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VAT DYEING OF ALKALI-SENSITIVE FIBERS, INCLUDING AN ACID REDUCTION OF THE VAT DYE IMPREGNATED FIBERS

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This invention relates to the art of dyeing with vat dyestuffs. It relates more particularly to improvements in the method of dyeing fibers that are sensitive to alkali with vat dyestuffs, especially animal fibers, in the form of textiles, such as woolen piece-goods.

The dyeing of animal fibers with vat dyestuffs, and especially indigo, presents a number of difficulties which ordinarily are not encountered in the dyeing of cotton and other vegetable fibers. The vat dyestuffs are insoluble in water in the unreduced form; but upon reduction with a reducing agent, such as sodium hydrosulfite, they are converted to reduced forms (leuco forms) which are soluble in alkaline solutions in the form of salts of the reduced compounds with the alkali. The latter are taken up by textile fibers from such solutions and, upon oxidation, become fixed on the fiber by being again converted to the unreduced form. In dyeing with these dyestuffs, a number of procedures are used, the principal ones of which involve (1) reducing the dyestuff, forming an alkaline solution or suspension of the dyestuff in the reduced form, contacting the material to be dyed with the solution or suspension, and then oxidizing the dyestuff on the fiber; or (2) applying the unreduced vat dyestuff to the fiber, reducing the vat dyestuff in contact with the fiber in an alkaline bath, to render the dyestuff soluble, and then oxidizing the dyestuff to the unreduced form on the fiber.

An advantageous method of carrying out the second of these procedures involves padding piece-goods with the unreduced vat dyestuff by passing the goods through a padding liquor comprising an aqueous suspension of the unreduced vat dyestuff in water which may also contain a thickener and/or a wetting agent and/or a dispersing agent or the like, whereby the goods are impregnated with the unreduced vat dyestuff, and then passing the goods through an alkaline hydrosulfite bath wherein the unreduced dyestuff is converted to the reduced form (leuco form) in the presence of the goods, after which the goods are subjected to an oxidation treatment which regenerates the unreduced vat dyestuff on the fiber.

Because of the chemical nature of the animal fibers, it is necessary to avoid the use of strongly alkaline dyebaths. Similarly in the dyeing of organic derivatives of cellulose, strongly alkaline dyebaths are harmful because of their hydrolytic action upon the esters. In the dyeing of animal and other sensitive fibers with vat dyestuffs, it has been proposed heretofore to add to

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the alkaline dyebaths substances which protect the fibers from the corrosive action of strong alkalies (such as glue, sulfite cellulose waste liquor, degradation products of albumen, glucose, etc.) in order to avoid the harmful effect of the alkalies. It has also been proposed to work with vats containing weaker alkalies than caustic soda, such as ammonium hydroxide, sodium carbonate, sodium silicate, trisodium phosphate, etc., in the presence or absence of protective colloids, thereby eliminating the strong alkali and its attendant harmful effects. Further, it has been proposed to dye with aqueous suspensions of free leuco compounds of the vat dyestuffs prepared by reducing the vat dyestuffs in a strongly alkaline medium and then acidifying the resulting aqueous alkaline solutions or vats with acids, such as boric, acetic or sulfuric acid, in the presence of protective colloids and/or dispersing agents.

While such expedients overcome the aforesaid disadvantages of the strongly alkaline vats, they do not make it possible to dye heavy, especially tightly woven worsted, fabrics in shades, especially full shades, which possess good uniformity, penetration, and fastness to rubbing.

For the production of blue shades with indigo on woolen piece-goods for military and civilian uniforms, it has hitherto been necessary to weave the goods from predyed raw stock, which is objectionable, or to employ special dyeing machinery capable of dyeing the goods in the open width.

I have discovered that the use of special dyeing apparatus is unnecessary, and that in accordance with the present invention heavy woolen piece-goods, as well as other textile fabrics, can be dyed in the rope form in ordinary piece-dye kettles (winch or reel machines).

According to the present invention a vat dyestuff is applied to the fiber to be dyed, in the unreduced form from an aqueous suspension thereof, and the dyestuff is converted to the reduced form (leuco compound) by treating it with a reducing agent for the dyestuff in an acid medium, after which the dyestuff on the fiber is oxidized to the unreduced form, to develop the ultimate dyeing.

The process of the present invention is particularly suitable for dyeing animal fibers, especially wool. I have discovered that the penetration, uniformity and fastness to rubbing of the dyeings on tightly woven fabrics, notably woolens and worsteds, are improved by applying the vat dyestuff to the fabric in the unreduced

form and carrying out the reduction of the dyestuff to the leuco form in an acid medium, rather than in an alkaline medium. Indeed, by the process of this invention it has been found possible to dye "tippy" wool with indigo in shades having strength, evenness and fastness properties which could not be obtained by dyeing with indigo from an ammoniacal vat. The process of the present invention is also suitable for coloring organic derivatives of cellulose (e. g., cellulose acetate) since it avoids alkaline conditions which are detrimental to such materials.

The application of the unreduced vat dyestuffs to the material to be dyed, and the reduction in situ may be effected in ways known in the art. For instance, an aqueous suspension of the unvatted vat dyestuff may be padded onto the cloth in a padding machine or mangle, and the resulting cloth then worked in an acid reducing bath on a jigger or other suitable apparatus. It is a feature of the invention, however, that no special equipment is required and that well-penetrated dyeings can be obtained, even on tightly woven heavy fabrics such as 16-ounce melton worsted cloth, merely by working the fabric in an ordinary piece-dye kettle (winch or reel machine), and even when the goods are treated in rope form.

Accordingly, in the preferred practice of the present invention when applied to a fabric, the fabric is worked in a piece-dye kettle containing an aqueous suspension of the unreduced vat dyestuff until the fabric has become impregnated with the unreduced dyestuff, an acid reducing agent is added to the liquor in the kettle and the temperature and other conditions are adjusted to bring about reduction of the vat dyestuff, and the fabric is then worked in the resulting reducing bath, whereby the dyestuff on the the fabric is reduced (vatted) in situ and is absorbed by the fiber. After the reduction has been carried to the desired extent, the dyestuff can be oxidized to the unreduced form on the fiber by working the fabric in cold running water in the kettle (oxygen dissolved in the water and in the air acting as the oxidizing agent), or, if necessary, by forming a bath containing an oxidizing agent in the kettle and working the fabric therein. The fabric is then subjected to scouring and other usual finishing treatments.

It is a feature of the present invention that the impregnation of the fabric with the unreduced vat dyestuff and the reduction (vatting) of the dyestuff can be carried out in a single bath. Thus, by the selection of a reducing agent which is stable at temperatures suitable for the impregnation of the fabric with the unreduced vat dyestuff, but which, upon heating to a higher temperature under the acid conditions existing in the dyebath, becomes effective as a reducing agent for the dyestuff, it is possible to work the fabric in a single bath and yet obtain dyeings of excellent quality.

The concentration of the impregnation liquor, namely, the amount of vat dyestuff per unit amount of impregnation or padding liquor, as well as the ratio of such liquor to the amount of material to be dyed are not critical and may be varied widely, as desired, depending on the type and amount of material to be dyed, size and type of dyeing apparatus, strength of dyeing desired, etc. Thus, in dyeing pieces in rope form in the usual piece-dye (winch) machines, the ratio of liquor to the goods is such that the fabric is adequately covered and works easily in the kettle. For example, such ratio may range from 30 to 1, when one piece is dyed, to say, 15 to 1 when a number of pieces, for instance ten, are treated simultaneously. In the latter case, the concentration of the components in the impregnation and reduction liquors is also increased so as to maintain the preferred weight ratio between dyestuff and goods.

To obtain good penetration of the goods by the unreduced dyestuff it is desirable that the vat dyestuff particles form highly dispersed suspensions in the impregnation or padding liquors and do not precipitate or form coarse aggregates during the treatment. For this purpose, dispersion assistants may be added to the liquors, for example, protective colloids (e. g., glue, dextrine, etc.), organic dispersing agents (e. g., sulfite waste liquor, aldehyde condensation products of aromatic sulfonic acids, etc.), lower alkyl sulfates, etc.

Many vat dyestuff preparations in paste, powder, flake, etc., form are on the market, containing dispersion and other assistants which render them suitable for use in the process of this invention, especially those containing the vat dyestuff particles in a very fine state of division and specially prepared for use in padding.

Wetting agents, padding oils, and other assistants employed in the art to promote wetting, penetration, etc., of fibers also may be added to the vat dyestuff impregnation liquor, as desired. One group of such agents which I have found advantageous are the higher alkyl aryl sulfonates. An outstanding surface-active agent of this type is a mixture of sodium alkyl benzene sulfonates derived from kerosene (herein identified as "NR") which acts to improve the penetration of the impregating liquor into the fibers and to facilitate the action of the reducing liquor on the vat dyestuff in and on the fibers in the subsequent reduction step.

Preferably the padding or impregnating bath or liquor is heated; since the absorption and penetration of the unreduced dyestuff into the fabric is facilitated by heating, especially to the boiling point.

In the impregnation of wool, the absorption by the fiber of the unreduced dyestuff particles is facilitated by the presence of dilute acids, and is preferably effected in a medium having a pH of from 5 to 6. The use of strongly acidic media, e. g., having a pH less than about 4, tends to decrease the amount of unreduced vat dyestuff which can be taken up by the fiber and ultimately to lead to less penetrated dyeings. Alkaline media are undesirable because they tend to attack and weaken the wool fiber and to cause foaming, especially when dispersion assistants are used. Preferably the wool is acidified by pretreating it with a weakly acid liquor before applying the vat dyestuff in unreduced form; but beneficial action of the acid also may be secured by employing a weakly acid aqueous suspension of the unreduced vat dyestuff as the impregnating or padding liquor.

In effecting the reduction of the vat dyestuff in acid medium according to the present invention, reducing agents are preferably used which are not readily decomposed by acid media. Thus, derivatives of hydrosulfurous acid which are active and relatively stable in acid media, are suitable; such as, sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate, etc.

The amount of reducing agent required to convert the vat dyestuff to the leuco compound depends on the particular reductant employed, the

type and amount of vat dyestuff, type of dyeing equipment, and to some extent on the acidity and temperature of the medium. When insufficient amounts of reducing agent are employed, some of the vat dyestuff escapes reduction and fixation with resulting loss in tinctorial strength of the dyeings; whereas excessive amounts of reductant promote over-reduction, which may be reflected by a dullness or alteration in the shade of the dyeing. Optimum amounts may be determined by trial; for example, by determining the amount of reducing agent which yields the strongest dyeings possessing satisfactory shades.

In addition to their stability in acid media, many of the derivatives of hydrosulfurous acid (such as those mentioned above) exhibit substantial reducing action only at elevated temperatures. Hence, they are especially useful in carrying out the process of the invention by the procedure involving impregnation of the fabric with a suspension of the dyestuff containing the reducing agent and effecting the reduction of the dyestuff in place on the fiber by heating the resulting dye liquor to a higher temperature. The stability at elevated temperatures further permits carrying out the dyeing in hot aqueous media, thereby promoting thorough penetration of the reducing liquor to the particles of unreduced dyestuff in the fabric, which aids in producing superior fixation of the color in the fibers with consequent improved fastness to rubbing.

While it is possible to obtain fixation of vat dyestuffs with sodium hydrosulfite alone, or in the presence of an acid (such as acetic acid), the resulting dyeings are relatively weak, owing to the instability of sodium hydrosulfite in acid media. It has been found, however, in accordance with the present invention that the employment of sodium hydrosulfite in conjunction with a stable hydrosulfite, especially, zinc formaldehyde sulfoxylate, gives rise to brighter and somewhat better penetrated shades, in the production of light and medium dyeings on woolen pieces (e. g., when 10% to 20% of Indigo NAC 20% paste, based on the weight of the goods, is used), than are obtained in the absence of sodium hydrosulfite. Mixtures containing about 1 to 2 parts of sodium hydrosulfite per 3.5 to 5 parts of zinc formaldehyde sulfoxylate are particularly suitable and are preferred. The total amount of these reductants employed with respect to the material to be dyed may be varied, depending upon the conditions obtaining; for example, the nature and amount of vat dyestuff employed, whether the reduction is effected in apparatus open or closed to the atmosphere, etc. The following table illustrates the relationship between the amount of reducing agent and the amount of indigo required to produce good dyeing results on wool (the percentages are by weight, based on the weight of the goods):

Indigo NAC 20% paste	1%	4%	10%	20%	30%
Zinc formaldehyde neutral sulfoxylate	0.5%	2.5%	4.0%	6%	10%
Sodium hydrosulfite	0.25%	0.5%	1.0%	2%	2%

On the other hand, it has been found in accordance with the invention that somewhat stronger dyeings can be obtained by the use of stable hydrosulfite derivatives alone, especially zinc formaldehyde sulfoxylate, as reducing agents than are obtained by the use of mixtures of such reducing agents with sodium hydrosulfite. This is especially marked in the preparation of heavy (full) shades on woolen pieces; e. g., by the use of from 25% to 40% of Indigo NAC 20% paste (based on the weight of the material).

Further, it has been found, in accordance with the invention, although the use of sodium hydrosulfite in acid media results in weak dyeings, as previously mentioned, probably because of the instability of sodium hydrosulfite in acid solutions, the addition of a soluble zinc salt (for example, zinc acetate) to an acid reducing bath containing sodium hydrosulfite improves the strengh of the dyeings. Presumably the zinc salt stabilizes the hydrosulfite considerably, possibly with the formation of a zinc hydrosulfite salt, since the degree of reduction and fixation of the vat dyestuff on the fiber is noticeably greater, although short of the results obtained with zinc formaldehyde sulfoxylate, and with mixtures of the latter with sodium hydrosulfite.

It has also been found in accordance with this invention that the presence in the reducing liquor of a small amount (say ½ to 5% of the weight of the material to be dyed) of a strong dispersing agent, for example a synthetic tanning agent obtained by condensing formaldehyde with beta-naphthalene sulfonic acid, or sodium lignin sulfonate, promotes the production of considerably stronger and redder shades of indigo than are obtained in the absence of such a dispersing agent. The tinctorial strength of the dyeings also may be improved by similarly employing cationic dispersing agents; for example long chain quaternary ammonium compounds, e. g., cetyl pyridinium bromide, lauryl and other high molecular alkyl dimethyl benzyl ammonium chloride, etc.

The reduction of the vat dyestuff in accordance with the present invention is accomplished in a medium having a greater acidity than pH 7 (i. e., having a pH less than 7), and preferably having an acidity greater than pH 5. The most suitable pH or condition of acidity depends upon a number of factors, e. g., the particular type of fiber treated, and the nature of the vat dyestuff and reducing agent employed. In general, strongly acid media (e. g., those having a pH of 1 or less) are preferably avoided. While they may be suitable for vatting the dyestuff, they tend to be harmful, especially at elevated temperatures, to sensitive fibers such as wool. In vatting indigo on wool with stable hydrosulfites, such as sodium and zinc formaldehyde sulfoxylates, it has been found desirable to maintain the pH of the reducing liquor below 5, and preferably between 3.5 and 5.

Acids and acid-reacting compounds (e. g., acetic acid, boric acid, phthalic acid, sulfuric acid, ammonium bisulfate, etc.) may be employed as sources of the required acidity. In some cases, the reducing agents (e. g., zinc formaldehyde sulfoxylate) may themselves provide an acid medium by hydrolysis, without the addition of other acidic substances.

The oxidation of the leuco vat dyestuff on the fiber may be accomplished by any suitable means as, for example, by simple air oxidation, by rinsing with water, or by treatment with oxidizing agents, for example, perborates (e. g., sodium perborate), hydrogen peroxide, bichromates (e. g., sodium bichromate, potassium bichromate), sodium chlorite, etc. It has been found that in coloring wool with indigo, a dyeing possessing superior fastness to crocking is obtained by treating the material carrying the reduced vat dyestuff with water in the absence of added oxidants. The relatively slow oxidation which is obtained with molecular oxygen (dissolved in the rinse water and present in the atmosphere to which the goods are exposed), as compared with atomic

oxygen produced by chemical oxidants, appears to improve the fastness of the dyeings.

The invention will be illustrated by the following specific examples, but it will be understood that the invention is not limited to the details thereof and that changes may be made without departing from the scope of the invention. The percentages in all cases refer to the weight of the goods. Strength of reagents is by weight unless otherwise indicated.

Example 1.—One piece of 16-ounce melton worsted cloth (see American Dyestuff Reporter, 1943, page 29), which had been carbonized with sulfuric acid, was processed in the following manner, in rope form, in a conventional piece-dye kettle (winch machine). The goods were continuously passed over the winch (reel) during all operations (e. g., charging of chemicals, neutralization, impregnation, reduction, rinsing, etc.) except as noted. The ratio of the treatment liquor to the goods was maintained at all times at about 25 to 1 by weight, except as otherwise noted. In discharging the treatment liquor, water was run in at a rate sufficient to maintain substantially the volume of the bath, so that the goods were properly covered by the liquor and worked easily without dragging.

Neutralization.—In order to neutralize the goods, an aqueous neutralizing bath was prepared by charging water to the dye kettle and adding 5% of ammonium hydroxide (26% strength) and ½% of "NR." The goods were entered and the bath was heated to 130° F. and maintained at that temperature for about 10 minutes, whereupon it was discharged and the fabric was rinsed for 30 minutes with cold water.

Impregnation with Indigo.—10% of Indigo NAC 20% paste (Color Index 1177), stirred up with about five times its weight of water, and ½% of "NR" were introduced into the water in the dye kettle. The bath was then heated to boiling during about 30 minutes and boiled for 15 minutes, at the end of which time the liquid was colorless and completely exhausted of indigo. The bath was cooled to 110° C. by adding cold water.

Reduction.—To the resulting bath were added 5% acetic acid (56% strength), 10% of glucose, and ⅓% of anthraquinone (100% strength), followed in about ten minutes by 7% of normal zinc formaldehyde sulfoxylate: $Zn(HSO_2.CH_2O)_2$, and 3% sodium hydrosulfite powder. The bath was heated to 180° F. in 45 minutes and maintained at that temperature for 10 minutes, after which it was allowed to cool slowly. The pH of the liquor at the start and end of this heating period was 3.5.

Oxidation.—The fabric was then rinsed with running cold water for 45 minutes, whereby a pronounced blue dyeing was developed.

Scouring.—3% ammonium hydroxide (26% strength) and ⅓% "NR" were added, after which the bath was heated to 130° F. during 15 minutes and maintained at that temperature for 10 minutes. The fabric was rinsed with cold water for 30 minutes until the liquor was colorless. The purpose of this last treatment was to wash off superficially-attached, loosely-held indigo particles which otherwise would reduce the crocking fastness of the dyeing.

The fabric was thereby dyed a good medium blue shade characterized by excellent evenness, and penetration.

Topping with chrome colors.—½% "NR," 10% Glauber's salt, 3% acetic acid, and 1.7% ammonium hydroxide (26% strength) were added to the water in the kettle. 2.8% of National Superchrome Blue B high conc., 2.5% of National Superchrome Red ECB, and 0.18% of National Superchrome Black TS, each dissolved in a small amount of water, were then added, and the dyebath was heated to boiling during 45 minutes and boiled for 30 minutes. 1% of acetic acid (56% strength) was added, the dyebath was boiled for 30 minutes, followed by another addition of 1% of acetic acid and subsequent boiling for 30 minutes to substantially exhaust the color. 2% sodium bichromate was then introduced, and the bath was boiled for 45 minutes to complete the chromation of the dyestuffs. The fabric was rinsed with cold water until the liquor was free from color.

The fabric was then transferred to a washer where it was washed and scoured with soap and soda ash in conventional manner, rinsed and dried.

The resulting fabric was dyed a full navy blue shade characterized by excellent evenness, penetration, and fastness to rubbing.

Example 2.—Six pieces of uncarbonized 11 oz. woolen flannel, totaling 350 pounds, were dyed in an ordinary piece-dye kettle in rope form in a manner similar to that described in the preceding example, the ratio of goods to liquor being maintained at 1:15 at all times. The procedure was as follows:

Impregnation.—2% of acetic acid (56% strength) was added to the water in the dye kettle, followed ten minutes later by 10% of Indigo NAC 20% paste, diluted with four times its weight of water, and ½% of "NR." The bath was heated with direct steam to boiling in 30 minutes and boiled for 15 minutes, at the end of which time the liquor was free from color, showing that the indigo had been completely taken up by the fabric. The bath was then cooled to 110° F. by adding cold water while maintaining the volume of the liquor.

Reduction.—To the dye kettle liquor at 110° F. were added 2.5% of acetic acid (56% strength), 10% of glucose, ¼% of "NR" and ¼% of anthraquinone, followed in about ten minutes by 4% of normal zinc formaldehyde sulfoxylate and 2% of sodium hydrosulfite. The resulting bath, whose acidity in terms of pH was 4.1, was heated during 45 minutes to 150° F., 3% of acetic acid (56% strength) was added, and the bath was then heated to 180% F. in 20 minutes to complete the reduction. At the end of this period, the acidity of the bath in terms of pH was 3.8.

Oxidation.—The pieces were rinsed for 45 minutes in running cold water to develop the dyeing, while maintaining the bath volume.

Scouring.—2% of ammonium hydroxide (26% strength) and ½% of "NR" were added to the bath, which was then heated to 120° F. in 20 minutes and maintained at that temperature for 10 minutes. The pieces were thereafter rinsed for 30 minutes with cold water. The resulting fabrics were dyed a medium shade of blue.

Topping with chrome colors.—10% of Glauber's salt, 8% of acetic acid (56% strength), 2% of ammonium hyroxide (26% strength) and ¼% of "NR" were stirred into the water contained in the dye kettle, after which 2.75% of Superchrome Blue B high conc. and 1.5% of Superchrome Red ECB, each dissolved in a small amount of water, were added. The dye-bath was heated to boiling during an hour and a half and boiled for an hour, whereupon 1.7% of sodium

bichromate was introduced and the boiling was continued for 45 minutes. The pieces were then rinsed with cold water for 30 minutes until the liquor was colorless.

The resulting pieces were carbonized with sulfuric acid, and then scoured with soap and soda ash in the usual manner.

The pieces were thereby dyed full navy blue shades possessing excellent evenness, penetration, and fastness to crocking.

Example 3.—A piece of 16 oz. melton worsted cloth was dyed in rope form in a piece-dye kettle in a similar manner with Carbanthrene Brilliant Green, the ratio of the goods to the liquor being 1:30. The procedure was as follows:

5% of Carbanthrene Brilliant Green double paste (Color Index 1101) containing about 15% of dyestuff solids, ½% of "NR", and 2% of acetic acid (28% strength) were stirred into the water in the dye kettle. The cloth was entered and the bath was heated to boiling during 30 minutes and boiled for 15 minutes substantially to exhaust the color. The dyebath was displaced with fresh water, 5% of sodium formaldehyde sulfoxylate and 2% of acetic acid (28% strength) were added, and the bath was heated to 150° F. during 25 minutes. 3% of acetic acid (28% strength) was then introduced, after which the bath was heated to 180° F. during 1 hour and maintained at that temperature for 15 minutes, to complete the vatting of the dyestuff. The piece was rinsed in cold running water to oxidize the leuco vat dyestuff, and then scoured. A level, bright green dyeing was thereby obtained.

Example 4.—A piece of 16-ounce melton worsted cloth was dyed in rope form in a piece-dye kettle in the manner of Example 3 with a mixture of 4,4'-dimethyl-6,6'-dichlor-thioindigo and 6,6'-diethoxy-thioindigo, the ratio of the goods to the liquor being 1:30. The procedure was as follows:

10% of a commercial vat dyestuff composition in the form of flakes comprising, per 100 parts by weight, 18.2 parts of a mixture of 4,4'-dimethyl-6,6'-dichlor-thioindigo and 6,6'-diethoxy-thioindigo (the remainder being non-dyeing water-soluble matter, including sugar, sodium isobutyl sulfate and a dispersing agent), ½% of "NR," and 2% of acetic acid (28% strength) were stirred into the water in the kettle. The piece was entered and the bath was heated to boiling during 30 minutes and boiled for 15 minutes to exhaust the color, after which the liquor was displaced with fresh water. 10% of sodium formaldehyde sulfoxylate, 2% of sodium hydrosulfite, 10% of glucose, ⅓% of anthraquinone, and 10% of acetic acid (28% strength) were added with agitation to the bath. To effect reduction of the dyestuff, the liquor was heated to 180° F. during 1 hour and maintained at that temperature for 15 minutes. The piece was then rinsed in cold running water to oxidize the leuco vat dyestuff and the resulting dyeing was scoured in the usual manner. An even, well-penetrated salmon-pink dyeing was thereby obtained.

Example 5.—A piece of 16-ounce melton worsted cloth was dyed in rope form in a piece-dye kettle in the manner of Example 3 with 5,6,5',6'-dibenzo-thioindigo, the ratio of the goods to the liquor being 1:30. The procedure was as follows:

5% of a commercial vat dyestuff composition in the form of flakes comprising, per 100 parts by weight, 18 parts of 5,6,5',6'-dibenzo-thioindigo (the remainder being non-dyeing water-soluble matter, including sugar, sodium isobutyl sulfate and a dispersing agent), ½% of "NR" and 2% of acetic acid (28% strength) were stirred into the water in the kettle. The piece was entered and the bath was heated to boiling during 30 minutes and boiled for 15 minutes to exhaust the color, after which the liquor was displaced with fresh water. 5% of sodium formaldehyde sulfoxylate, 10% of glucose, ¼% of anthraquinone and 6% of acetic acid (28% strength) were added with agitation to the bath. The liquor was heated to 180° F. during one hour and maintained at that temperature for 15 minutes, to effect reduction of the dyestuff. The piece was then rinsed in cold running water to oxidize the leuco vat dyestuff and the resulting dyeing was scoured in the usual manner. A tan dyeing characterized by good uniformity and penetration was obtained.

Example 6.—A piece of 16-ounce melton worsted cloth was entered into about thirty times its weight of warm (100° F.) water in a piece-dye kettle, and the goods were circulated in rope form. 20% of Indigo NAC 20% paste was added to the water in the kettle and about ten minutes thereafter, 5% of zinc formaldehyde sulfoxylate was sprinkled in. The pH of the dyebath at this point was 5.0. The dyebath was heated to 190° F. during 45 minutes, maintained at that temperature for 30 minutes, and allowed to cool for 30 minutes. At the end of this period, the pH of the dyebath was 3.7. The goods were rinsed and oxidized with cold running water until the blue dyeing was fully developed, as described in Example 1, and were then scoured with soap and soda ash to remove unfixed indigo particles.

A good medium-heavy blue shade of good evenness, penetration and fastness to crocking was thereby obtained.

Example 7.—A piece of 16-ounce melton worsted cloth was dyed in rope form in a piece-dye kettle, the ratio of goods to liquor being 1:30. The goods were placed in circulation, and 20% of Indigo NAC 20% paste, 12% of acetic acid (28% strength), 5% of zinc formaldehyde sulfoxylate, and finally 2% of sodium hydrosulfite were added, the additions being made at 5 to 10 minute intervals. The dyebath was heated during 45 minutes to 190° F., maintained at that temperature for 30 minutes to complete the fixation of the dyestuff, and allowed to cool for 30 minutes. The pH of the dyebath at the start and end of the heating period was 3.7. The goods were then rinsed and oxidized with cold water until the full strength of the blue dyeing was obtained, as described in Example 1, and finally scoured.

A good blue shade was thus obtained, which was weaker but somewhat brighter than that produced by the process of Example 6.

Example 8.—A piece of 16-ounce melton worsted cloth was dyed in rope form in a piece-dye kettle, the ratio of goods to liquor being 1:30. The goods were placed in circulation, 20% of Indigo 20% paste and 12% of acetic acid (28% strength) were stirred into the water in the kettle, and then 5% of sodium formaldehyde sulfoxylate was sprinkled in. After each addition, the goods were circulated for 5 to 10 minutes. The dyebath was heated to 190° F. during 45 minutes, maintained at that temperature for 30 minutes, and allowed to cool for 30 minutes. The pH of the liquor was 3.9 at the start and 4.0 at the end of this period. The goods were then rinsed and oxidized in cold running water until the full blue shade was developed, as in the foregoing examples, after which they were scoured in the usual manner.

A good blue dyeing was thereby obtained.

Example 9.—A piece of 16-ounce melton worsted cloth in rope form was entered into forty times its weight of warm (110° F.) water in a piece-dye kettle. The goods were circulated, and ½% of "NR," ½% of a synthetic tanning agent obtained by condensing formaldehyde with beta-naphthalene sulfonic acid, 35% of Indigo NAC 20% paste, 4% of acetic acid (28% strength) and 12% of normal zinc formaldehyde sulfoxylate were added to the water in the kettle, the additions being made in the named order at 5 to 10-minute intervals. The dyebath was heated to 190° F. during 30 minutes, and maintained at that temperature for 30 minutes. The goods were then rinsed and oxidized in cold running water to develop the dyeing, scoured with ammonia and "NR," and finally washed and soaped, as described in Example 1.

A good full shade possessing excellent evenness, penetration and fastness to crocking was thereby obtained.

The invention is not limited to the use of the vat dyestuffs employed in the foregoing examples. Water-insoluble vat dyestuffs of various kinds (whether of the indigoid or anthraquinone series) may be applied according to the process of the present invention. For instance, in addition to the vat dyestuffs referred to above, the following may be specifically mentioned, all of which produced satisfactory dyeings when applied by the process exemplified in the specific examples:

Thioindigo (Color Index 1207)
Brilliant Indigo KMR (Color Index 1182)
Brilliant Indigo 4BR (Color Index 1184)
Carbanthrene Blue GCD (monochloro-N,N-dihydro-1,2,2',1'-anthraquinoneazine).

The presence of small amounts of anthraquinone in the acidic reducing bath, as illustrated in certain of the examples, is advantageous in that it decreases the amount of reducing agent required to effect vatting and fixation of the dyestuff. Anthraquinone presumably acts as an oxidation inhibitor and hydrogen transfer agent, probably catalytically, preventing the premature oxidation of the leuco vat dyestuff and facilitating reduction of the vat dyestuff to the leuco form, respectively. While its use is an advantage, especially in dyeing with indigoid vat dyestuffs, it is not essential to the process. Derivatives and substitution products of anthraquinone containing oxygen in at least one meso position thereof (such as, anthraquinone-alpha and beta-sulfonates) or other quinones (e. g., benzoquinone, naphthoquinone sulfonates, phenanthrene quinone, etc.) may be similarly employed. While quinones are not antioxidants per se, they are reduced during the vatting operation to corresponding hydroxy derivatives, which are the actual antioxidizing agents. Accordingly the quinones may be added in the form of their reduction products, if desired. Even very small amounts are effective; hence the use of anthraquinone or other quinones in amounts larger than are employed in the examples is unnecessary, although not harmful.

As above noted, other dyeing assistants than those employed in the specific examples may be used. While none need be used, the degree of impregnation, levelness and fastness of the dyeings are improved by including in the padding or impregnating bath assistants such as Turkey-red oil, soaps, alkyl aryl sulfonic acids, higher alkyl sulfates, etc. Furthermore, by using a strong dispersing agent in the reducing bath, enhanced dyeings may be obtained. Thus, by including the strong dispersing agent (synthetic tanning agent) in the single impregnating and reducing bath of Example 9, the dyeing which was obtained had greater tinctorial strength and was a redder shade than a corresponding dyeing made from the same material in the same manner but omitting the dispersing agent.

The chrome colors employed in certain of the examples to supplement the indigo dyeings are preferably employed to secure heavy navy blue shades with indigo on heavy woolen goods. Their proportions, amounts and method of application are merely illustrative. They may be replaced by other wool colors (including acid dyestuffs as well as chrome colors) and may be employed prior to the vat dyestuff (bottoming) or subsequent to the vat dyestuff (topping).

Besides being useful for the dyeing of woolen fibers illustrated in the examples, the process of the present invention may be used for the dyeing of other animal fibers, fibers of ester derivatives of cellulose, and fibers of other substances which are sensitive to alkalies. Further, it may be utilized for coloring other materials, such as cotton and rayon; although it is less adapted for dyeing the latter materials, since the free leuco compounds possess relatively poorer affinity for cellulosic fibers than for animal fibers. The term "animal fibers" is used herein in the generic sense, including natural animal fibers (such as wool, silk, hair, and the like) and artificial animal fibers (such as those derived from casein, soybean, and the like).

Further, the invention is not limited to the treatment of fabrics nor to the use of piece-dyeing equipment, but may be applied to other masses of fibers, in the form of skeins, jackspools, cops, rawstock, or otherwise, and in other types of dyeing machines or apparatus (e. g., the Franklin machine, etc.).

I claim:

1. A method of dyeing organic textile fibers sensitive to alkalies, with a vat dyestuff which is reducible under acid conditions, which comprises impregnating a mass of the fibers with the vat dyestuff in unreduced form, reducing the vat dyestuff in contact with the fiber in an acid medium having an acidity of less than pH 1, and then oxidizing the reduced vat dyestuff on the fiber to the unreduced form.

2. A method of dyeing animal fibers with a vat dyestuff which is reducible under acid conditions, which comprises impregnating a mass of the fibers with the vat dyestuff in unreduced form, reducing the vat dyestuff in contact with the fibers in an acid medium having an acidity less than pH 1, and then oxidizing the reduced vat dyestuff on the fiber to the unreduced form.

3. A method of dyeing woolen fibers with a vat dyestuff which is reducible under acid conditions, which comprises padding a mass of the fibers with the vat dyestuff in unreduced form in an acid medium having an acidity of pH 4 to pH 6, reducing the vat dyestuff in contact with the fibers in an acid medium having an acidity less than pH 1, and then oxidizing the reduced vat dyestuff on the fiber to the unreduced form.

4. A method of dyeing woolen fibers with an indigoid vat dyestuff which is reducible under acid conditions, which comprises padding a mass of the fibers with the vat dyestuff in unreduced form, reducing the vat dyestuff in contact with

the fibers, in a medium having an acidity of pH 1 to pH 5, and then oxidizing the reduced vat dyestuff on the fiber to the unreduced form.

5. A method of dyeing woolen fibers with indigo which comprises impregnating a mass of the fibers with indigo in unreduced form, reducing the indigo in contact with the fibers, in a medium having an acidity of pH 3.5 to pH 5, and then oxidizing leuco-indigo on the fiber to the unreduced form.

6. In the dyeing of woolen fibers with vat dyestuffs which are reducible under acid conditions, by a process in which the vat dyestuff in unreduced form is applied to the fibers and the vat dyestuff is then reduced in contact with the fiber, the improvement which comprises impregnating a mass of the fibers with the unreduced vat dyestuff, reducing the dyestuff in contact with the fiber by means of a formaldehyde sulfoxylate in an acid medium having an acidity of pH 3.5 to pH 5, and then oxidizing the reduced dyestuff on the fiber to the unreduced form.

7. In the dyeing of woolen piece-goods with a vat dyestuff, the improvement which comprises padding woolen piece-goods with an indigoid vat dyestuff by working the piece-goods in rope form in a dyebath containing an aqueous suspension of an indigoid vat dyestuff in unreduced form, reducing the dyestuff in contact with the goods by working the resulting goods in rope form in an acid bath containing a reducing agent for the dyestuff and having an acidity of pH 1 to pH 5, and then oxidizing the reduced dyestuff on the fiber to the unreduced form.

8. In the dyeing of woolen piece-goods with indigo, the improvement which comprises padding woolen piece-goods with indigo by working the piece-goods in a dyebath containing an aqueous suspension of indigo in unreduced form, reducing the indigo in contact with the goods by working the resulting goods in rope form in an acid bath containing a reducing agent for indigo and having an acidity of pH 3.5 to pH 5, and then oxidizing the reduced indigo on the fiber to the unreduced form.

9. In the dyeing of woolen piece-goods with indigo, the improvement which comprises padding woolen piece-goods with indigo by working the piece-goods in a dyebath containing an aqueous suspension of indigo in unreduced form, reducing the indigo in contact with the goods by working the resulting goods in an acid bath having an acidity of pH 3.5 to pH 5 and containing a formaldehyde sulfoxylate as a reducing agent for the indigo, and then oxidizing the reduced indigo on the fiber to the unreduced form.

10. In the dyeing of woolen piece-goods with indigo, the improvement which comprises padding woolen piece-goods with indigo by working the piece-goods in a dyebath containing an aqueous suspension of indigo in unreduced form, reducing the indigo in contact with the goods by working the resulting goods in an acid bath having an acidity of pH 3.5 to pH 5 and containing zinc formaldehyde sulfoxylate as a reducing agent for the indigo, and then oxidizing the reduced indigo on the fiber to the unreduced form.

11. In the dyeing of woolen piece-goods with indigo, the improvement which comprises padding woolen piece-goods with indigo by working the piece-goods in a warm dyebath containing indigo in unreduced form and zinc formaldehyde sulfoxylate and having an acidity of pH 4 to pH 6, reducing the indigo in contact with the goods by heating the resulting bath to a reducing temperature and working the resulting goods in said bath, and then oxidizing the reduced indigo on the fiber to the unreduced form.

12. In the dyeing of woolen piece-goods with indigo, the improvement which comprising padding woolen piece-goods with indigo by working the piece-goods in a dyebath containing an aqueous suspension of indigo in unreduced form, reducing the dyestuff in contact with the goods by working the resulting goods in an acid bath having an acidity of pH 3.5 to pH 5 and containing a formaldehyde sulfoxylate and a hydrosulfite as a reducing agent for the indigo, and then oxidizing the reduced indigo on the fiber to the unreduced form.

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