cc. of the N/10 solutions. The first end-point should be taken for with the presence of the other salts in the solution the end-point will shift as the solution stands. The entire determination should therefore be carried out as quickly as possible. The amount of sodium bicarbonate or sodium hydroxide may then be determined by the following formula

$$\frac{\text{cc. NaOH} \times \text{N} \times 8.4}{50} = \text{percent NaHCO}_3$$

$$\frac{\text{cc. HCl} \times \text{N} \times 4.0}{50} = \text{percent NaOH}$$

Having determined the amount of either caustic or bicarbonate present in the developing bath by the barium chloride titration method as above described the total alkalinity of the bath may be titrated directly with HCl using phenolphthalein as the indicator. By taking into consideration the barium chloride finding the difference in the titrations may be considered as sodium carbonate.

The necessary sodium hydrosulfite concentration should, of course, be maintained in the development bath. The amount of sodium hydrosulfite can readily be determined by titrating a known amount of a standard solution of sulfonated indigo as follows:

Pipette 5 cc. of standard indigo solution into a 250 cc. Erlenmeyer flask, dilute with 75 cc. of water. Titrate as rapidly as possible with the $\text{Na}_2\text{S}_2\text{O}_4$ solution taken directly from the development bath with a 25 cc. calibrated pipette until 1 drop causes the blue color of the indigo to disappear.

Calculation

$$\frac{5 \text{ cc. standard indigo solution} \times 0.25}{\text{cc. Na}_2\text{S}_2\text{O}_4 \text{ (developing solution)}} = \text{percent Na}_2\text{S}_2\text{O}_4 \text{ by volume}$$

The sulfonated indigo solution may be prepared as follows: Weigh 3.76 grams of finely powdered 100% indigo (or an equivalent amount of weaker product) into a 400 cc. beaker. Add 100 cc. of concentrated H_2SO_4 , stir well, and heat at 80° C. for one hour stirring occasionally. Cool the sulfonated material and pour into 400 cc. of water at 20° C. Dilute the solution to one liter in a volumetric flask. Mix thoroughly and allow the solution to stand for at least one-half hour before using. Keeping tightly stoppered in a dark bottle. This solution is equivalent to 0.0025 gram of commercial $\text{Na}_2\text{S}_2\text{O}_4$ per cc.

The following examples are given to illustrate the invention:

EXAMPLE 1

Jean cloth running 2.85 yards to the pound in the form of piece goods is dyed in desirable tan shades suitable for cotton work clothing by the continuous process as follows:

The cloth is impregnated or padded in the open width by passing it through a padding bath held at 120° F. and containing 20 gallons of the vatted color made up as follows:

	Ounces per gallon
"Ponsol" Brown AG dbl. pst.	1.97
"Ponsol" Olive AR dbl. pst.	0.29
"Ponsol" Brown VR Paste	0.565
Caustic soda (dry)	1.80
Sodium hydrosulfite	1.33
A penetrating and foam control agent such as the fatty alcohol sulfate "Modinal" D	0.1

at the rate of about 70 yards per minute. The goods is then passed through squeeze rolls mounted over the pan or pad box adjusted so that the material carries approximately 60% of its dry weight of the padding solution. The pad liquor taken out by the cloth is constantly replaced by additional pad liquor known as the pad feed made up as follows:

	Ounces per gallon
"Ponsol" Brown AG dbl. pst.	2.27
"Ponsol" Olive AR dbl. pst.	0.33
"Ponsol" Brown VR pst.	0.65
Caustic soda (dry)	1.80
Sodium hydrosulfite	1.33
"Modinal" D	0.10

After padding, the cloth is passed at the same speed, with the color still in substantially reduced state, through a development bath where it is treated for three minutes. This development bath consists of two 1700 gallon boxes fitted with rollers to lead the cloth up and down through the boxes in a progressive manner in such a manner that approximately 210 yards of cloth are immersed in the 3400 gallons of solution at any one time. These boxes are charged with a developing solution comprising 3400 gallons of water containing 1.5 oz. per gallon of sodium carbonate and 0.25 oz. per gallon of sodium hydrosulfite. The temperature is brought to 150° F. and a color solution made up as follows is added:

	Pounds
"Ponsol" Brown AG double paste	4.68
"Ponsol" Olive AR	0.05
"Ponsol" Brown VR	0.18

are reduced in 20 gallons of water with 2 pounds of sodium hydroxide, and 1½ pounds of sodium hydrosulfite. Two-thirds of this color mixture are added to the first 1700 gallons of solution in the first bath and one-third is added to the 1700 gallons of solution in the second bath. Seven hundred pounds of salt (NaCl) are added to each 1700 gallons of water. This amount of color closely approximates equilibrium at the start. The solution is then titrated to determine if any sodium bicarbonate is present in the solution by the barium chloride method above described and any bicarbonate present is converted to sodium carbonate with the necessary amount of caustic soda. This usually requires from .05 to .1 oz. per gallon of caustic soda. After the continuous dyeing has started periodic tests are made to determine the amount of sodium bicarbonate or sodium hydroxide present in the development bath to insure uniform alkalinity. Experience has shown that a tolerance of .05 oz. per gallon of either sodium bicarbonate or caustic soda is permissible on this type of goods to give the desired uniformity of shade. The starting total sodium carbonate alkalinity of the development bath of 1.5 oz. per gallon should be main-

tained. Experience has shown that a tolerance of 1.4 to 1.6 oz. per gallon of sodium carbonate in the development bath is permissible for this type of cloth. The amount of hydrosulfite present in the development bath should also be checked from time to time and the starting concentration of .25 oz. per gallon of sodium hydrosulfite should be maintained. Experience shows that a drop to .18 oz. per gallon of hydrosulfite is permissible on this type of cloth. Approximately 15 pounds of sodium hydrosulfite must be added to the development per hour to maintain proper concentration, where the goods is being passed through the solutions at the speed mentioned.

Under the above conditions the alkalinity of the development bath stays within the degree of tolerance mentioned without auxiliary feeds of sodium bicarbonate or sodium hydroxide. However, auxiliary feeds of these materials and an auxiliary feed of sodium carbonate should be made conveniently available for use should the control tests indicate a trend requiring their use.

After development, the goods is washed with water, oxidized with a solution of sodium dichromate and acetic acid, rinsed, soaped, rinsed, dried and finished in the usual manner.

By this method, a saving of 11.2 pounds of color in the development bath is made for a 20,000 yard run as compared with the amount of color necessary where caustic soda is employed with the same amount of salt in the developing solution, or a saving of 70% in color used in the developing. A further material saving in alkali and other chemicals employed was experienced due to the use of sodium carbonate in place of caustic soda, for additional feed of alkali is not required, and because with the lower alkalinity, less acid is required in the subsequent operations. If the amount of color in the development bath is not exactly the amount required to establish equilibrium at the start, this equilibrium is established very quickly due to the small amount of color required in the solution for maintaining this color equilibrium, and because the alkalinity of the solution is readily controlled, much more uniform dyeings are obtained than where caustic soda is employed.

While in the mild alkaline developing bath the addition of inert salts such as sodium chloride and sodium sulfate further reduces the amount of color required to establish equilibrium in the same manner as when caustic alkali is used, with many colors and certain fabrics the use of large amounts of salt is not advisable. With the weak alkalies however, salt is not necessary for the solubility of the colors is small as compared with their solubility in caustic alkali. Where caustic alkali is used without salt almost prohibitive amounts of color are required in the developing bath, particularly where the more soluble colors are used and more particularly where small yardages of goods are being dyed, for the dye remaining in the developing bath cannot be recovered. Furthermore, color equilibrium is exceedingly difficult to reach in the caustic alkali developing bath when salt is not employed.

While a single developing bath may be employed, a series of two or more is ordinarily used with diminishing amounts of color in each bath. This materially reduces the amount of color required in the development for as more and more of the color is fixed on the fiber, less color is required in the developing bath to establish the color equilibrium. Where only a single bath is

employed the entire amount of solution must contain the higher percentage of color that must be discarded at the end of the run.

By means of the Leeds and Northrop pH meter the developing bath under the conditions originally established is pH 10.8.

EXAMPLE 2

A mixed fiber fabric for mens' suiting comprising 50% cotton, 42.5% mohair and 7.5% viscose rayon is dyed in light brown shades with vat colors by the continuous dyeing process as described in Example 1. The padder which is equipped with a 30 gallon pad box is charged with 30 gallons of the vatted color made up as above described with:

	Ounces per gallon
"Ponsol" Brown VR paste.....	0.567
"Ponsol" Olive GGL paste.....	0.413
"Ponsol" Brown AR dbl. paste.....	0.495
Caustic soda (dry).....	1.750
Sodium hydrosulfite.....	1.500
"Modinal" D.....	0.10

and is held at a temperature of 120° F. The pad feed is made up as described in Example 1 with:

	Ounces per gallon
"Ponsol" Brown VR paste.....	0.63
"Ponsol" Olive GGL paste.....	0.59
"Ponsol" Brown AR dbl. paste.....	0.55
Caustic soda (dry).....	1.75
Sodium hydrosulfite.....	1.50
"Modinal" D.....	0.10

After padding the cloth, it is passed while the color is still substantially in reduced form into a developing bath where it is treated for three minutes at 145° F. In this case, a developing bath consists of 4 six hundred gallon boxes fitted with rollers to lead the cloth from the top to the bottom of the boxes in such a fashion that 90 yards of cloth are immersed in the 2400 gallons. The boxes are charged with the total of 2400 gallons of water containing sodium carbonate equivalent to 1.25 oz. per gallon and sodium hydrosulfite equivalent to 0.25 oz. per gallon.

	Ounces
"Ponsol" Brown VR paste.....	7.40
"Ponsol" Olive GGL paste.....	3.00
"Ponsol" Brown AR dbl. paste.....	6.50

are reduced and dissolved in 11 gallons of water with 2 pounds caustic soda (dry) and 2 pounds sodium hydrosulfite at 120° F. Six gallons of this color solution is added to the first box. Three gallons to the second and one gallon each to the third and fourth boxes. The developing solution is then titrated for sodium bicarbonate and adjusted as in Example 1. The dyeing is run at 30 yards per minute. By periodical determinations the alkalinity of the developing solution is maintained as closely as possible to the starting conditions. Tolerances of from 1.20 to 1.35 oz. per gallon of sodium carbonate, .01 oz. per gallon of caustic soda and .05 oz. per gallon of sodium bicarbonate are permissible.

Under these conditions and with this type of cloth it is not desirable to control the alkalinity in the developing bath by increasing the amount of caustic soda in the pad feed because of the deleterious effect it may have on the alkaline sensitive fibers in the fabric and since in dyeing fabrics containing animal fibers by this method there is a faster neutralization of the alkali in the development bath, auxiliary feeds of caustic

soda are usually necessary. After development, the goods is given a running rinse with water, skyed to the air to oxidize the color, and then soaped, rinsed, dried, and finished. The goods thus dyed is fast to laundering and dry cleaning and tests indicate that there is substantially no deterioration of the alkali sensitive fibers.

EXAMPLE 3

Suiting material comprising spun viscose rayon with an acetate stripe and blend in which the acetate is left white is dyed in bright blue shades with vat colors by padding the goods at 130° F. in the continuous padder as described in Example 1, wherein the pad box is charged with 20 gallons of properly reduced and dissolved vat color made up as follows:

	Ounces per gallon
"Ponsol" Blue 3G paste.....	4.73
"Ponsol" Violet BNX Supra.....	0.425
Caustic soda (dry).....	1.75
Sodium hydrosulfite.....	1.50

The auxiliary pad feed of this color comprises:

	Ounces per gallon
"Ponsol" Blue 3G paste.....	5.5
"Ponsol" Violet BNX Supra.....	0.5
Caustic soda (dry).....	1.75
Sodium hydrosulfite.....	1.50

which is made up and held at 130° F. The padded goods may be developed in either of two ways:

A. By the continuous process in which the goods passes directly from the padder while the color is still in the substantially reduced state into a developing bath consisting of three eight hundred gallon boxes fitted with rollers which lead the cloth from the top to the bottom of the boxes in a progressive manner and in such a fashion that approximately 120 yards of cloth are immersed in a total of 2400 gallons at a time. The developing boxes are charged with 2400 gallons of water containing 1.25 ozs. per gallon of sodium carbonate and 0.25 oz. per gallon sodium hydrosulfite. Seven gallons of color for use in the developing bath was prepared by dissolving in 7 gallons of water:

	Ounces per gallon
"Ponsol" Blue 3G paste.....	22
"Ponsol" Violet BNX Supra.....	2
Caustic soda (dry).....	6
Sodium hydrosulfite.....	6

at a temperature of 130° F. Four gallons of this mixture were added to the first box after the padder, two gallons to the second box and one gallon to the third box. The temperature of the development bath is brought to 150° F. after the usual correction for any sodium bicarbonate present. The run of the goods through the developing bath is started and the sodium carbonate alkalinity is maintained within the tolerance of from 1.20 to 1.35 ozs. per gallon. The caustic soda should not go above .02 oz. per gallon and the bicarbonate should not go above .05 oz. per gallon while the sodium hydrosulfite should be maintained at not less than .18 oz. per gallon. Under the above conditions with this type of cloth it is not desirable to control the alkalinity in the developing bath by increasing the amount of caustic to pad feed and therefore auxiliary feeds of caustic soda, sodium carbonate and sodium bicarbonate are made conveniently available should the control tests made during the continuous run indicate a trend beyond the tolerance above indicated.

The goods as it passes from the development bath is rinsed with water, oxidized with sodium perborate, rinsed, soaped, rinsed, dried and finished in the usual manner.

B. The development may also be carried out on the reel or dye beck type of apparatus in which case the goods as it passes from the padder is given a wash in a 1% solution of sodium carbonate. Four hundred and eighty yards of goods at a time are then transferred and loaded on to the reel dye machine or dye beck where it is handled in the rope form. The dye beck is previously charged with 1050 gallons of water containing 1.25 ozs. of sodium carbonate per gallon. The temperature is brought to 150° F. and the goods is turned in this solution for five minutes. While the goods is in motion sodium hydrosulfite equivalent to 0.25 oz. per gallon and caustic soda equivalent to .05 oz. per gallon are added. The goods is moved in the solution for 15 minutes after which it is given a running wash with clear water, oxidized with hydrogen peroxide, rinsed, soaped at 150° F., rinsed, dried and finished in the usual manner. Since the development in this case is carried out as a unit with continued re-passage of the goods through the same bath and the hydrosulfite is added after the goods are in motion in the solution color need not be added to this developing bath.

EXAMPLE 4

A mixed fiber fabric containing 50% cotton and 50% acetate suitable for use for fused collar interlinings is dyed in blue shades by the process as outlined in Example 3 without any noticeable saponification of the acetate fiber.

EXAMPLE 5

Upholstery pile fabric having a cotton back and mohair face may be dyed with vat colors by the process as above described. The vat colors are selected to produce certain styling or color balance between the cotton back and mohair face and also to produce superlative fastness particularly to light. The following examples are given which illustrate the dyeing of these mixed fiber fabrics and the possibility of color selections for such materials. In these examples the fabric is padded with the caustic alkaline solution of the vat color and while the color is still in substantially reduced state it is subjected to development in a bath containing 1.25 ozs. per gallon of sodium carbonate and .25 oz. per gallon of sodium hydrosulfite and the ascertained amount of color to effect equilibrium for a period of three minutes at 145° F. In all cases the padding liquors are prepared by dispersing the vat colors in water, adding 1.75 ozs. per gallon of caustic soda (dry), bringing to the proper vatting temperature and adding 1.5 ozs. per gallon of sodium hydrosulfite. The concentration of color and the vatting temperatures are given with the description of the dyeing effects produced.

- A. Eight ozs. per gallon "Ponsol" Red BN double paste, padded at 120° F., dyes both the cotton back and mohair pile in red shades of about the same depth and shade. It shows excellent fastness to light.
- B. Six ozs. per gallon "Ponsol" Brilliant Red B paste, padded at 130° F., dyes the cotton backing considerably heavier in depth and brighter in shade than the mohair pile. It exhibits good light fastness.

C. Eight ozs. per gallon "Ponsol" Yellow AR, padded at 120° F., dyes cotton to about the same depth but greener and brighter than the mohair pile. It exhibits excellent fastness to light.

D. Two ozs. per gallon "Ponsol" Yellow G double paste, padded at 130° F., dyes the cotton very much heavier than the mohair.

E. Three ozs. per gallon Sulfanthrene Brown G paste, padded at 140° F., dyes the cotton very much lighter shade than the mohair.

F. The mixture of 0.5 oz. per gallon Sulfanthrene Brown G paste, 1.0 oz. per gallon "Ponsol" Yellow G double paste, padded at 130° F., dyes the cotton backing a golden shade while the mohair is dyed brown thereby imparting a novelty effect.

G. A mixture of 1.75 ozs. per gallon "Ponsol" Blue GD double paste, 1.90 ozs. per gallon "Ponsol" Golden Orange 2RT paste, 2.50 ozs. per gallon "Ponsol" Brown AG double paste, padded at 120° F., dyes this material a desirable taupe shade, fast to light.

H. A mixture of 0.5 oz. per gallon "Ponsol" Brilliant Violet 4RN paste, 1.12 ozs. per gallon "Ponsol" Golden Orange 2RT paste, 2.00 ozs. per gallon "Ponsol" Khaki 2G double pdr., padded at 130° F., dyes the mohair pile fabric a taupe shade fast to light.

The cotton back mohair face pile fabric, dyed as above described, was subjected to a standard abrasion test and no deterioration of the mohair fiber was discernible.

EXAMPLE 6

A mixed fiber for men's suits made of cotton, viscose staple rayon and wool is dyed in a stone green shade with vat colors giving desirable contrasting color effects by padding the cloth with the vat dye padding solution in a manner described in Example 1 in which the padding liquor is made up of:

	Ounces per gallon
Ponsol Direct Black 3B dbl. paste	2.4
Ponsol Green 2BL	0.4
Caustic soda (dry)	1.75
Sodium hydrosulfite	1.75

The padding is carried out at a temperature of 130° F. The pad feed was made up as follows:

	Ounces per gallon
Ponsol Direct Black 3G dbl. paste	3.0
Ponsol Green 2BL	0.5
Caustic soda	1.75
Sodium hydrosulfite	1.75

After padding, the cloth is batched on a shell and immediately transferred to a jig. The jig is previously charged with 80 gallons of a solution containing 1½ ozs. of sodium carbonate maintained at a temperature of 150° F. The cloth is given two passages through the sodium carbonate solution by running the cloth down from the shell on to the jig beam and then passing back on to the second jig beam.

0.25 oz. per gallon of sodium hydrosulfite is then added to the carbonate solution and after titrating for sodium bicarbonate, alkalinity and total alkalinity it is adjusted so as to contain 1½ ozs. per gallon sodium carbonate and 0.05 oz. per gallon of caustic soda. While the solution is maintained at 150° F., the cloth is given a passage through the solution. This development bath is again titrated and adjusted. The development requires from 2 to 4 passages, depend-

ing on the depth of shade, size of roll and the number of yards on the roll. The bath should be tested for alkalinity between the passes and indicated adjustments made. After development the cloth is given two passages in cold water, two passages through an oxidizing bath, then rinsed, soaped, rinsed and dried in the usual manner.

EXAMPLE 7

A mixed fiber fabric containing 80% spun viscose rayon and 20% wool is dyed a solid bright blue shade with vat colors by the process of Example 1, by employing for the padding solution

Ounces per gallon	
Sulfanthrene Navy Blue MR.....	4.0
Ponsol Green 2 BL.....	0.5
Caustic soda dry.....	1.5
Sodium hydrosulfite.....	1.5

The dyeing is carried out at 140° F. The cloth is passed directly from the padder into a continuous reel dyeing machine containing the development bath of sodium carbonate, sodium hydrosulfite, and sufficient amount of the colors to approximate equilibrium with the padded material. Limits of .02 oz. per gallon of caustic soda and .05 oz. per gallon of sodium bicarbonate should be maintained. The sodium carbonate concentration should be held at 1.20 to 1.35 ozs. per gallon, and the sodium hydrosulfite should not fall below .18 oz. per gallon. The reel dyeing machine is so arranged that the cloth is still in the open width when it enters the machine. After immersion in the open width the cloth goes into the rope form in which form it remains for the development, oxidation and soaping operations.

EXAMPLE 8

A viscose staple spun rayon fabric is dyed in blue shades fast to light and washing by nip padding with a solution of the vatted color prepared from

Ounces per gallon	
"Ponsol" Blue BF double paste.....	2.0
"Ponsol" Violet BN supra.....	.25
"Ponsol" Olive GGL paste.....	.25
Potassium hydroxide.....	1.75
Sodium hydrosulfite.....	1.5

The goods is passed from the padder through a developing bath, as described in Example 1, in which the required amount of colors have been added to approximate color equilibrium at the start. The alkalinity of the developing bath is maintained from 1.4 to 1.6 ozs. per gallon of sodium carbonate and from 0.02 to 0.05 oz. per gallon of sodium hydroxide. Due to the nature of this combination of colors, bicarbonate alkalinity in the bath is to be avoided. The hydrosulfite should not be allowed to fall below .18 oz. per gallon.

Other alkaline salts than sodium carbonate may be employed for the development of these vat colors, provided they are sufficiently alkaline to maintain the reduced vat dye in solution, and, where the process is used on alkali sensitive fibers, the alkalinity is not of such a strength that it injures such materials in the time required for development. Alkaline solutions of between pH of 8 and pH 12 have been found to be satisfactory.

The following salts and combination of salts, which in water solutions have a pH value in the concentrations used as indicated, have been found to be suitable for developing vat dyes of all types

that have been dyed on cotton, and on mixed fiber fabrics containing spun rayon and wool without showing any harmful effect on the alkali sensitive fibers where the goods were padded at 130° F. with a vat solution made up as follows:

Ounces per gallon	
"Ponsol" Direct Black 3G double paste.....	4.0
Caustic soda (dry).....	1.80
Sodium hydrosulfite.....	1.50

The padded goods were developed for 3 minutes at 150° F. in a developing bath containing 0.25 oz. per gallon of sodium hydrosulfite and the following amount of alkaline salt or mixture of salts:

- (a) 1.5 oz. per gallon sodium carbonate (pH 11.25)
- (b) 1.5 oz. per gallon sodium phosphate (Na_3PO_4) (pH 11.93)
- (c) Mixture of:
 - 0.938 oz. per gallon Na_3PO_4
 - 0.56 oz. per gallon Na_2HPO_4 } (pH 11.44)
- (d) 2.5 ozs. per gallon potassium carbonate (pH 10.89)
- (e) 1.5 ozs. per gallon 42° Bé. Na_2SiO_3 (pH 10.49)
- (f) 6.93 ozs. per gallon 42° Bé. Na_2SiO_3 (pH 11.24)
- (g) Mixture of:
 - 1.53 ozs. per gallon sodium carbonate
 - .05 oz. per gallon sodium bi-carbonate } (pH 10.93)
- (h) Mixture of:
 - 1.5 ozs. per gallon sodium carbonate
 - .05 oz. per gallon sodium hydroxide } (pH 11.8)

Satisfactory color shade development was obtained in all cases.

The pH measurements for the above solutions were made prior to the addition of the hydrosulfite with a hydrogen electrode using a saturated calomel electrode as a reference electrode. The hydrogen electrode was checked against a standard buffer solution of pH 10.00 before and after the measurements were made.

While in the above examples, standard commercial vat dyes of the anthraquinone and indigoid types are used, it is to be understood that the invention is not limited to these particular colors but is applicable to all vat dyes, such as those of the anthraquinone, indigo, thioindigo and sulfur vat dye classes. The invention is of particular importance in the dyeing of those colors that must be used in caustic alkali solutions for by the present process these colors can be applied to fabrics containing wool, silk and cellulose acetate rayons.

As illustrated in the above specific examples it is usually necessary in dip padding to have the pad feed somewhat stronger in dye content than the initial padding solution, for, due to the affinity of the color for the cloth there is relatively more color than water retained by the cloth. This causes a partial exhaustion of the color in the pad box. To correct this the pad liquor fed into the pad box to replace that taken up by the cloth must contain a proper amount of additional color to maintain the starting concentrations. Unless this is done a taper or progressive loss in depth of shade will result when a single color is used and a taper in both depth and shade will result when a mixture of colors is used which have different rates of exhaust.

It has been found that complete development of the color in the mild alkaline development

bath requires about three minutes or more. The time of development may be decreased but only with a possible sacrifice of fastness and color economy.

It will be obvious that this process for developing vat dyes is not limited to piece goods dyeing. This process makes possible the dyeing of fibers, and particularly the alkali sensitive fibers with vat dyes in any form such as in skeins, warps, slivers, etc., provided the material can be impregnated, squeezed and passed into the development bath before deterioration of the alkali sensitive fibers takes place.

It is to be understood that the amount of sodium carbonate in the developing bath can vary within wide limits provided the starting amounts are maintained within relatively narrow limits. From the standpoint of control the starting sodium carbonate concentration should be set high so that the total alkalinity of the developing bath is not subject to wide variations in short periods of time.

I claim:

1. In the process for dyeing textile fibers with vat colors the steps which comprise padding the fibers with a caustic alkali solution of the reduced colors and developing the colors on the fibers by subjecting them, while the color is, in substantially the reduced form, to a mild alkaline solution of an alkali metal hydrosulfite until development of the color is substantially complete, said developing solution having an alkalinity of from about pH 8 to about pH 12, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

2. In the process for dyeing textile fibers with vat colors the steps which comprise padding the fibers with a caustic alkali solution of the reduced colors and developing the colors on the fibers by subjecting them, while the color is in substantially the reduced form, to a mild alkaline solution of an alkali metal hydrosulfite until development of the color is substantially complete, said developing solution having an alkalinity of from about pH 8 to about pH 12 and maintaining the alkalinity of the solution relatively constant at any chosen value within these limits, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

3. In the process for dyeing textile fibers with vat colors the steps which comprise padding the fibers with a caustic alkali solution of the reduced colors and developing the colors on the fibers by subjecting them, while the color is in substantially the reduced form to a mild alkaline solution of an alkali metal hydrosulfite until development of the color is substantially complete, said developing solution having an alkalinity of from about pH 8 to about pH 12 and maintaining the alkalinity of the solution relatively constant at any chosen value within these limits said developing solution containing at the start a sufficient amount of the colors employed in the padding operation to approximate the amount necessary to establish equilibrium between the amount of color coming off of the fibers being dyed and the amount going onto the fibers from the developing solution during the developing operation, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

4. In the process for dyeing textile fibers with vat colors the steps which comprise padding the fibers with a caustic alkali solution of the re-

duced colors and developing the colors on the fibers by subjecting them, while the color is in substantially the reduced state to a mild alkaline solution of an alkali metal hydrosulfite, the alkalinity of which solution is between pH 10.5 and pH 12 while maintaining the alkalinity relatively constant at any chosen value within these limits, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

5. In the process for dyeing textile fibers with vat colors the steps which comprise padding the fibers with a caustic alkali solution of the reduced colors and developing the colors on the fibers by subjecting them, while the color is in substantially the reduced state to a mild alkaline solution of an alkali metal hydrosulfite the alkalinity of which solution is between pH 10.5 and pH 12 while maintaining the alkalinity relatively constant at any chosen value within these limits, said developing solution containing at the start a sufficient amount of the colors employed in the padding operation to approximate the amount necessary to establish equilibrium between the amount of color coming off of the fibers being dyed and the amount going onto the fibers from the developing solution during the developing operation, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

6. In the dyeing of fibers with vat colors by continuous dyeing processes wherein the fiber is padded with a caustic alkali solution of the reduced color, the steps which comprise passing the fibers into a developing bath while the dye is in substantially the reduced state, said developing bath being an alkaline hydrosulfite solution having a pH of from 10.5 to 12 and maintaining the alkalinity of the developing solution relatively constant at any chosen value within these limits during the developing operation, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

7. A process of dyeing textiles containing caustic alkali sensitive fibers which comprises padding the textiles with a caustic alkali solution of a reduced vat color and immediately passing the padded fabric into a development solution of sodium carbonate and an alkali metal hydrosulfite, maintaining the alkalinity of the solution at a sodium carbonate content of from 0.5 to 2.5 ounces per gallon of solution, sufficient alkali hydrosulfite being present in the development solution to retain the color in the reduced state at all times, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

8. A process of dyeing textiles containing caustic alkali sensitive fibers which comprises padding the textiles with a caustic alkali solution of a reduced vat color and immediately passing the padded fabric into a development solution of sodium carbonate and an alkali metal hydrosulfite, maintaining the alkalinity of the solution at a sodium carbonate content of from 0.5 to 2.5 ounces per gallon of solution with sufficient alkali hydrosulfite in the solution to retain the color in the reduced state at all times, said developing solution containing at the start a sufficient amount of the colors employed in the padding operation to approximate the amount necessary to establish equilibrium between the amount of color coming off of the fibers being dyed and the amount going onto the fibers from the developing

solution during the developing operation, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

9. A process of dyeing textiles containing caustic alkali sensitive fibers by the continuous piece goods dyeing processes which comprises, padding the textiles with a caustic alkali hydrosulfite solution of a vat color and developing the color on the textile by subjecting the padded material while the color is in substantially the reduced form and before the alkali sensitive fiber has been materially affected with the caustic alkali to a solution of sodium carbonate and an alkali metal hydrosulfite containing a sufficient amount of the color in solution to approximate color equilibrium at the start of the run, and maintaining a sodium carbonate alkalinity in the solution within relatively narrow limits during the run, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

10. In the process for dyeing textile fibers with vat colors the steps which comprise padding the

fibers with a caustic alkali solution of the reduced colors and developing the colors on the fibers by subjecting them to a mild alkaline solution of an alkali metal hydrosulfite until development of the color is substantially complete, said developing solution having an alkalinity of from about pH 8 to about pH 12, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

11. In the process for dyeing textile fibers with vat colors the steps which comprise padding the fibers with a caustic alkali solution of the reduced colors and developing the colors on the fibers by subjecting them to a mild alkaline solution of an alkali metal hydrosulfite until development of the color is substantially complete, said developing solution having an alkalinity of from about pH 8 to about pH 12 and maintaining the alkalinity of the solution relatively constant at any chosen value within these limits, and after the development of the color is substantially complete oxidizing the reduced dye on the fibers.

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