

March 13, 1945.

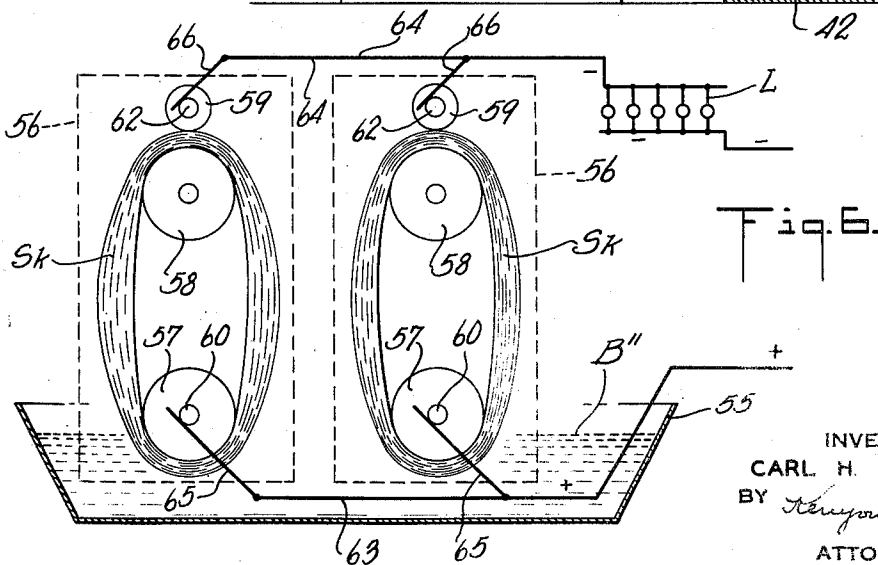
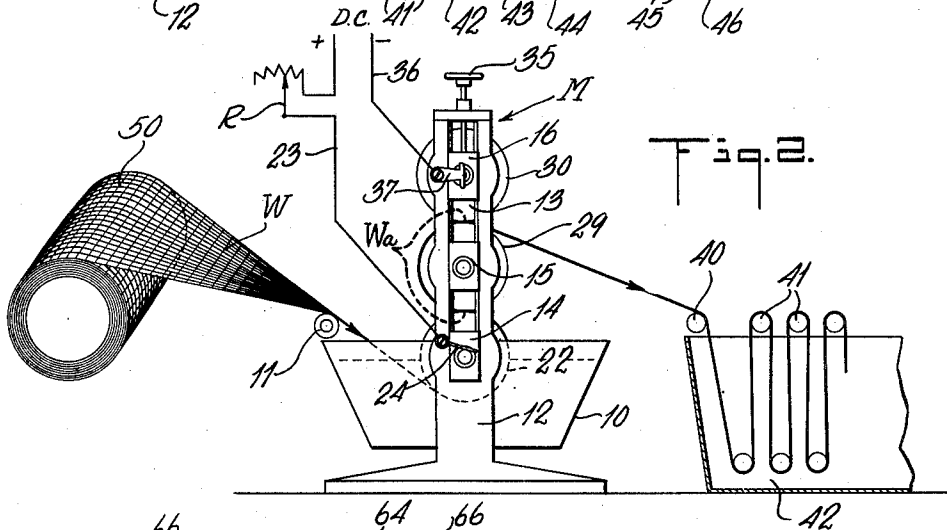
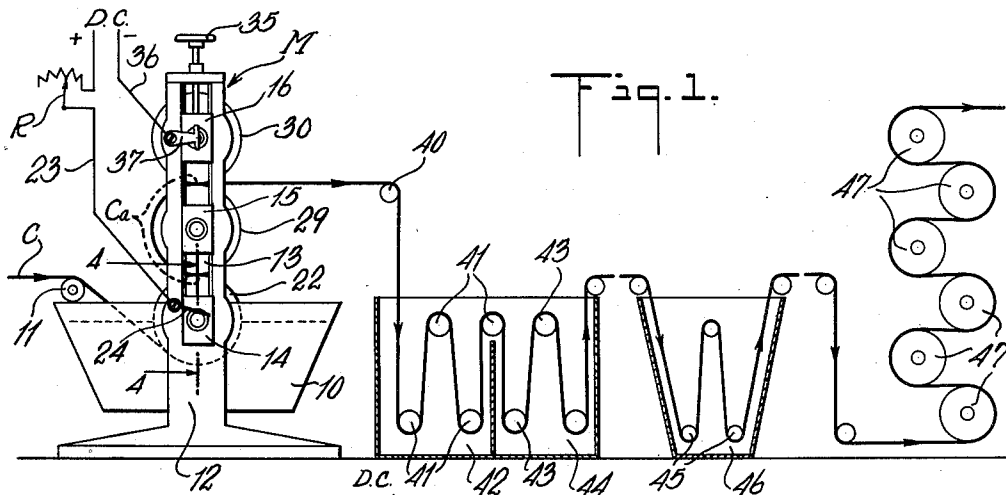
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2,371,145

VAT DYEING PROCESS

Filed Jan. 6, 1942

3 Sheets-Sheet 1



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VAT DYEING PROCESS

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3 Sheets-Sheet 2

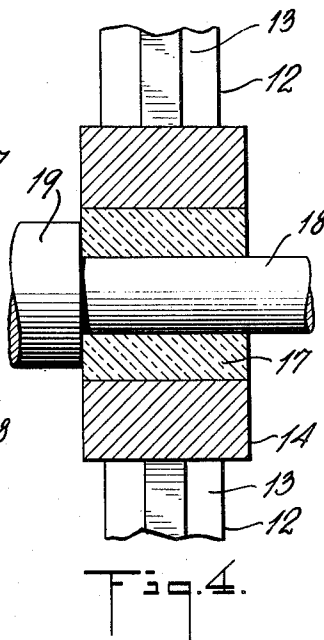
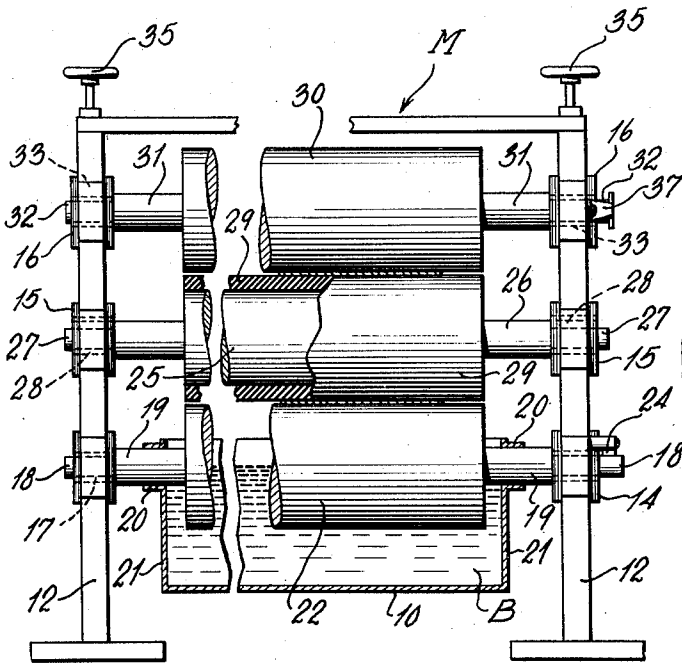
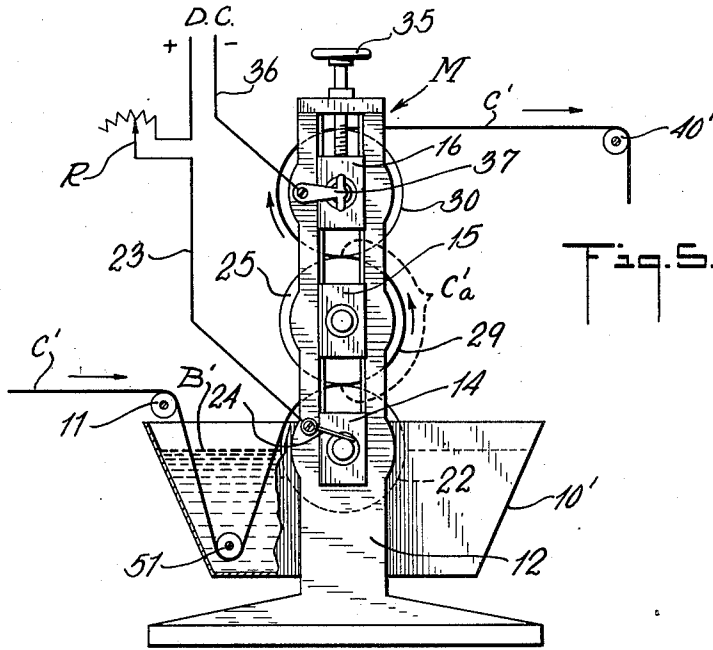


Fig. 3.

Fig. 4.

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3 Sheets-Sheet 3

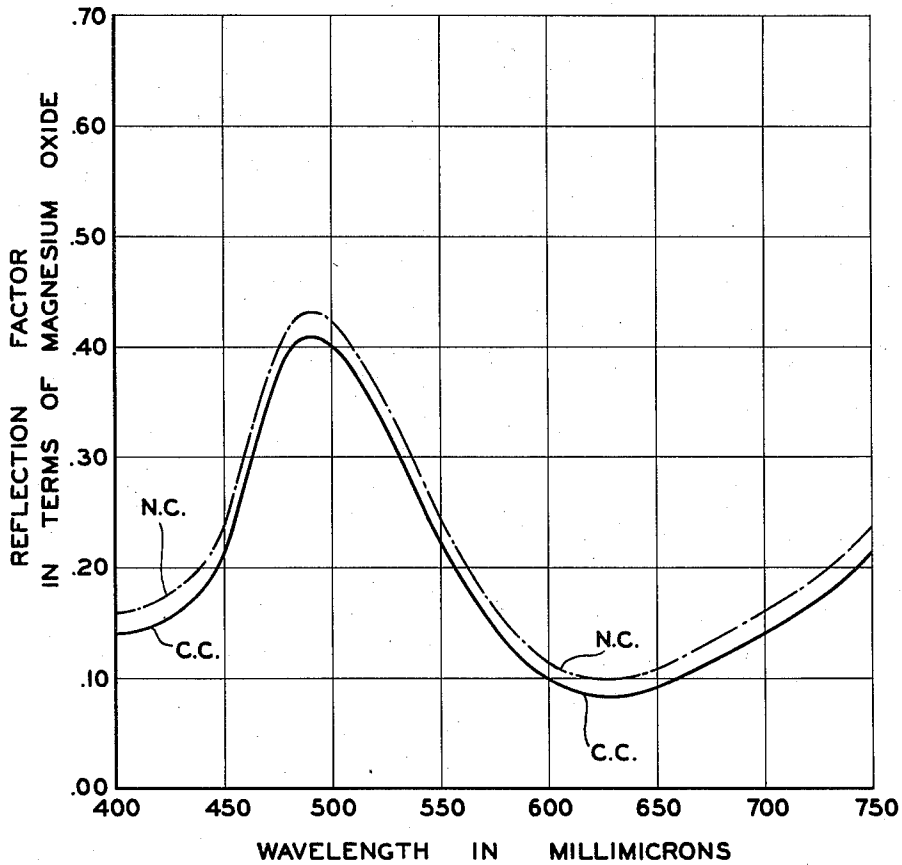


Fig. 2

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# UNITED STATES PATENT OFFICE

2,371,145

## VAT DYEING PROCESS

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Application January 6, 1942, Serial No. 425,727

9 Claims. (Cl. 204—134)

The present invention relates to apparatus for and methods of dyeing or coloring textiles, yarns, fibres, fabric, skeins and the like and is applicable particularly to those fibres and fabrics which are capable of being dyed with those colors known to the trade as "vat" colors or dyes.

Such dyes, namely "vat dyes," are dyes which have to be used in a manner similar to indigo, by being reduced chemically to a soluble substance having a different color from the original dye, but which when dyed and reoxidized will then reproduce the original color. They are each a comparatively insoluble pigment which when chemically reduced becomes a soluble "leuco compound" which dissolves in relatively weak alkali present in the vat bath (usually sodium or potassium hydroxides or sodium or potassium carbonates). Such dissolved leuco compound upon reoxidation after application to the textile is restored to its original color. Oxidation may be either by oxidation in air, in water or by some other means as by sodium perborate, sodium bichromate and acid, or other means known to the dyers' art.

In older methods of mill practice many variations are found. In some cases, for example, vat dyestuff is suspended in a slightly thickened bath, then padded into a woven web of cloth between pad rollers. The cloth or web is then transferred to a dye jig wherein the cloth is run back and forth through an alkaline reducing bath. In other cases the fabric is immersed or worked in a bath of such dye stuff, an alkali, or reducing agent, sometimes a thickening agent, and with or without salts like sodium chloride or sodium sulphate. Such methods are familiar in the dyeing art, are tedious and produce varied results. Many are not completely satisfactory from the point of view of penetration, color yield and levelness of dyeing.

An object of this invention is the provision of a continuous dyeing process utilizing vat or leuco base dyes wherein by the proper application of an electric current in the process improved color yields, faster and better penetration over known methods, improved levelness and other benefits result. The application of electric current to a dyeing process as required by the application results also in a reduction in the quantity of dye necessary to produce any desired color and in an increase in the number of dyes that can be used in a continuous process. Some vat or leuco dyes that heretofore have required "batch" method of dyeing on a dye jig,

can now be dyed continuously with applicant's process.

It is another object of this invention to make use of an electric current applied in such a manner that the wet fabric, fibre or yarn wet out or saturated by the dye bath becomes wholly or partially the electrolyte through which the current acts. In other words, the electric current is so applied to the dye-wetted fabric, yarn or fibre that in its passage between electrodes it is constrained to flow through the dye-wetted fabric, the latter constituting in most cases substantially the sole electrical connection between the two electrodes.

A further object of this invention is to provide a vat dyeing process in which it is possible to utilize smaller quantities of vat dyes over what have heretofore been required, and to produce with such smaller quantities improved color yields, faster and better penetration over known methods and improved levelness thereover.

To the accomplishment of the foregoing and such other objects as may hereinafter appear, this invention consists in the novel methods and apparatus hereinafter to be described and then sought to be defined in the appended claims, reference being had to the accompanying drawings forming a part hereof which show merely for the purposes of illustrative disclosure preferred embodiments of the invention, it being expressly understood, however, that various changes may be made in practice within the scope of the claims without digressing from the inventive idea.

In the drawings in which similar reference characters denote corresponding parts:

Fig. 1 is a diagrammatic elevational view of one form of apparatus for dyeing fabric with the method of the invention;

Fig. 2 is a similar partial view of the application of the method to the dyeing of warps;

Fig. 3 is an end elevational view partially in section and on an enlarged scale of the apparatus in Fig. 1;

Fig. 4 is an enlarged section taken along line 4—4 of Fig. 1 and viewed in the direction of the arrows;

Fig. 5 is a vertical elevation of a modified threading arrangement of material to be dyed useful in place of that of Fig. 1;

Fig. 6 is a diagrammatic elevational view of a modified form of apparatus for dyeing skeins according to the method of the invention; and

Fig. 7 is a graph comparing the results of dyeing a piece of fabric in a dye bath utilizing the

method of the invention, with a similar piece of fabric dyed by the same dye bath but without the use of an electric current.

In general, the process of this invention comprises wetting the fabric, yarn or other material to be dyed in a bath containing the desired dye, in quantity sufficient to obtain the desired color, a reducing agent in sufficient quantity to partially at least reduce the dye to its soluble form, water and a caustic in quantity at least sufficient to dissolve all of the reduced dye together, optionally, with dextrine or other suspending agents, such as glues, gums, starches or the like commonly used to hold the dye stuff in suspension until applied to the material to be dyed. The material to be dyed is wetted in a warm dye bath and the wetted material is then passed between a pair of electrodes of alkali resisting metal such as an iron-positive and a nickel-negative electrode to which an electric potential has been applied, positive to the iron and negative to the nickel. Current between the electrodes necessarily flows in the path created by the wetted material lying between the electrodes, which there constitutes the electrolyte and the sole path for such current. The speed of passage of the material to be dyed through the bath and between the electrodes is rapid. The material is in continuous motion. In the electrolytic zone of treatment, it is probable that the electric current quickly completes the reduction of any unreduced dye to its soluble form (leuco-base) and, in the excessive alkali present, speeds the solution of said reduced dye in the dye bath retained on said wetted material and effects quick uniform penetration of the fibres of the material being dyed with the reduced leuco-base dye.

Thereafter the still wetted material leaving the electrolytic zone is subjected to reoxidation in any of the known ways to reoxidize the reduced leuco base dye to its original state producing thereby the desired color in the material. Subsequently this material is finished by being treated by customary rinsing, soaping, rinsing, calendering and dyeing or other finishing processes. The finished material is found to have improved color penetration, improved levelness and better color yield over earlier processes, and even over the product of the same process but from which the step of electrolytic treatment has been omitted.

This process is applicable to the treatment of woven cloth, yarn, warps, skeins and other fibres capable of being dyed with vat dyes.

Suitable apparatus for carrying out this process will now be described.

Referring to the drawings, the first to Figs. 1, 2, 3 and 4, 10 denotes a dye vat. This vat, in the embodiment shown, is comparatively shallow. Suitable means (not shown) for heating the contents of the vat may be provided. A guide roller 11 is supported suitably from said vat. A mangle M is arranged to be used with this vat. This mangle comprises suitable standards 12 (Figs. 1, 2, 3) arranged at opposite ends of the vat 10. Each standard has a substantially vertical slot 13. A set of bearing blocks 14, 15 and 16 are slidably mounted in each slot 13. The bearing blocks 14 each rest respectively on the bottom of its slot 13 and the two are provided with axially aligned bored bearings 17 (Fig. 4) in which the opposite ends 18 of a rotatable roller shaft 19 are carried. The bearings 17 preferably are non-conductive electrically. Shaft 19 ex-

tends through suitable openings 20 in the opposite end walls 21 of the vat 10 and carries an anode roller 22. The roller is so located with respect to vat 10 that it is only partially submerged in the dye bath B therein. Both shaft 19 and roller 22 are of metal and, preferably, roller 22 is of low carbon content iron. (It may be of some other alkali-resistant metal.) The roller 22 is conveniently connected to the positive terminal (+) of a power source, for example by a lead 23 and a suitable contact brush 24 insulatively carried by one of the standards 12 and in electrical contact with a shaft end 18. A simple rheostat R or other means such as a lamp bank for controlling the current may be connected in the circuit of lead 23. It may be connected elsewhere in the circuit.

An intermediate roller 25 is supported above roller 22 on a shaft 26 extending between the bearing blocks 15, the shaft ends 27 of shaft 26 being supported in suitable bearings 28 similar to bearings 17. This roller 25 is either entirely of rubber or other insulating material or is provided with a covering or casing 29 of rubber or other suitable insulating material. Roller 25 is movable toward and away from roller 22 by corresponding movement of slide blocks 15 in slots 13.

A cathode roller 30 is supported above roller 25 on a shaft 31 extending between the bearing blocks 16, the shaft end 32 of shaft 31 being supported in suitable non-conductive bearings 33 similar to bearings 17. This roller 30, and its shaft 31 are both electrically conductive. Roller 30 is of metal and preferably nickel or some other metal having a nickel coating. The coating or roller in toto may be of some other alkali-resistant metal. It is movable toward and away from the roller 25 by corresponding movement of the blocks 16 in slot 13. The pressure between the surfaces of rollers 25 and 22 and between the surface of rollers 30 and 25 may be adjusted in any suitable manner. For example, pressure screws 35 mounted on standards 12 and adapted to engage the respective blocks 16, may serve to provide required pressure on blocks 16 and consequently on rollers 30 and 25.

Roller 30 is conveniently connected to the negative terminal (-) of a power source for example by a lead 36 and a suitable contact brush 37 insulatively carried by one of the standards 12 and in electrical contact with the shaft end 32. Since the shaft end 32 is movable vertically, provision is made, in any well known manner, to insure contact between it and brush 37 notwithstanding any vertical movement of the roller.

The web of cloth C to be dyed is drawn from a bolt or roll (not shown), passed over guide roll 11, and threaded through the mangle M by being passed under and part-way around roller 22, between it and the surface 29 of roller 25, part-way around the surface of the latter roller, and then between the surface 29 of roller 25 and the surface of roller 30. From there the cloth may be led over a guide roller 40 and a series of guide rolls 41 into an oxidizing bath 42 of a developer. It then may pass over another series of guide rolls 43 into a rinsing bath 44 of a rinser and from there over a series of guide rolls 45 into a soaping bath 46 of a soaper and then to other conventional rinsers and other apparatus (not shown), and finally over a set of drying rolls 47 in a dryer. The developer, rinser, soaper, etc., and dryer are optionally provided and arranged

as necessary, constitute finishing means and may be of any known types.

In Fig. 2 the web of cloth C is replaced by warp W drawn from a warp beam or roll 50. The warp is guided over roller 11 and is threaded through the mangle M about rollers 22, 25 and 30 in the same manner as cloth C and then led to equipment like the developer, rinser and other finishing devices in the same manner as cloth C.

In Fig. 5 a modified method of threading the web of cloth C', through mangle M, around rollers 22, 25 and 30 is shown. Vat 10' is provided with an auxiliary guide roll 51 located below the usual level of the dye bath B' in said vat. The web of cloth C' here is led over guide roll 11, into the bath and around roll 51, up out of the bath, then between rollers 22 and surface 29 of roller 25, part way around the surface 29 of the latter, then between the surface 29 of roller 25 and the surface of roller 30, and part way around the surface of the latter, and over the top of the roller 30 to a guide roll 40' from whence it may be led to a developer rinser, and other finishing equipment (not shown) similar to that beyond roller 40 of Fig. 1.

In each instance, it will be noted that the web of cloth C, warp W or web of cloth C' passes out of the dye bath before it passes between rollers 22 and the surface 29 of rollers 25, and that the dye-wetted portion of the web of cloth C, or warp W, or web of cloth C' which extends partly around the rubber covering 29 of roll 25 completes the electric circuit from the iron-positive roll 22 to nickel- or nickel-covered-negative roll 30, the path of the current being of necessity through the respective dye-wetted portions Ca, C'a or Wa of the webs of cloth C, C' or warp W.

The process of this invention is applicable also to skein dyeing. Apparatus for such purpose is illustrated in Fig. 6. Herein a shallow vat 55 is provided. Frames 56 are suitably supported with respect to the vat. Each frame has vertically aligned horizontally extending rotatable rollers 57, 58, 59. Each of the rollers 57 is so positioned on its frame 56 as to be partially submerged in the dye bath B'' contained in the vat 55. Rollers 57 and their axles 60 are electrically conductive and rollers 57 are preferably of low carbon content iron. They may be of other material mentioned as suitable for rollers 22.

Each of the rollers 58 is positioned on its frame 56 well above the surface of the dye bath and at a distance determined by the size of the skeins Sk, one of which is removably mounted between each pair of rollers 57 and 58. Rollers 58 are preferably rubber or rubber covered. They may be of other suitable insulating material.

Each of the rollers 59 is adjustably positioned on its frame 56 by its axle 62 whereby it may be used to press against the skein Sk passing over the top of the corresponding roller 58 and moved away from the latter to permit removal of the skeins. The frames 56 are movable vertically to permit such removal of the skeins. The rollers 59 and their axles 62 are electrically conductive and rollers 59 are, preferably, either of nickel or have nickel-coated surfaces. They may be of the other material mentioned as suitable for rollers 30. They or all of the rollers 57, 58 and 59 may be suitably driven to rotate the skeins Sk removably threaded around them as described. Rollers 57 and 59 are respectively connected to the positive (+) and negative (-) terminals of an electric power source through conduits 63, 64 and electrical brushes 65, 66 conveniently applied to

the axles 60 and 62. Other suitable means of applying a potential to the rollers 57 and 59 may be employed. A lamp bank L may be provided in the electric circuit to control current therein or a rheostat may be used.

As with the apparatus of Fig. 1, the dye-bath-wetted skeins Sk constitute substantially the electrolyte and the sole electrical path between pairs of rollers 57 and 59 so that the wetted skein portions serve as an electrolyte and the electric current is forced to flow through such wetted skeins and produce the same superior results in skein dyeing as with web and warp dyeing.

In carrying out the dyeing process of the invention, specific examples of actual runs are as follows:

#### Example 1

Using apparatus similar to that of Fig. 1, a vat dye bath was prepared from the following ingredients:

8 gms. Ponsol Jade Green S.  
6 gms. caustic soda  
5 gms. dextrine  
25 Water  
1.8 gms. sodium hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$   
400 ml.

In preparing the mixture the dextrine was heated to paste, then the caustic and dye and water were added. Just before use, the sodium hydrosulfite was added. This bath was placed in the vat 10 and heated to approximately 145° F. ( $\pm 2^\circ$ ). A cloth web C from a roll of bleached and mercerized, white cotton cloth 80 x 80—39"—4.00/yd. grey construction (that is 80 threads to the inch both warp and filling, 39 inches wide and weighing 4 yards to the pound in the grey construction) was passed through the vat and threaded through mangle M around rollers 22, 25 and 30 as shown in Fig. 1. A potential of about 100 volts D. C. was applied across rollers 22 and 30 and the cloth web C moved through the dye bath and around rolls 22, 25 and 30 by rotation of the rolls. When the wetted cloth lay on the rollers the potential was then found to drop to 100 to 105 volts. In its passage through the dye bath the cloth web C became wetted thereby and then passed around rolls 22, 25 and 30. From the tangent contact line between roll 22 and surface 29 of roll 25 to the tangent contact line between the surfaces of rollers 25 and 30, the dye saturated cloth web Ca lying on the rubber surface 29 of roller 25 acted as an electrolyte and constituted the sole electrical conductor completing the electrical circuit between the two rolls 22 and 30.

From roll 30 the electrically treated web was passed through a developing and rinsing bath 42 containing approximately 1/2% sodium perborate maintained at approximately 120° F. in any suitable way to oxidize the leuco-base color back to its insoluble form. The fabric then was rinsed at 44, soaped at the boil at 46, rinsed and dried in well known manner.

The resulting dyed fabric web showed superior results as to fabric penetration, levelness of dyeing and color yield, over a length of similar cloth treated in the identical bath and in all other ways the same but without the use of electric current.

Fig. 7 illustrates the superior results by spectrophotometric curves obtained with a recording spectrophotometer. The curve marked C. C. is

for cloth dyed with the ponsol jade green S bath of Example 1 and treated electrically as described. That marked N. C. is for similar cloth similarly dyed in the same bath but without the use of electricity. For the curves the abscissae represent wavelengths in millimicrons over the visible range of the spectrum. The ordinates represent spectral reflection factors in terms of magnesium oxide. A spectrophotometric curve for magnesium oxide would be a substantially horizontal line in the region of the ordinate 1 (not shown). The lower the spectral reflection factor, the darker the color. Curve C. C. shows that the electrically treated sample is darker throughout the visible range of the spectrum. Since both samples were dyed in the same bath, this indicates clearly superior fabric penetration and color yield for the electrical dyeing process.

Visual inspection of the swatches from which the spectrophotometric tests were made gives the same impression. The electrically processed swatch is uniformly darker, more pleasing and more levelly dyed.

The dye bath used in Example 1 as well as in the other examples is similar to conventional dye baths except that in general it has a relatively smaller quantity of vat dye and a higher caustic soda content over such conventional vat dye baths. Tests show that increased caustic soda content and electric treatment results in better color yields. In general, about 10% less dye-stuff is needed, i. e. only about  $\frac{1}{10}$  of the dyestuff necessary for conventional vat baths is necessary. Such saving amounts to at least about 60 cents per pound of dyestuff. Since the cost of excess alkali is small, only 2 to 3 cents per pound, the saving is considerable. This example and those following show excess alkali in various increased quantities over that in conventional baths.

The dextrine is used to help hold the dyestuff in suspension until applied. It and other agents such as glues, gums, and starches are regularly used for this purpose.

#### Example 2

Using the same apparatus of Fig. 1 with a cloth web C from a roll of bleached white cloth 64 x 60, 38 $\frac{1}{2}$ "—5.35 grey construction (that is 64 warp threads and 60 filling threads to the inch, 38 $\frac{1}{2}$  inches wide and weighing 5.35 yards to the pound in the grey construction) threaded through the apparatus as there shown, the vat 10 was filled with a vat dye bath having ingredients in the following proportions:

8 gms. Indanthrene Orange RKWP  
8 gms. caustic soda  
5 gms. dextrine  
Water  
2 gms. sodium hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$   
400 ml.

This dye bath was warmed to approximately 160° F. A potential of about 110 volts D. C. was applied to the rollers 22 and 30 (+ to roller 22 and - to roller 30) and the cloth web C moved through the bath, squeezed between the surfaces of rollers 22 and 25, then squeezed between the surfaces of rollers 25 and 30, being subjected to the action of the electric current passing through the dye saturated cloth lying on the rubber covered surface 29 of roller 25, said portion of the cloth Ca acting as the electrolyte between the rion-positive roller 22 and the nickel- or nickel-surfaced-negative roller 30. The cloth web C was

then passed through a developing (oxidizing bath) warmed to about 120° in suitable manner, then rinsed, soaped at the boil, rinsed or otherwise finished and dried in the usual way. The resulting dyed web of cloth produced a product superior as to fabric penetration, levelness of dyeing and color yield over that in similar cloth treated in the same bath but without the use of electricity.

It is to be noted that in this bath, the 2 grams of sodium hydrosulfite (reducing agent)  $\text{Na}_2\text{S}_2\text{O}_4$  was insufficient to reduce the leuco dye compound completely to its leuco base.

#### Example 3

With the same apparatus as Fig. 1 and with a roll of bleached white plain cotton cloth of 64 x 60, 38 $\frac{1}{2}$ "—5.35 grey construction (the same type of cloth as in Example 2) a dye bath as follows was used:

8 gms. Indanthrene Red Violet BRNWP  
16 gms. caustic soda  
8 gms. dextrine  
Water  
4 gms. sodium hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$   
400 ml.

The dye bath was warmed to 140°—160° F. placed in vat 10 and the cloth passed therethrough and the other apparatus of Fig. 1 in a manner similar to that of the other examples. The voltage similarly applied across rolls 22 and 30 was substantially the same, namely 110 volts. The cloth was finished as in the other examples.

The resulting dyed cloth was superior as to fabric penetration, levelness of dyeing and color yield over that in similar cloth treated in the same bath but without the use of electricity. This was so withstanding the fact that in this dye bath sufficient reducing agent sodium hydrosulfite was present to produce a bath that was in dyehouse language "dye reduced," i. e. sufficient to reduce the leuco dye compound substantially completely to its leuco base. It will be noted further that the caustic soda content was still higher than in Example 2.

#### Example 4

With the same apparatus and a cloth roll whose grey construction was 80 x 80, 39"—4.00 yd. (that is 80 warp and filling threads to the inch, 39 inches wide and weighing 4 yards to the pound in the grey construction) was bleached and then threaded through the apparatus of Fig. 1. A dye bath consisting of the following was used:

8 gms. Indanthrene Red FBBO  
8 gms. sodium hydroxide (caustic soda)  
8 gms. dextrine  
Water  
1 $\frac{1}{2}$  gms. sodium hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$   
400 ml.

This bath heated to approximately 160° F. was placed in vat 10 and the cloth passed therethrough and the other apparatus of Fig. 1 in a manner similar to that of the other examples. The D. C. voltage similarly applied across rolls 22 and 30 was substantially the same, namely 110 volts. The cloth was finished as in the other examples.

The resulting dyed cloth was superior as to fabric penetration, levelness of dyeing and color yield over that in a portion of its length which was dyed without the use of the electric current.

A clear demarcation was visible between the portion dyed, using electricity, and that portion dyed in the same bath without the application of electric current. In this bath, the caustic soda content was about the same as in Example 2, while the hydrosulfite content (1½ grams) was in the least quantity of all the examples and insufficient to produce a "dye reduced" bath.

The symbols following the name of the dye in each example are conventional identification marks well known in the dyeing art.

A characteristic of all the examples is that the caustic or alkali (caustic soda) is in excess of that conventionally used in vat dye baths. Another characteristic in most cases is that less reducing agent is used than is required to provide a "dye reduced" bath. Even when sufficient reducing agent is used to produce a "dye reduced" bath, superior results are obtained upon the use of electric current as described. Since the examples show that smaller quantities of reducing agent are sufficient, it is preferable practice to utilize the reducing agent sodium hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$  in quantities less than that which in any instance will produce a "dye reduced" bath. Of course, other suitable reducing agents may be used. They may be glucose, or any reducing agent that is active in an alkaline medium such as zinc dust or sulphoxylate-formaldehyde compound.

Many other experimental trials have been made in determining the efficacy of the process herein described.

For example, various methods of applying the electric current were tried, such as moving the cloth web between contact plates, bars and rollers. The best results were obtained when the current carrying devices were also made the rollers of the dye jig or pad mangle or mangles or similar machine. Two roll pad mangles as well as three roll pad mangles and also pluralities of each type have been tried. A pair of two roll pad mangles, the rolls of one being nickel and the rolls of the other being iron, were also tried. The two mangles were separated and the cloth threaded between, and the lower roll of each mangle dipped in the dye bath. Negative potential was connected to the nickel rolls and positive potential to the iron rolls. The lower roll of each mangle was partially submerged in the dye bath and the cloth between the two mangles lay above the dye bath constituting, when wet, one of the paths for current between the two mangles. Good results were obtained by this method, too. The best results were obtained when using two metallic contact rollers separated by one or more rubber or other insulating rollers. Particularly, the structure of Figs. 1-5 inclusive herein described proved most satisfactory.

Also many metals and combinations of metals were tried for the rollers 22 and 30. Since "vat" type colors are more soluble in the reduced state in caustic or alkaline mediums ( $\text{NaOH}$ ,  $\text{KOH}$  or  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ ), the choice of metals necessarily was restricted to those within a practical price range which can be used in alkalis. The best results were obtained with a low carbon content iron roller 22 and a nickel or nickel-coated roller 30.

This invention is capable of many variations in its application but a principal feature of the invention lies in the use of electric current applied by any means of contact bars, rods, plates, rollers, etc., in such a manner that the bath saturated fibre, yarn or fabric becomes the electrolyte or

an electrolyzed dye bath. This fibre, yarn or fabric may also be only partially saturated or partially wet out by said dyebath, or it may have previously been wet out by the dyebath and wholly or partly dried and then re-wet by means of a spray or pad rollers or otherwise without departing from the spirit of this invention. All these methods were tried and only a few of the many examples can be stated herein.

By means of this method continuous dyeing of many of the reduced or reducible type colors is much improved over former methods. The tendency of reduced dyebaths to oxidize back and yield streaky and uneven dyeings is almost entirely eliminated.

Penetration and color yield from the same strength dyebath are also much improved by this method. In the experiments with a certain dyebath run in the usual way and then with the current applied as described and on a mangle similar to the sketch of Fig. 1, the electrolyzed portion was darker in shade and with better penetration and of more even appearance than that portion run in the same dyebath and similar dyebaths of the same color content without the current flow.

After the fibres, yarn or fabric have passed through the machine or process as described, the color may be oxidized back in the usual ways used in the art of dyeing this class of colors. Thus oxidation may be done by "skying" or passing the textile through the air over a plurality of rollers or otherwise. It may be carried out by repeated passage in or through fresh water. Oxidation may be completed by chemical means as for example by passing through such agents as sodium bichromate and acid or through a solution of sodium perborate or other oxidizing agents.

Thus this invention may be used alone as a dyeing method replacing an ordinary pad mangle, or a dye jig or other device, or it may be placed in a continuous range thus widening the scope of the continuous dyeing process. The textile may thus after passing through one or more of the electrolyzing units, pass directly to a suitable oxidizing unit, then to rinsing, soaping, framing, drying, calendering, or other finishing machines. All these are known to the art of textile dyeing and finishing, and in various combinations might be used as a continuous dyeing range in connection with the electrolyzed dyebath method of this invention. This invention makes it possible to dye some colors on a continuous range which by older methods were necessarily dyed by a batch method.

The direction of current flow was tried in many trials using direct current. When both electrodes were made of the same metal, it made no difference as to the direction of flow, but in using certain combinations of metals, better results were obtained with the current flowing in a definite direction. Thus for example, when the best results were obtained using one iron (low carbon iron) roller and one nickel roller, the positive lead was connected to the iron contact and the negative lead to the nickel contact roller.

Varying voltages were applied, starting with 6 v. D. C. from a storage battery up to 120 v. D. C. from the usual power line. Other conditions being equal, increased voltages in general shortened the time necessary for the dyeing. This, however, seemed to reach a practical limit, with the dyebaths normally employed, at from 80 v. to 120 v. Different widths and different weights of fabric naturally hold varying amounts of the dyebath and therefore offer more or less resistance

to the voltage applied and hence carry less or more current. A simple rheostat or lamp bank was employed to regulate conditions for the best results.

Varying strengths of dyebaths were employed. Naturally the amount of the vat pigment itself is governed by the resulting shade or color desired. Quite a few of the common vat colors were tried, of the indigo, thio-indigo and mixed types. Most of the trials were purposely kept in the range that might be employed in practical mill usage. The amount of caustic present was varied from barely sufficient to dissolve the reduced leuco compound up to several times this amount. A slightly higher caustic content than would be employed in older methods was found desirable. On the other hand, a very small amount, less than that required to produce a dye-reduced bath, of the chemical reducing agent sodium hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$  yields good results. The presence or absence of the usual suspending agents (gums, dextrines, etc.) is immaterial except that as with older methods, they are used to maintain an even or uniform dispersion of the pigment prior to its reduction and solution. Baths can be used containing in each 400 ml. about 8 grams of a vat dye, 4-16 grams of an alkali, 1-4 grams of a reducing agent and 5-8 grams of a suspending agent.

On a comparative scale conventional dye baths would contain in each 400 ml. of bath less than 6 grams of caustic soda or potash and specifically approximately 5 grams of caustic soda or 5 grams of caustic potash. Similarly, if used, less quantities of sodium or potassium carbonates  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  would be necessary. Such bath also would require more than 8 grams of vat dye in each 400 ml. of bath and probably in the neighborhood of 10 or more grams to produce coloring in the dyed material even approximately similar to that produced by any of the examples recited herein. In addition, such a conventional bath would require the reducing agent sodium hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$  or other reducing agent in larger quantities than that specified in any of the dye baths used in applicant's process. Specifically in each 400 ml. of bath more than 4 grams of sodium hydrosulfite or other reducing agent would be necessary. In fact as much as 5 or more grams of sodium hydrosulfite would be required for the purpose of effecting complete reduction to its soluble leuco base of the necessarily increased quantity of vat dye in such conventional bath. Accepted conventional practice appears to require substantially equal parts by weight of caustic and of reducing agent.

It is apparent, therefore, that applicant's process has economy among its advantages. There are considerable savings in the quantities of the more expensive ingredients needed, namely, of the vat dye and of sodium hydrosulfite. The reduction in production costs resulting from such saving is materially greater than the cost of additional caustic so that a substantially cheaper, more economical and more effective dyeing process results.

While specific apparatus and process have been described, it is to be understood that variations in apparatus and process within the scope of the appended claims is contemplated. There is no intention of limitation to the exact details shown and described.

What is claimed is:

1. That improvement in the process of dyeing with vat dyes comprising, providing a vat dye

bath containing a vat dye, a reducing agent in a quantity not exceeding that required to reduce said dye to its soluble form and produce a completely dye-reduced bath, and a caustic alkali in sufficient quantity to dissolve all the reduced soluble dye, wetting material to be dyed with said dye bath, and so subjecting said so wetted material at and between iron positive and nickel negative electrodes spaced apart a distance greater than the thickness of said material to the action of a direct electric current at a voltage lying between 6 and 120 volts that it constitutes a substantially long path for said electric current to effect substantially complete penetration of said material with said dye and effective dyeing thereof, and subsequently developing the dye.

2. In the process of dyeing with leuco-base dyes, the steps of providing a dye bath containing at least one of said dyes, water, a reducing agent in sufficient quantity to reduce said dye partially at least to its soluble leuco base, and caustic alkali in sufficient quantity to dissolve the dye when in its reduced soluble form, wetting material to be dyed with said dye bath, and then subjecting said wetted material at and between iron positive and nickel negative electrodes spaced apart a distance greater than the thickness of said material to the action of a direct electric current at a voltage lying between approximately 6 and 120 volts so that the wetted material constitutes a substantially long completing path for the circuit of said electric current to effect substantially complete reduction of said dye to its soluble form and its penetration into and dyeing of said material, and then finishing said dyed material to reoxidize the reduced dye therein to its original insoluble state.

3. In the process of dyeing textiles or the like with leuco-base dyes, the steps of providing a dye bath containing at least one of said dyes, water, sodium hydrosulfite in sufficient quantity to reduce said dye partially at least to its soluble leuco base, and caustic soda in sufficient quantity to permit complete solution of that of said dye in its reduced soluble form, warming said bath and wetting material to be dyed with said dye bath, then subjecting the wetted material at and between iron positive and nickel negative electrodes spaced apart a distance greater than the thickness of said material to the action of a direct electric current at a voltage lying approximately between 6 and 120 volts so that the wetted material constitutes a substantially long path for the electric current between said electrodes to effect substantially complete reduction of the dye in said wetted material to its soluble form and its penetration into and dyeing of said material.

4. In the process of continuous dyeing of textiles or the like with leuco base dyes, the steps of providing a dye bath containing at least one of said dyes, water, a reducing agent in sufficient quantity to reduce said dye partially at least to its soluble leuco base, and caustic alkali in sufficient quantity to permit complete solution of any of said dye in its reduced soluble form, warming said bath, wetting material to be dyed with said dye bath, then in continuation of said process and directly following the wetting, subjecting the wetted material at and between iron-positive and nickel-negative electrodes spaced apart a distance greater than the thickness of said material to the action of a direct current at a voltage lying between 6 and 120 volts so that the wetted material as it moves between said electrodes com-

stitutes a substantially long path for the electric current between said electrodes to effect a substantially complete reduction of the dye in said wetted material to its soluble form and its penetration into and dyeing of said material, and thereafter in continuation and directly following the electric current treatment, subjecting the current-treated material to oxidation to reoxidize the reduced dye retained therein to its insoluble form and then finishing said material, all of said steps following each other sequentially in a continuous manner.

5. In the process of dyeing with leuco-base dyes, the steps of providing a dye bath containing at least one of said dyes, water, sodium hydrosulfite in sufficient quantity to reduce said dye partially at least to its soluble leuco base, and caustic soda in sufficient quantity to permit complete solution of any of said dye in its reduced soluble form, warming said bath to 145° to 160° F. and wetting material to be dyed with said dye bath, then subjecting the wetted material at and between iron positive and nickel negative electrodes spaced apart a distance greater than the thickness of said material to the action of a direct electric current at a voltage lying approximately between 6 and 120 volts so that the wetted material constitutes a substantially long and sole path for the electric current as it moves between said electrodes to effect substantially complete reduction of the dye in said wetted material to its soluble form and its penetration into and dyeing of said material, and thereafter subjecting said material to oxidation to reoxidize the reduced dye therein to its insoluble state and then finishing said dyed material.

6. That improvement in the process of dyeing with vat dyes which are normally insoluble and require reduction to make them soluble comprising, providing a vat dye bath containing besides water in each 400 ml., a sufficient quantity of a vat dye to produce a desired color, more than 4 grams of a caustic alkali and in excess of that required by a conventional dye bath, and not more than 4 grams of a reducing agent, and in a quantity less than that required by said conventional dye bath, warming said vat dye bath, wetting material to be dyed in said warmed bath, so subjecting said so wetted material at and between iron positive and nickel negative electrodes spaced apart a distance greater than the thickness of said material to the action of a direct electric current at a voltage lying approximately between 6 and 120 volts that it constitutes a substantially long completing path for the circuit of said electric current as the material moves between said electrodes to effect substantially complete reduction of said vat dye to its soluble form and its penetration and dyeing of said material, and thereafter reoxidizing the reduced dye retained in said material to its original insoluble state.

7. That improvement in the process of dyeing with vat dyes which are normally insoluble and require reduction to make them soluble comprising providing a vat dye bath containing besides water, in each 400 ml., about 8 grams of a vat dye, 4-16 grams of a caustic alkali, 1-4 grams of a reducing agent, 5-8 grams of a suspending agent, warming said bath to between 140-160° F., wetting material to be dyed with said warmed bath, so subjecting said so wetted material at and between iron positive and nickel negative electrodes spaced apart a distance greater than the thickness of said material to the action of a direct electric current at a voltage lying between 6 and 120 volts that it constitutes a substantially long completing path for the circuit of said electric current as the material moves between said electrodes to effect substantially complete reduction of said dye to its soluble form and its penetration into and dyeing of said material, and thereafter reoxidizing the reduced dye in said material to its original insoluble state.

8. That improvement in the process of dyeing textiles with vat dyes which are normally insoluble and require reduction to make them soluble comprising providing a vat dye bath containing besides water, in each 400 ml., about 8 grams of a vat dye, 4-16 grams of a caustic alkali, 1-4 grams of a reducing agent, 5-8 grams of a suspending agent, warming said bath to between 140°-160° F. wetting material to be dyed in said warmed bath, so subjecting said so wetted material at and between iron positive and nickel negative electrodes spaced apart a greater distance than the thickness of the material to the action of a direct electric current at a voltage lying between approximately 6 and approximately 120 volts to effect substantially complete reduction of said dye to its soluble form and its penetration into said material, and subsequently developing the dye.

9. That improvement in the process of dyeing textiles or the like with vat dyes which are normally insoluble and require reduction to their leuco-base to make them soluble comprising providing a vat dye bath containing besides water, in each 400 ml., about 8 grams of a vat dye, 4-16 grams of caustic soda, 1-4 grams of sodium hydrosulfite and 5-8 grams of dextrine, warming said bath to between 140°-160° F., wetting the textile to be dyed in the warmed bath, and then so subjecting said so wetted textile at and between iron positive and nickel negative electrodes spaced apart a greater distance than the thickness of the material to the action of a direct electric current at a voltage lying between approximately 6 and approximately 120 volts to effect substantially complete reduction of said dye to its soluble leuco-base form and its penetration into and dyeing of said textile, and subsequently developing the dye.

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