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**Continuation-in-part of application Ser. No. 660,167, Aug. 3, 1967, now Patent No. 3,498,086, Continuation-in-part of application Ser. No. 614,520, Feb. 7, 1967, now abandoned.**

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] **PROCESS FOR PRODUCING HEAT-INDUCED EFFECTS ON TEXTILE FIBERS AND FABRICS**  
**5 Claims, 12 Drawing Figs.**

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 8/1 A, 8/4, 8/8, 8/34, 8/35, 8/39, 8/41 R, 8/42 R, 8/62,  
 8/69, 8/74, 8/116.3, 8/120, 8/65, 34/41, 117/16,  
 117/25, 117/119.8, 8/176

] Int. Cl..... **D06p 5/00**

] Field of Search..... 8/176, 2.5,  
 62, 14, 74, 34, 37, 41, 42, 65, 69; 34/144, 41;  
 117/16, 26, 119, 8

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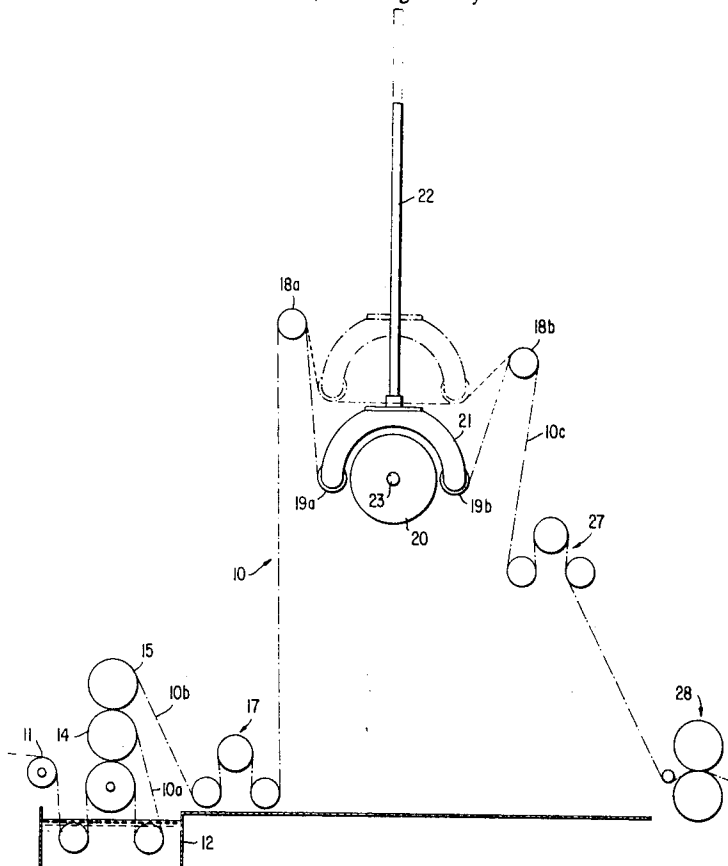
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**ABSTRACT:** A process for producing heat-induced effects on textiles, films or other suitable flexible substrata such as for example:

1. physical migration of dyes, chemicals or pigments;
2. heat fixation of dyes, chemicals or pigments;
3. development of dyes, chemicals or pigments by the reaction of two or more components, or by heat-induced transformation of an intermediate;
4. curing of creaseproofing agents, cross-linking agents, synthetic resins, natural gums, etc.;
5. discharging or destroying of dyes, pigments, etc.;
6. drying of said flexible substrata.

Localized and overall chemical reactions and physical changes on or in such substrata are obtained by application of heat, i.e. a temperature from about 500° F. to about 1,500° F., by contact of the flexible substrata with a heated surface within a short period of contact, e.g. a fraction of a minute, generally.



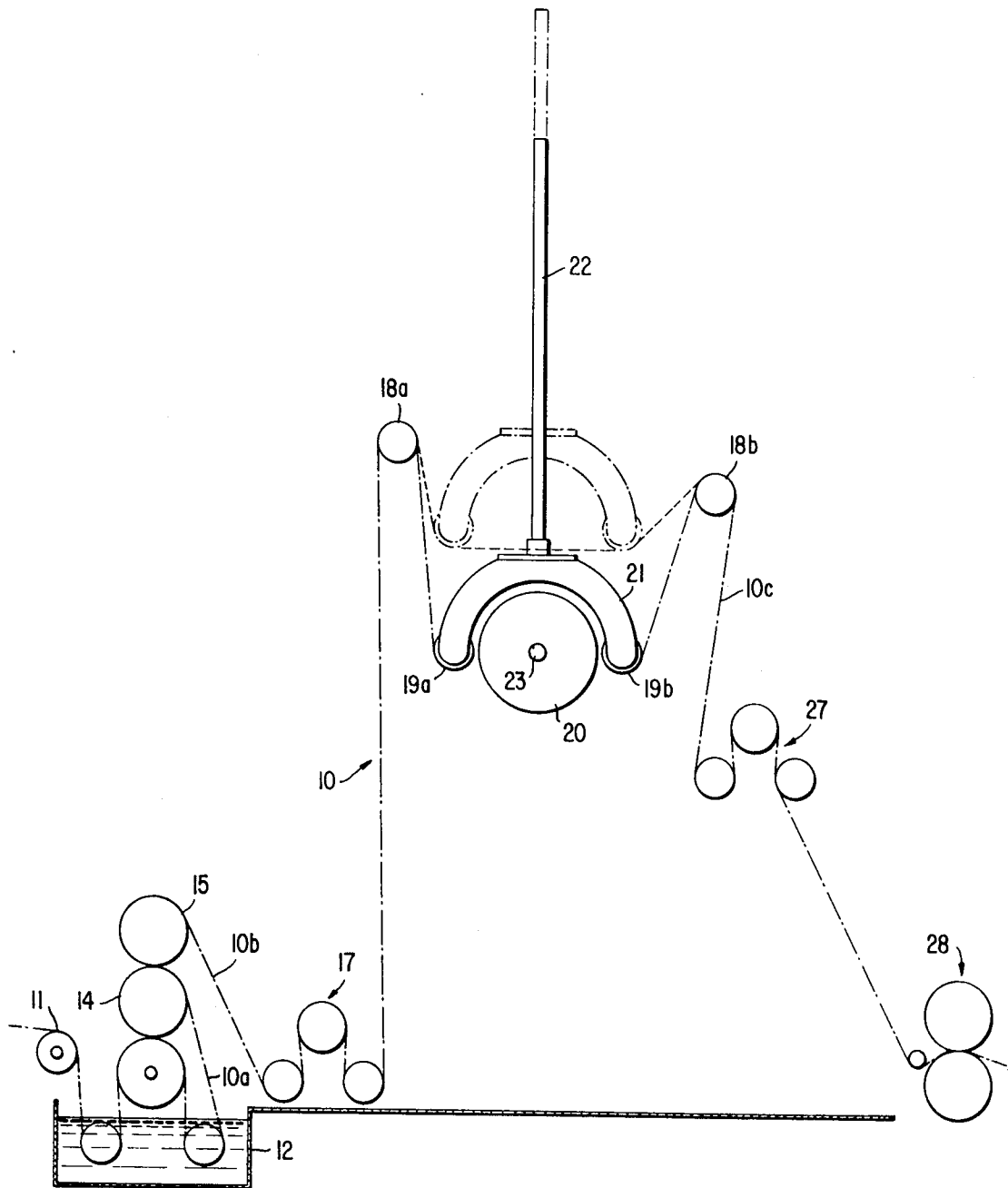


FIG. I

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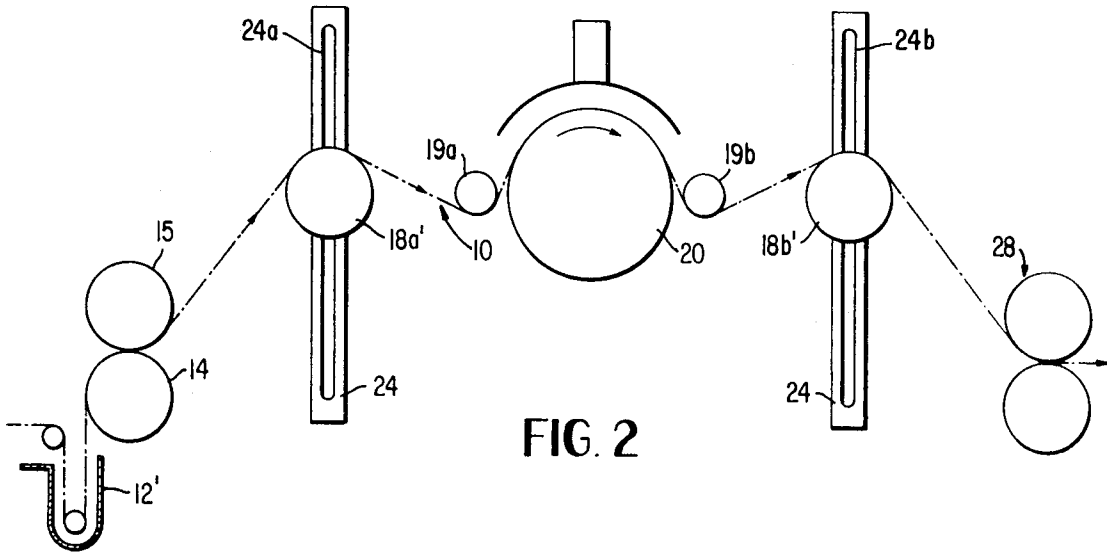


FIG. 2

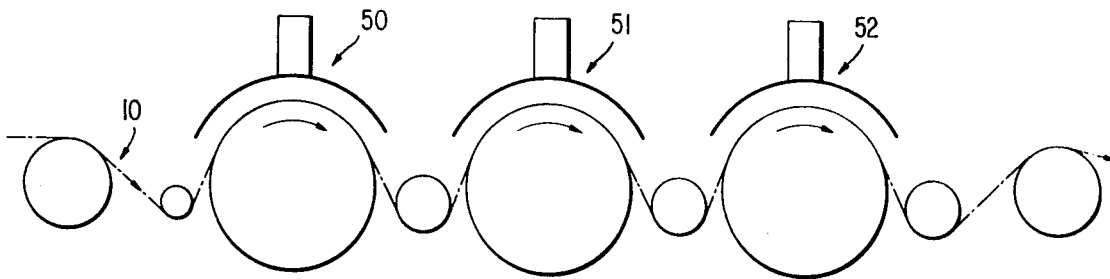


FIG. 3

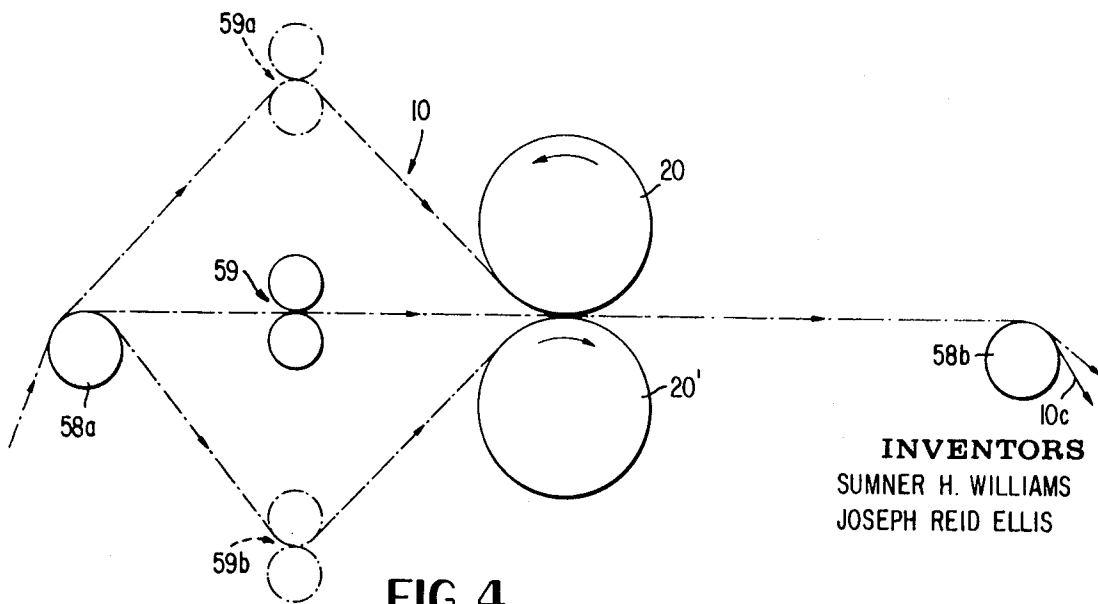


FIG. 4

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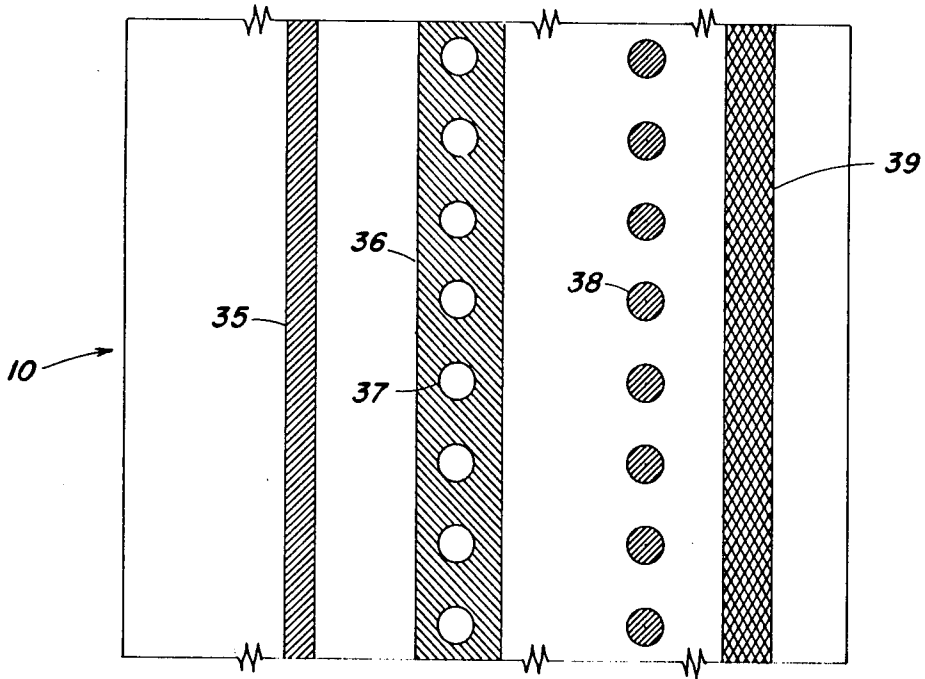


Fig. 6.

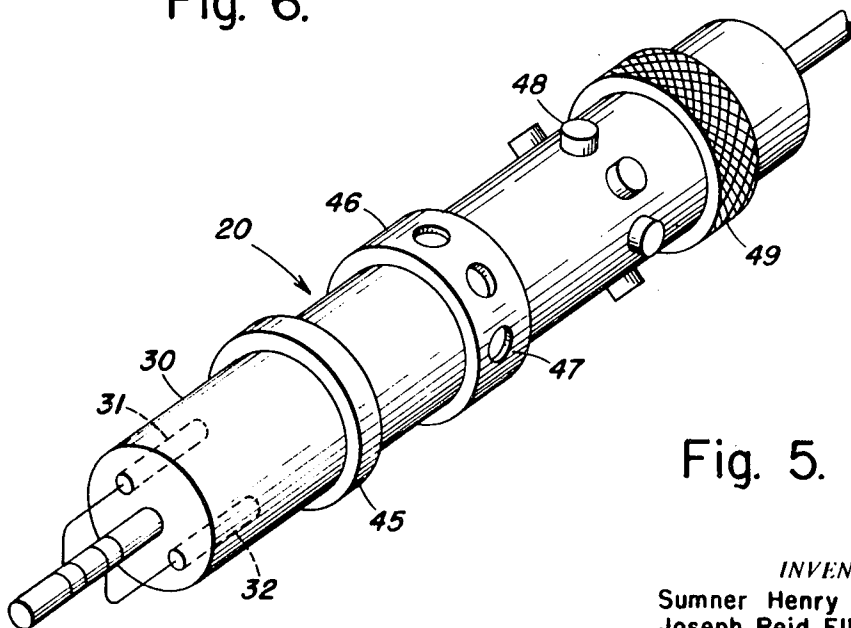


Fig. 5.

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Fig. 7.

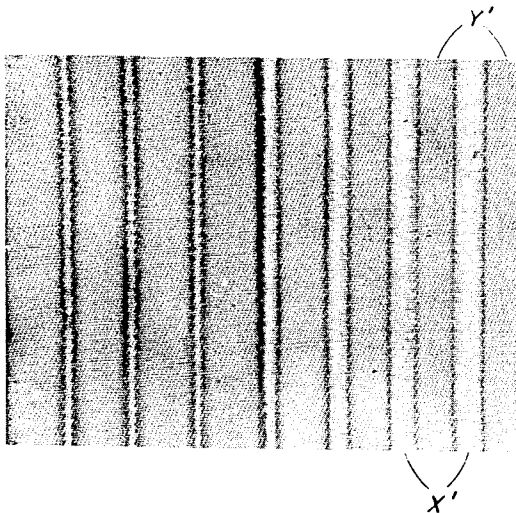
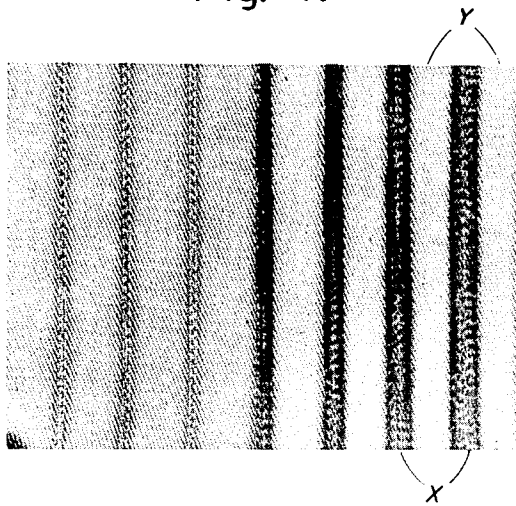


Fig. 8.

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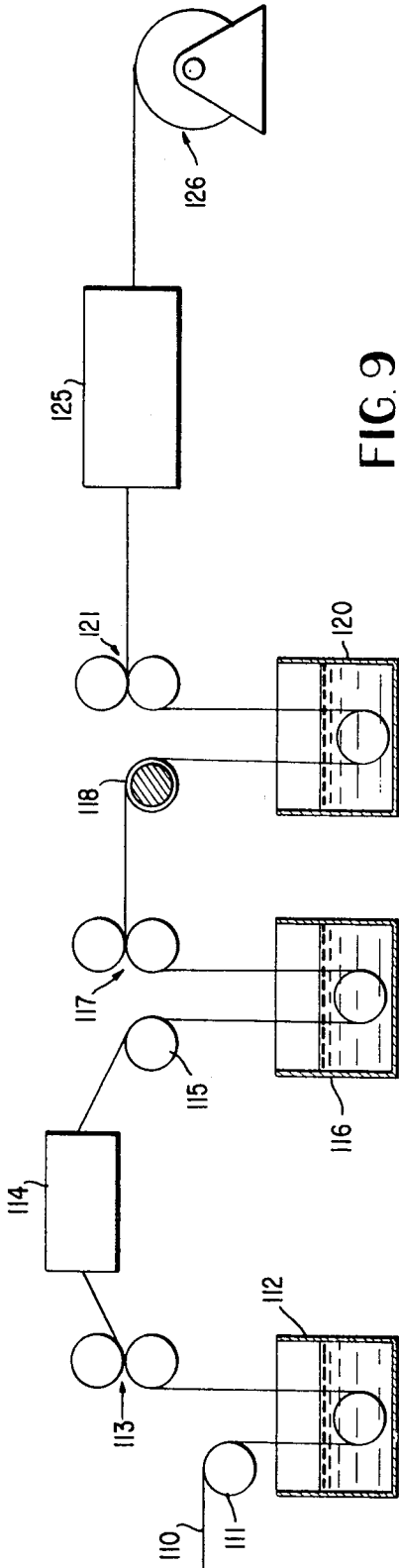


FIG. 9

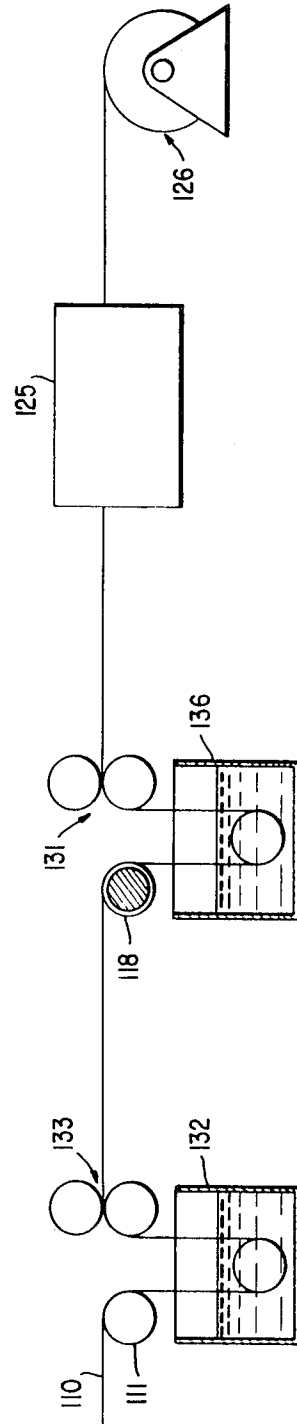


FIG. 10

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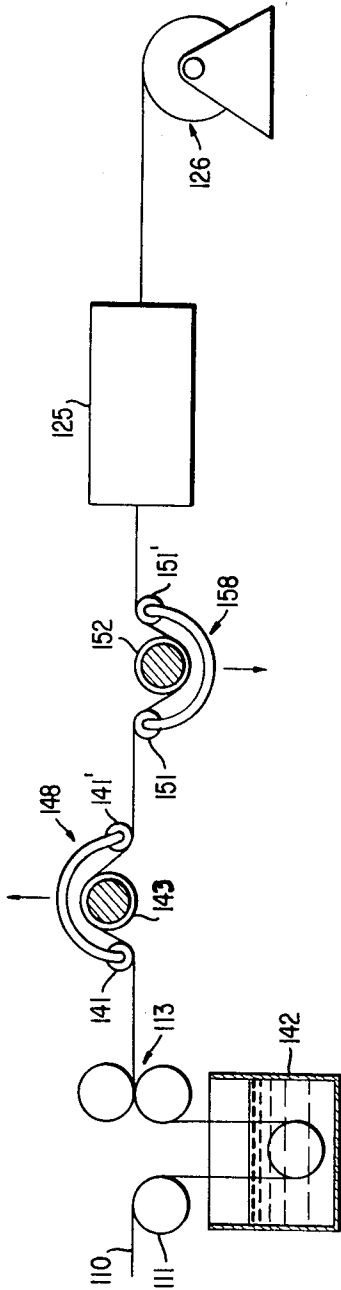


FIG. 11

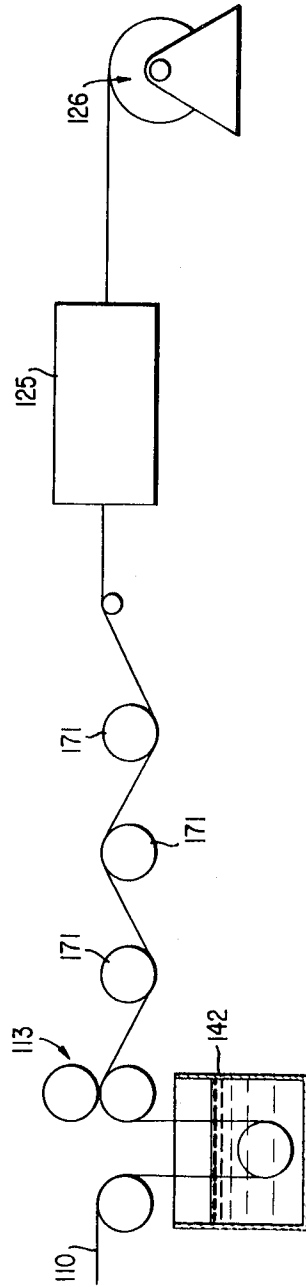


FIG. 12

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## PROCESS FOR PRODUCING HEAT-INDUCED EFFECTS ON TEXTILE FIBERS AND FABRICS

This application is a continuation-in-part of copending application Ser. Nos. 614,520 now abandoned and 660,167 now U.S. Pat. No. 3,498,086 filed respectively Feb. 7, 1967 and Aug. 3, 1967.

The present invention is directed to a novel process for conducting overall or localized chemical reactions and/or physical changes on or in flexible substrata such as textiles, films, etc. by the application of heat through contact with a heated surface, e.g. a patterned surface. More particularly, the present invention is directed to a process of producing overall or localized chemical reactions and/or physical changes such as physical migration or heat fixation of dyes, chemicals or pigments, development of dyes, chemicals or pigments through a reaction of two or more components or transformation from an intermediate therefor, curing of creaseproofing and cross-linking agents, synthetic and natural resins, discharging or destroying of dyes and pigments, and drying of fibers, fabrics and other flexible substrata through the application of an intense heat, i.e. from about 500° to about 1,500° F., for a short period of time, i.e. generally a fraction of a minute, the contact and reaction time being as little as one-fifth of a second or less.

While the process of the present invention is applicable to any and all of the above-noted chemical and physical changes, the process of the present invention is particularly applicable to a process for producing patterns and/or physical designs on a textile fabric through a phenomenon known as migration. By such a process, it is possible to produce a fabric having patterns of enhanced or intensified color values with respect to the background and fabrics with patterns in contrasting multishade or variable physical effects.

In a generally employed practice of coloring fabrics with soluble or dispersed dyes or pigments by a continuous process, the fabric is passed through a bath containing the coloring material, whereby the fabric is padded to a substantially uniform shade of intensity. Generally, the bath contains the dye or pigment in solution or dispersion containing a variety of dyeing assistants. Generally, the fabric as it is removed from the bath through squeeze rollers is saturated therewith, and in many prior art processes the fabric so saturated is then dried or semidried before further treatments. When water-soluble dyes or dispersed dyes or pigments are applied to a fabric, the excess liquid is squeezed off and the fabric is dried or semidried for best results prior to reduction or oxidation or other chemical treatment and further processing including drying as a final step. In either process, the first drying step is carried out by a controlled heating system which can comprise a variety of different apparatus. Thus for example, the controlled heating system may consist of a series of heated cylinders, hot air ovens, radiation driers, or any combinations thereof. In such drying processes, variable factors such as humidity, temperature, air velocity and speed of the fabric web are carefully controlled to prevent the fabric from having uneven coloration.

In this regard, wherein it was desired in the past to produce fabrics containing patterns, designs or other similar physical effects involving contrasting coloration or variance in color intensity, such effects have been produced by weaving the various colored yarns in the desired design or pattern, or alternatively, by direct or discharge printing the designs onto the fabric. Additional methods for producing such effects have included, for example, the weaving of a color effect thread and then over dyeing the fabric or embossing designs under high pressures. All of such previous methods for producing the design or pattern effect of contrasting colors and/or color intensities on the dyed fabric have been relatively costly and time consuming. Accordingly, such previous prior art methods have not been found to be sufficiently economical for the production of many diverse effects such as obtained by the processes described below.

Such inherent disadvantages and deficiencies of the prior art have been overcome in accordance with the present invention wherein it has been discovered that various chemical and/or physical changes can be produced on fabrics or similar surfaces by contacting such surfaces with a heated surface at a temperature of at least 500° F. preferably at least 525°-550° F. and up to 1,500° F. or more for a period of time of a fraction of a minute.

These inherent deficiencies and disadvantages or prior art methods have, of course, been overcome in accordance with at least one embodiment of the present invention. Again, this embodiment relates to effecting a local or overall chemical and physical migration of a dye or pigment through the local application of a high temperature through contact of the fabric saturated with color with a heated roller, e.g., a patterned roller. In this way, the application of a high temperature locally or overall to effect the migration of the dye to those points of the fabric to which the heat is applied is such that the fabric will appear as a patterned material having variances in color density and variances in color intensity according to the character of the heated surfaces.

Further, while the present invention has presented a great improvement with respect to such processes of producing patterns or similar physical effects or designs on textiles and similar fabrics, the present invention also provides improvements in other processes involving chemical and physical mechanisms susceptible to initiation and acceleration by heat.

Moreover, the character of many of the effects produced in accordance with the present invention are new and are not reproducible by any of the processes or mechanisms heretofore known in the prior art.

Thus, for example, conventional heat fixation processes have generally involved the fixing of dyes or pigments onto a fabric by heating the fabric in ovens, agers or steamers or cylinders or combinations with radiant heating for periods of time of about 90 seconds or more. These conventional uses of such equipment have generally been carried out at lower temperatures and over prolonged periods of time since the materials being treated could not withstand any higher temperatures, within the conventionally utilized apparatus.

In accordance with the present invention, however, by carrying out a heat fixation process at a temperature of 500° F. to 1,500° F., for example, by contacting the fabric containing the dye or pigment to be fixed with a heated roller or other surface it is possible to complete the heat-fixation reaction in a time comprising a fraction of a second or of a minute, rather than the fixation time now required in previous prior art processes.

While some attempts have been made to eliminate the generally employed long heating periods required in conventional heat fixation processes, such attempts have not been satisfactory for a number of reasons. Thus for example, U.S. Pat. No. 3,171,711 discloses a process for the fixation of vat dyestuffs on cellulose fabrics which comprises steaming for a period of less than 2 minutes. Such a process, however, is complicated by the fact that a particularly costly catalyst composition must be utilized in order to achieve even this shortened fixation time. Thus, the patent discloses that the cellulose fabric to which the vat dyestuff is to be fixed has applied thereto a thickened vat dyestuff dispersion, an alkali, a reducing agent for the vat dyestuff, and as a reduction catalyst a complex of cobalt with a  $\beta$ -hydroxyanthraquinone. It can be obviously seen that such a process which may be effective to reduce the heat fixation period to slightly less than 2 minutes, because of the necessity of employing an expensive catalyst material in a particular type of system, cannot be economically competitive with the improved process of the present invention wherein fixation of a dyestuff is accomplished within a fraction of a minute by contact of a dyed fabric with a heated roller or other surface at an elevated temperature as specified above.

Similarly, with respect to the development of dyestuffs on fabrics, that is, a development process involving a chemical reaction such as in situ azoic dye formation, reduction, oxida-



tion, etc., processes effecting the same in the past have generally involved the application of heat over a relatively extended period of time. Again, such prior art processes can be greatly improved in accordance with the process of the present invention, by which the development of dyes can be achieved in a fraction of a minute under the conditions specified above. Thus, in accordance with the present invention, it has been discovered that it is possible to greatly reduce the development time generally employed in the development of dyestuffs on fabrics by contacting the fabric containing the necessary chemical reagents with a heated roller or other surface at a temperature in the order of  $-500^{\circ}\text{F.}$  to  $1,500^{\circ}\text{F.}$ , or higher so as to effect the necessary chemical reaction in a shortened period of time and in a manner not heretofore contemplated by any previously employed prior art processes.

In a similar manner, previously employed processes for curing synthetic resins, for example, on textile fibers and fabrics such as in the preparation of permanent press fabrics, have involved long aging or curing processes wherein the fabric treated with a synthetic resin has been treated in an oven for an extended period of time. Here again, such a process for curing synthetic resins on textile fibers and fabrics can be greatly improved in accordance with the process of the present invention, by which it is possible to reduce the curing time to a fraction of a minute. In this respect again, in accordance with the present invention it has been discovered that a synthetic resin can be cured on or in a textile fiber, fabric or other flexible substrata within a fraction of a minute by contacting the substrata containing the synthetic resin to be cured with a heated roller or the like at an elevated temperature within the order of about  $500^{\circ}\text{F.}$  to  $1,500^{\circ}\text{F.}$  In this way, it is possible to rapidly cure a resin to fix a dye or pigment to the material or simply cure the resin itself to effect various changes in the physical properties of the material.

In addition, the process of the present invention is particularly applicable in discharging printing wherein esthetic effects are produced by the localized discharging or destroying of dyes applied to textile fabrics.

Discharge printing is the destructive removal of dye or dye components from selected areas of textiles containing the dye or dye components. Thus, in white discharge printing the selected areas are left as white on a colored background, while in colored or illuminated discharge printing the selected areas lose their original color and are dyed a different color by a dye incorporated in the discharge composition. The discharging reaction must take place where the dye to be discharged, that is destroyed, is located.

Generally employed discharge printing processes have involved the application of the discharge composition followed by steaming over a prolonged period of time at a somewhat elevated temperature. Thus for example, U.S. Pat. No. 3,103,404 discloses a discharge printing process, wherein the textile material printed with the discharge composition is dried in air and thereafter steamed to effect the discharging, followed by conventional scouring. As pointed out in this patent such a generally employed process of discharging printing involves a steaming operation which generally lasts for at least 5 to 10 minutes to effect an adequate discharge. Thus, the steaming is said to be conducted at atmospheric pressure for at least 5 to 10 minutes at a temperature of about  $216^{\circ}\text{F.}$

The present art of producing discharge effects is done by applying the discharge paste, which includes gums, chemicals, dyes, pigments, etc., to localized surfaces of the fabric, then drying, then steaming or aging, and washing of the fabric.

Such applications carried out on a conventional roller printing machine require a roller to carry the discharge paste and a doctor blade riding the roller to scrape the paste that is not applied within the engraving. The fabric is then dried, and aged for color destruction, rinsed and finished in the conventional manner.

Again, such conventional prior art processes of discharge printing can be greatly improved in accordance with the process of the present invention, such improvement residing

in a substantial reduction in the time necessary to effect the discharging or destroying of the dye previously dyed or printed on the textile fabric, in addition to enhanced effects.

This invention applies the discharge formula using a gum or water solution (conventional processes must use thickener). The entire fabric is saturated and squeezed through conventional rollers. The localized effects are then produced by contact with heated rollers at  $500^{\circ}\text{F.}$ , to  $1,500^{\circ}\text{F.}$ , depending on production speed required and no doctor blades or brushes are required on the rollers.

The discharging and drying are therefore carried out on the same rollers used to produce the pattern.

Thus, it has been found in accordance with the present invention that a discharge printing process, both white and colored discharge printing, can be conducted by heat treating the fabric containing the discharge composition for a fraction of a minute by passing such fabric over a heated patterned roller or cylinder maintained at a temperature of from about  $500^{\circ}\text{F.}$  to  $1,500^{\circ}\text{F.}$  Even with such high temperature, because of the limited contact, it is possible to obtain discharge of the dye without accompanying yellowing of the discharge areas as associated with conventional printing processes. Here again, the ability to reduce the necessary treating time from several minutes or more to a time comprising a fraction of a second or minute with accompanying drying is an industrial and economical advantage associated with the improved process of the present invention.

Accordingly, it is a principal object of the present invention to provide for a process of localized or overall chemical reactions and/or physical changes on textile fibers and fabrics and other flexible substrates in a manner which eliminates inherent deficiencies and disadvantages of prior art processes and provides an improvement not heretofore contemplated by previously employed processes.

It is a further object of the present invention to provide an improved process for conducting localized chemical reactions and/or physical changes on such substrates, the improvement residing in allowing such localized chemical reactions and physical changes to be conducted in a substantially shortened period by contacting the substrate containing the necessary reagents with a heated roller at a temperature of about  $500^{\circ}\text{F.}$  to  $1,500^{\circ}\text{F.}$

A still further object of the process of the present invention comprises an improved method for applying patterns or designs to such a substrate while utilizing the phenomenon of controlled color migration.

Yet a further object of the process of the present invention is to provide a method for applying a pattern or design to such substrate through the phenomenon of color migration whereby both the background and the intensifying color effect may be achieved in a single operation.

A further object of the process of the present invention comprises an improved process for the heat fixation of dyes and pigments on and/or in such substrates whereby such thermofixation can be achieved in a shortened period of time.

Yet a further object of the process of the present invention comprises an improvement in the development of dyes on and/or in such substrates, such improvement again relating to allowing the development of such dyes in a greatly shortened reaction time.

A further object of the process of the present invention relates in the curing of synthetic resins on and/or in such substrates, including the curing of synthetic resins containing pigments, the improvement relating to allowing such curing within a greatly reduced time period.

A still further object of the present invention comprises an improved process for discharging or destroying dyes with respect to obtaining either a white or colored background, such improvement relating to effecting such discharging or destroying of the dyes in a shortened period of time by contacting the substrate containing the discharge composition with a heated roller at a temperature of about  $500^{\circ}\text{F.}$  to  $1,500^{\circ}\text{F.}$

Still another object of this invention is the provision of an improved, highspeed process for drying such substrates.

Still further objects and advantages of the novel process of the present invention will become more apparent from the following more detailed description thereof.

As indicated previously, the process of the present invention comprises an improvement in a process for effecting localized or overall chemical reactions and/or physical changes on textile fibers or fabrics and the flexible substrates, such reactions and/or physical changes being those requiring the application of heat. Such improvement essentially comprises improved effects and/or a substantial shortening of the necessary treatment time by a very brief contacting of the substrate containing the necessary reagents or other substances with a heated solid member, e.g., a roller maintained at a relatively high temperature sufficient to effect the desired chemical reaction and/or physical change, yet insufficient to cause damage to the flexible substrate under the conditions of operation. Generally, such temperature is in the order of from 500° to about 1,500° F., preferably 525° to 1,000° F.

In accordance with a further feature of the present invention, it has been found that still further improved results are obtained when the substrate is under tension to obtain better contact with the heated solid member. Generally, the tension is controlled and governed by the type of substrate, and the effect desired at the production speeds used. Tension is controlled by a PIV (positively infinitely variable) driven governing the speed between entering and delivering nips of the apparatus.

Generally, the processes of the present invention utilize rollers as the heating means, with contact of the surface to be heated never being tangential i.e., contact being along a surface of a sector of the roller preferably but not necessarily less than 180°. Preferably, the tension may range from just above that necessary to remove wrinkles (or slackness) to the breaking point of the substrate.

Thus, as examples of processes involving localized or overall chemical reactions and/or physical changes embodied by the present invention are:

1. The physical migration of dyes, chemicals or pigments within a textile fabric or other flexible substrate so as to produce a multishade or a patterned effect;
2. the heat fixation of dyes such as where the color is developed by diffusion of the dye into the textile fiber or other such substrate;
3. development by heating such as where two or more components of a dye or pigment react under the influence of heat to form the final dye or pigment in situ;
4. the curing of a resin and fixing of the same in or on a textile fiber or fabric or other flexible substrate to change its physical properties or to fix and bind a dye or pigment to the substrate;
5. discharging or destroying dyes, pigments or resins, etc., to provide a patterned effect upon a white or colored background; and
6. the drying of a moist textile fiber or fabric.

In addition, other effects which can be brought about in accordance with the present invention include a redistribution of dyes, pigments or chemicals after a padding operation to improve coverage of a fiber or fabric or other flexible substrate so as to eliminate original defects, weaving defects, e.g., thick and thin appearances, dead cotton, etc., on plain shades or solid-colored substrates. This can be accomplished in accordance with the present invention by only slightly migrating the saturated and padded substrate before final drying.

Of course, the above processes involving localized or overall chemical reactions and/or physical changes on flexible substrates are only exemplary of those which can be improved in accordance with the process of the present invention. In this regard, it is pointed out that any and all chemical processes or physical changes involving the application of heat to such substrates can be similarly improved in accordance with the present invention.

The improved process of the present invention, in addition to having the advantage of greatly reducing the time needed to perform the desired chemical reaction and/or physical change on the flexible substrate has the advantages relating to elimination of acid or neutral agers for the development of some types of dyes, the elimination of doctor blades required in conventional roller printing and the eliminating of curing ovens for fixation of certain types of dyes, resins, pigments, etc. These and other advantages of the novel process of the present invention will become more apparent as the description proceeds.

With respect to the various embodiments of the present invention to be described hereinafter, it is noted that the materials which can be treated in accordance with the present invention may be of any construction such as yarns or woven or nonwoven fabrics containing examination of or synthetic materials. Similarly, they may contain little or no moisture and may have been printed, dyed or treated with resins or other compounds conventionally employed in conjunction with processes such as herein described.

As will become apparent, the present invention is additionally applicable to the treatment of all and any flexible sheet material, including, for example, paper and plastic films as well as the preferred textiles. Accordingly as employed herein, the terms "flexible sheet material" and "flexible substrate" are meant to embrace all of such applicable materials. The preferred fabric materials embraced by the present invention can comprise any flexible fibers or fabrics as described above.

#### MIGRATION

In accordance with one embodiment of the present invention, the phenomenon of chemical migration which has been primarily avoided in the prior art, is utilized to produce a desired effect, pattern or design on a textile fabric or similar flexible substrate, such designs having prior the present invention been obtained by weaving, printing or embossing the design onto the substrate. In general, the chemical migration is effected by contacting the moist substrate, e.g. fabric impregnated with dye, pigment or other chemical suitable for changing the color or physical effect of the fabric with a heated roller, smooth, knurled or having the desired pattern or design. Upon contact of the roller with the fabric the unfixed color or chemical products contained on or in the moist fabric migrate to the heated contacted surface and thereby cause predominance or intensity of color or physical effects at that portion of the fabric which has been contacted by the heated surface. For purposes of the instant application, the term "-dye" is intended to embrace products applied to the fabric whether or not they visually contrast in color with the fabric to which they are applied. In addition to dyes and pigments, desirable changes may be produced by the migration of resins or other chemical products that will migrate in a similar fashion as dyes and pigments and thus, produce a contrast in color or other physical effects in or on the fabric. It is only necessary that the dye or similar material that is migrated in accordance with the present invention be unfixed prior to migration so that that the contacting of the textile fabric with the heated roller can effect the desired migration or movement of the unfixed dye or similar material.

In order to accomplish the rapid migration by fast or even flash vaporization in accordance with the present invention, an apparatus is utilized which generally comprises a feeding device for feeding the material to be dyed to and through a trough containing the liquid bath of dye, pigment, etc., a hot surface, preferably a roller device, heated to a temperature ranging from 500° to 1,500° F., and an egress device for transporting the fabric from the roller. In operation, fabric which has been impregnated with the liquid bath in the trough is fed to the rotating heated roller, whereupon contact of the fabric with the roller, flash vaporization and product migration occurs at the surface area contacted, thereby producing the desired color intensity or other physical effects.

The effect which is produced by this embodiment of the present invention can best be illustrated, for example, by reference to the production of a cloth having a light background color with parallel equidistant stripes of a darker tone of the same color running across the fabric. Such a fabric would be produced in accordance with the present invention by impregnating the fabric with the single light color liquid medium, such as a light blue shade, and subsequently contacting the moist fabric containing the light blue liquid medium with a heated roller having parallel equidistant ridges or extensions which contact the surface of the dyed fabric. Since the heated roller would contact the surface of the fabric only at the ridges or extensions, and the heat of the roller would be concentrated in these areas, the dye within the textile fabric would tend to migrate to these areas thus causing a predominance of dye or intensive color at those points at which the fabric was contacted with the heated roller surface. This would cause the fabric to take on the appearance of the light blue background with parallel equidistant lines or stripes of a darker blue or more intense coloration. This would be the same effect, for example, that could be produced by previous methods by weaving a different color thread or for example, printing the textile fabric with a dark blue color over a light blue background. Of course, in accordance with the present invention, it is possible to provide this effect merely in a single dyeing operation with utilization of the phenomenon of migration.

This embodiment of the process of the present invention can be further illustrated by reference to FIGS. 1 through 12 wherein:

FIG. 1 is a schematic view of an apparatus used to carry out the process according to the present invention;

FIG. 2 illustrates another embodiment of apparatus useful for carrying out the process;

FIG. 3 illustrates apparatus useful for providing a plurality of patterns;

FIG. 4 illustrates a schematic view of apparatus applying a two-sided pattern or plain shade development;

FIG. 5 illustrates a perspective view of a pattern-carrying roller;

FIG. 6 illustrates the type of pattern which may be obtained after contacting a moist fabric impregnated with a dye with the heated roller illustrated in FIG. 5;

FIG. 7 is a photograph of the contacted side of a cotton twill fabric which was impregnated with a moist dye and contacted by a 600° F., engraved roller for one-half second; and

FIG. 8 is a photograph of the uncontacted side of the fabric illustrated in FIG. 7;

FIG. 9 is a schematic diagram illustrating, in the manner of a flow chart, the process of a further embodiment of the present invention;

FIG. 10 illustrates an alternate embodiment of the present invention; and

FIG. 11 illustrates yet another alternate embodiment of this invention;

FIG. 12 is an illustration of still another alternative embodiment of the present invention.

Referring now to the drawings wherein like reference characters designate like or corresponding parts throughout the several views, there is shown in FIG. 1 a continuous web of material, such as a web of fabric 10, which may for example be cotton twill. The web is passed over a suitable input roller 11 into a pad box or dye vat 12, filled with a solution of dye, or pigment dissolved or dispersed in a suitable solvent, such as water, chemical solvent or the like. The particular dye and the solvent used, whether it is a dispersion or a true chemical solution, will depend on the material of the web 10, and the color of physical effect to be obtained. The only important requirement which the present invention places on the nature of the solvent and of the dye, pigment or chemical is that after having been applied to web 10 the dye, pigment, or chemical has the ability to migrate in the web under the influence of heat. The web 10 is padded or passed through the pad box 12 over rollers in a suitable manner and as well known in the art, and

not further described in detail. Web 10, upon leaving the pad box 12 in the region 10<sup>a</sup> is passed through a pair of squeeze rollers 14, 15 where a portion of the solution is removed to control the moisture content of the web. Thus, at station 10<sup>b</sup> the moisture content of the web is controlled to be in the region of 75 percent of the weight of the material, and preferably is generally controlled so that it is in the range of about 30 percent to 125 percent of the weight of the material. Rollers 14, 15 are preferably arranged in such a manner that any excess treating bath is returned automatically, for example, by gravity as shown in FIG. 1, to pad box 12.

Web 10, after leaving station 10<sup>b</sup> is passed over a group of tension rollers generally designated by reference numeral 17 which, as is well known in the art, also act as compensators. The tension rollers may be spring loaded or otherwise suitably arranged to maintain proper position and tension within web 10. The web then passes over a guide roller 18<sup>a</sup> and then over a pair of guide rollers 19<sup>a</sup>, 19<sup>b</sup> arranged on either side of a heated pattern-carrying roller 20.

Guide rollers 19<sup>a</sup>, 19<sup>b</sup> are mounted on a yoke 21, which is movable transversely with respect to the axis of rotation of heated pattern-carrying roller 20, for example by being retained on a longitudinally movable shaft 22, so that the extent of contact of web 10 with the circumference of pattern roller 20 may be controlled. If shaft 22 is moved to the dashed position, so that yoke 21 and guide rollers 19<sup>a</sup>, 19<sup>b</sup> will also be in the dashed position (FIG. 1), web 10 will be completely out of contact with the pattern-carrying roller 20. This position will be assumed if the entire apparatus is stopped, even if only momentarily, to prevent scorching of the material if it remains in contact with pattern-carrying roller 20 since all the solvent in the web will evaporate in the region where pattern-carrying roller 20 contacts the web. A suitable interlock, not shown, may be controlled for example from a shaft 23 which supports roller 20, whereby the interlock would permit shaft 22 to move to the dashed-line position if the speed of roller 20 falls below a predetermined value. Such interlocks are well known, and may be controlled by the centrifugal force acting on the shaft 23 and sensed by a small switch to deenergize a magnetic solenoid, which when energized, holds shaft 22 in the solid line position against the force of a spring, tending to retract shaft 22 into the dashed-line position. Such an arrangement, in which a spring tends to move shaft 22 away from the heated roller, upon deenergization of an electrical element, is, of course, also fail-safe in operation. When the web contacts the heated roller over a sector greater than 180°, and the distance between the guide roller surfaces on each side of the patterned roller is less than the diameter of the patterned roller, other obvious means must be employed to swing the guide rollers outwardly past the patterned roller during retraction to prevent scorching.

After leaving guide roller 19<sup>b</sup>, web 10 is passed over another idler roller 18<sup>b</sup>, then over another tension-controlled arrangement, generally designated as reference numeral 27, which also act as compensators similar to rollers 17. From the rollers 17, the web 10 is removed from the apparatus carrying out the present invention by means of rollers 28, and then the web may be further applied to treatment stations, such as hot-air drying ovens to dry the noncontacted portions of the fabric, and chemical treatment stations or reducing stations, as well known in the dyeing art, for further fixation and development of the migrated products.

A form of pattern-carrying roller 20 is shown in more detail in FIG. 5. It consists of a cylindrical element 30, supplied with means to heat the element, shown for example as internal electrical heating units 31, 32 suitable connected internally and brought out to electrical contacts by, for example, slip rings, as is well known in the art, (and as only schematically indicated in FIG. 5) for further connection to a supply of electrical power. In order to make a longitudinal stripe pattern, such as shown at 35 in FIG. 6, cylindrical body 30 is supplied with a circumferential ridge 45. Let it be assumed that the web 10 of FIG. 6 is originally of a neutral, such as unbleached, slightly

yellowish color, and consists of cotton twill, to be colored with a reactive dye, for example. The fabric 10 is thus dyed in general to a blue color. The application of the dye may be at room temperature, or at elevated temperatures as is customary in the dyeing field. After leaving pad box 12, the web may be squeezed between rollers 14, 15 to a moisture retention of 50 to 100 percent based on the weight of the material. On contacting the web for a period of time of about half a second, with a surface temperature at circumferential ridge 45 of about 500° to 600° F., approximately 90 percent of the dye is moved from the back and from within the web to the face thereof where it is being contacted by the heated roller. The face side of the material will thus have a dark turquoise stripe applied thereto, indicated at 35, FIG. 6. The back side of the material, in the same region where the dark stripe on the face appears, will have a light stripe. Upon subsequent drying of the entire fabric, and fixing (if the dye is of such material that this is called for), the uniform generally blue background due to the dye distribution will be retained where the material was not contacted by the ridge 45, and the extensive and intensified, dark strip 35 will likewise appear the surface of the material.

FIGS. 7 and 8 are representative of a portion of mercerized cotton twill fabric, which after padding with a reactive dye solution and squeezed to a moisture retention of 75 percent has been contacted with a roller having a plurality of circumferential ridges of different widths. It will be observed that in FIG. 7 the areas X which have been contacted by the ridges of the roller are clearly defined and darker than the background Y, whereas in FIG. 8 the corresponding areas X' on the back of the fabric are lighter than the background Y', thereby clearly showing the migration of the dye to the surface area X contacted by the roller.

If a pattern, such as a dark stripe interspersed with dots of lighter background color is desired, a ridge 46, with holes 47 (FIG. 5) is formed on the cylindrical body 30. The pattern will appear as the dark stripe 36, with background color spots 37, FIG. 6. Conversely, if dark dots are desired on material of general background color, projections 48 may be patterned on the cylindrical element 30, thereby forming intensified dots 38, standing out from the background color as seen in FIG. 6. A mottled aspect can be obtained by contacting an area of the material with a ridge which has a knurled or serrated appearance, as shown at 49 in FIG. 5; the material will then present spots of intensified color interspersed with spots of lighter, neutral background color, as seen generally at 39 in FIG. 6. A closely knurled roller will produce substantially an overall effect and is actually preferred for this purpose as compared with a smooth roller.

The intensity of the color, that is, the extent of the migration of dyestuffs or pigments to the surface, under the influence of contact with the heated roller depends not only on the surface temperature of the particular die pattern contacting the fabric web, but also on the time or duration of contact. If the temperature is towards the upper range, that is, between 600° and 1,500° F., a contact time of for example about half a second, for cotton, results in flash evaporation and effects migration of practically the entire dye material absorbed in the fabric web, towards the surface where it is being contacted. Experiments have shown that the lower the temperature, the greater the transfer of dye from the fabric web to the pattern roller 20. At the temperatures operative herein, i.e., 500° to 1,500° F., no transfer of dye or pigment material to the pattern roller 20 occurs, and there is no need for cleaning brushes previously required, because flash evaporation, and almost instantaneous drying, sets the pigment or dyes in the fabric web, and prevents further transfer to the pattern rollers 20. At lower temperatures, where a lower speed, or a larger circumferential contact area between roller 20 and the web 10 is required, more transfer of dye from web 10 to pattern roller 20 results.

The apparatus disclosed in FIG. 2 is similar to that of FIG. 1 except that the rollers 18<sup>a</sup> and 18<sup>b</sup> are movable transversely in respective slots 24<sup>a</sup> and 24<sup>b</sup> on supports 24, thereby per-

mitting easy adjustment of the circumferential contact area of the web to the pattern roller 20.

The apparatus in FIG. 1 has been modified as shown in FIG. 4 to produce contrasting effects on each side of the fabric. Thus, the apparatus of FIG. 4 includes pattern rollers 20 and 20', fixed guide rollers 58<sup>a</sup> and 58<sup>b</sup> and movable guide rollers generally designated as reference numerals 59. The guide rollers 59 are movable from the upper dashed position designated 59<sup>a</sup> to the lower dashed position designated 59<sup>b</sup>. Therefore, if the pattern or color intensity is to be the same on each side of the fabric, the guide rollers 59 are positioned carefully between positions 59<sup>a</sup> and 59<sup>b</sup>. However, if the intensity on one side of the fabric is to be greater than on the other side, the guide rollers 59 are moved toward either the upper or lower dashed position 59<sup>a</sup> or 59<sup>b</sup> depending upon which side the increased color intensity is desired. The guide rollers may be mounted on a support for motion in a slot similar to the mounting or roller 18<sup>a</sup> or 18<sup>b</sup>, hereinabove described or in any other suitable fashion well known in the art.

The degree of migration which can be produced can be varied by varying the temperatures across the roller. By suitable adjustment or provision of separate resistance elements within the roller, various temperatures at the surface of the roller, and at the pattern area can be arranged. The effect on migration is most pronounced on the back of the fabric; the visual aspect of the front side, even on the cooler region, for example, where a surface temperature of little more than 500° F. is obtained, varies but little from that where the surface temperature is 600° F. However, it appears in general that better color intensity may be obtained at the higher temperatures. In order to provide a multishade effect, for example with colors which are temperature sensitive, the fabric may be passed over a series of rollers having different patterns applied thereto, or contacting strips or ridges differently placed from the strips or ridges on another roller, and of a different temperature. An arrangement in accordance with this embodiment is shown in FIG. 3. The web material 10, as received from a tensioning arrangement similar to roller combination 17 (FIG. 1) is passed over a first guide-roller combination 50, which, for example, may be at a temperature of 500° F. A subsequent guide roller-pattern roller combination 51 is provided and the web is passed thereover. The roller of the guide roller-pattern combination 51 is heated to a different temperature, for example, 500° F.; and the roller of yet another guide roller-pattern roller combination 52, over which the web is subsequently passed, may be heated to 500° F. The general arrangement of the guide roller-pattern roller combinations 50, 51, 52 may be similar to that shown in FIG. 1, with the exception that variation of contacting area can be obtained not only by lateral movement of the guide roller support, but because a central guide roller can be common to a pair of pattern rollers, and swinging movement of the yokes retaining these central guide rollers may be provided for.

The length of time of contact of the fabric, as before, depends on the degree of heat transmitted to the surface of the material by the heated pattern rollers, the type of material used, and the amount of moisture to be evaporated or flashed off.

The rapid evaporation at the point of contact apparently moves the dyes, pigments or chemicals contained in the body of the fabric, which at this point in the process are not yet fixed to the surface. The accumulation of these substances in the restricted areas of contact with the heated pattern roller, enhanced by the rapid evaporation of moisture, result in color intensities of very high yields.

Variegated controlled coloring may be achieved by dye or chemical migration in yarns, warps, tow or other nonwoven materials processed in the same manner as described with fabrics. In addition, desirable physical changes in these materials as well as in fabrics may be accomplished by the use of migrating chemicals, resins and solvents that contain no coloring substance. For example, a web of material may be passed through a pad box containing a weak caustic soda solu-

tion which is too weak to effect subsequent dyeing. However, upon application of a heated roller to the material, in the same fashion as heretofore described on fabrics padded with dyes, migration and thus concentration of the caustic soda solution to the contacted areas will produce mercerizing effects which in a manner well known in the art may produce physical (i.e. plisse or puckering) changes in the material or if desired, produce ornamental effects in subsequent dyeing.

In yet a further embodiment of the present invention concerning a process for migration of dyes on a textile fabric, it has been found possible to obtain the preferential migration of one dye or colorant over another. In accordance with this embodiment of the present invention, such an effect is achieved by first dyeing the material with a certain background color, drying the background and then padding a solution of a second color over the first. The second color only is the migrated and fixed. This will allow, therefore, the preparation of a fabric wherein one dye is migrated preferentially with respect to another so as to produce a multicolor effect having an area with increased color intensity.

In an alternative process embodying this feature of the present invention, the textile fabric may be dyed with a first color which is subsequently migrated as for example, in accordance with that embodiment discussed above. The textile fabric having the migrated dye thereon can then be passed through a second bath containing a second dye or similar coloring agent together with a reducing, oxidizing or other agent to develop the migrated, as well as the second background color, in order to fix them to the textile material. This again will produce a similar effect, as discussed above, wherein a multicolor effect can be achieved, the material having areas of increased intensity due to the migration of the dye. In both cases, after migration and after fixing, the textile material may be steamed, rinsed, oxidized, rinsed, soaped and rinsed again by conventional procedures in a manner well known in the prior art.

In still another variation of this process wherein one dye is preferentially migrated with respect to another, it has been determined that the appearance of a pattern on a material may be improved to a great extent by migrating the dyes in an improved manner prior to fixation. This technique involves the migration of a single color by means of a pattern-carrying roller applied to one surface, the material being contacted at its other surface with a heated roller to migrate the remaining dye in the other direction with respect to the thickness of the material, so that the contrast of the material migrated in the first direction by the first roller is even more greatly enhanced. Thus, by migrating in opposite directions the different portions of the dyed textile material, it is possible to produce a patterned effect of even greater color intensity than possible by the embodiment previously discussed above.

This embodiment of the present invention can be described by reference to FIGS. 9 through 11.

Referring to these drawings there is shown in FIG. 9 a web material, for example, cotton twill cloth 110 which is transported over a guide roller 111 into a dye bath schematically indicated as pad box 112 where a first dyeing substance is applied to the material 110. The material 110 then passes through a pair of squeeze rollers 113, through a dryer 114 over another guide roller 115 and through a second pad box 116 where a second dye is applied on the web 110.

Material 110 is the passed through another set of squeeze rollers 117 where the moisture is reduced to be in the range of between 30 to 125 percent, preferably 50 to 100 percent, of the weight of the dry material and then contacted by a migrating device 118. Device 118 is comprised of a heated roller having the desired pattern embossed or engraved thereon. The exact structure of the migrating device 118 is disclosed and described in detail with respect to FIGS. 1 through 9. The web material 110, after having the dye migrated is then passed into a pad box 120 which may contain a developing, fixing or reducing bath, as will appear in detail below. The material is then passed through a pair of squeeze rollers 121 and

processed as desired, i.e. steaming, rinsing, etc., in a manner well known and designated in FIG. 9 as unit 125. The web is then reeled upon a takeup roll 126.

The following example will illustrate this process: As a first step the material is passed through the pad box 112 containing a reduced vat-color solution, for example, which fixes as soon as it is applied, thereby producing a shade which will not migrate. The material is then squeezed by rollers 113 and dried in dryer 114 where it oxidizes to the desired color.

In the next step, the material is passed through the second pad box 116 and saturated with an unreduced vat dye dispersion. The products of the second application are not fixed during saturation and extraction and thus are susceptible to migration. The material is then squeezed by rollers 117 to retain about 70-percent moisture and brought into contact for about ½ to 1 second with the migrating device 118 heated to about 650° F. The range of temperature of this migrating device may be as low as 500° F., and as high as 1,500° F. The important point is that the temperature is below the scorch point of the material, that is, the time of contact of the material with the migrating device, and the temperature thereof, are so adjusted that scorching or other heat damage is prevented. As the material is brought in contact with the migrating device, only the unreduced vat dispersion moves to produce the design or pattern leaving the vat coloring applied in pad box 112 unaffected. That is, the areas contacted by the heated die are dark in color, whereas the uncontacted areas are light in color.

In order to completely fix the dyes, the material is further treated by conventional reducing agents in pad box 120. The material is then squeezed and the color developed by the pad steam method and finished by rinsing, oxidizing, rinsing and soaping in the conventional manner in unit 125. The combination of the agents within pad box 120, and the steps in unit 125 complete the fixation of all the coloring products.

The results obtained, as previously described, are a light color background, with dark color stripes. When the stripes are narrow, for example, in the range of 1 or 2 mm. or so, they are completely solid and dark and have good and sharp contrast at the edges with respect to the background material. When the stripes are wider, for example, 5 mm. or more, the edges of the stripes are very dark, but the region between the edges is slightly lighter; if the width of the stripes is in the order of 1 cm. or so, the central area within the broad stripes may be almost as light as the background area. This very pleasing effect of dark contrasting stripes, which themselves have a variation in shade, can readily be obtained by the process according to the present invention.

Although the reason for the effect is unknown, it may be due to lateral migration of the color products from the uncontacted part of the fabric to the point of contact such that the color products can not migrate further toward the center of the broad stripe, since the water has evaporated. An alternative reason for the effect is that it may be due to the wider ridges of the engraved rolls causing a higher percentage of vat color, which was applied as an unreduced vat dispersion, to be migrated to the point of contact leaving a lighter area between the lines. The narrow lines, because of their limited degree of contact and consequently less evaporation, do not migrate the same percentage of color from the body of the material. Thus, varying shades of light color across the pattern may be obtained. This variance in ground shades, which is produced by the types of engraving used for migrating, is new and novel and not producible with vat colors by any of the presently used printing or dyeing systems.

If, for example, in accordance with the process outlined above, the initial vat color solution produced a shade of yellow on the textile fabric the application of a further dye dispersion comprising a blue paste, for example, when employing the sequence of process steps and the apparatus described would provide a very esthetic textile fabric having the areas contacted by the heated die of greenish-blue or dark green in color with the uncontacted areas of light green or greenish-

yellow in color. Again, variations in the color within the dark stripes themselves would result depending upon the width of the dark or more intense stripes.

FIG. 10 illustrates an apparatus and process which differs from the process and apparatus of FIG. 9 in that the colors, although at the same concentrations, are applied to the fabric in different order.

Again, web material 110 is passed over a roller 111 and into a first pad box 132 where it is saturated with a dye bath and squeezed to a moisture retention of about 70 percent of the dry weight of the material by squeeze rollers 133. The material is then brought into contact with the pattern migrating device 118, as in the prior description, for ½ to 1 second at 650° F. The pattern is produced on the material at the points of contact with heated surfaces of the device 118.

The ground shade is then produced by passing the material from migrating device 118 into a chemical pad 136 heated to about 120° F., and containing the same reduced vat color as that contained within pad box 112 in the first embodiment as explained in connection with FIG. 9.

From the chemical pad 136, which contained the reduced vat color, the material is passed directly into unit 125 for further reduction of the vat color and simultaneously reduction of the vat pigment dispersion which was applied to the material in the pad box 132 and then migrated. In the unit 125, the material is steamed, rinsed, oxidized, rinsed, soaped and rinsed again by conventional procedures and reeled upon the takeup roll 126.

The process as explained in connection with FIG. 10 is shorter as it uses the chemical pad operation for applying not only the reduction chemicals, but also the reduced vat color for the ground shade thereby eliminating a padding and a drying operation. This process, again, shows the production of wide variances of contrasting shades between the design and the ground shades while using the same reduced vat color and unreduced vat color dispersion as used in the previous example.

This process is not limited to vat colors and may be used with other classes of dyes, pigments and chemicals, by saturation and fixing on the web material those products not to be migrated, and applying separate solutions or dispersions containing the same or different products, which are to be migrated to a certain design or pattern.

Water-soluble vat colors may also be used. One pad box may contain products to be dried and fixed not by reduction, but by oxidation; the other pad box may contain products that are migrated within the moist material before fixation. Such products are available to the trade under the Algosol trademark.

Plain shade effects having a solid overall appearance by migrating the color to one side of the fabric, may be carried out by the same process, thereby producing wide variations of color effects from the back, as compared to the face of the fabric, when a plain surface heated roll is used in place of one having a pattern as will now be described.

Referring now to FIG. 11, web material 110 is passed through a pad box 142 which may contain any of the substances referred to above that have migrating properties. The dyed material is squeezed by squeeze rollers 113, as before, and passed over a first migrating device generally designated by reference numeral 148. The arrow indicates that the side rollers 141, 141' are movable with respect to the heated pattern-carrying roller 143, as explained in detail above. The opposite side of the surface of the web material is then contacted by a second migrating device generally designated as reference numeral 158, again having movable side rollers 151, 151' and a heated migrating roller 152. The roller 152 is a plain heated roller maintained at a temperature from about 500° to 1,500° F., although it, too, could be a pattern-carrying roller. Dyes, pigments or products which were not migrated by contact with the pattern-carrying roller 143 are now migrated to the opposite side of the material by roller 152, thereby producing greater color contrasts between the design and

ground shades. The time of contact, and the temperature in first migrating device 148 is so adjusted that material leaves the heated roller 143 at the point of dryness, at the areas contacted by the heated roller. Areas still containing moisture from the pad box 142 can then be migrated to the opposite side when contacted with the plain-faced roller 152, heated to produce the necessary migration. After migration, fixation of the products as used in the process is carried out in unit 125 in a manner well known in the art. If desired, intermediate the second migrating device 158 and the unit 125, an additional pad box may be inserted; for example, the pad box 142 may contain the same migrating dye as pad box 132 (FIG. 10) and since the migrating devices 148 and 158 functionally correspond to the migrating device 118 of FIG. 10, another pad box (not shown) which is similar to pad box 136 may be inserted between the migrating device 158 and unit 125. Alternatively, the material may already have a certain background shade, or be natural, bleached or unbleached thereby requiring the application of only one coloring solution. The contrast produced between the pattern of device 148 and the background is materially enhanced by the additional back side migration device 158.

In each of these latter two described processes, the same phenomenon results, that is, by the preferential migration of one dye with respect to the other, it is possible to produce a textile fabric having a very esthetic effect of a light background color and stripes or other patterns of a more intense darker coloration. Thus, with respect to the process outlined in connection with FIG. 10, this is achieved by first applying a color to the overall fabric and migrating the same with subsequent dyeing of the fabric with a second coloring agent and reducing the migrated as well as the second background color and fixing the same.

With respect to the embodiment of the process of the present invention as illustrated in reference to FIG. 11, a more intense coloration due to the migration of the dyestuff is obtained by migrating a single color by a pattern-carrying roll applied to one surface with contacting of the other surface with a heated roller to migrate the remaining dye in the other direction. This allows for a greater color contrast by a greater color concentration of dye at those points contacted by the pattern heated die or roller.

FIG. 12 shows a further embodiment of the present invention, illustrating the use of a multiplicity of heated rollers, in this case three, although more can be used, to produce the desired effect on the textile fiber or fabric. In accordance with this embodiment, the web material 110 is passed through a pad box 142 which may contain any of the previously described substances for application to the web material 110. Thereafter, the textile fiber or fabric which has been padded with the dye or similar material is squeezed by squeeze rolls 113 as previously described, to provide a web material having the desired moisture content for further contact with heated rollers or dies.

The web material 110 leaving squeezed rollers 113, then assumes the zigzag path shown by contacting successive sides with heated rollers 171, 172 and 173. It can thus be seen that in accordance with this embodiment of the present invention the web material is caused to pass in contact with a multiplicity of heated rollers which through their combined action, effect the desired chemical or physical change, e.g., migration of the dye padded on the web material. As shown in FIG. 12, the web material 110 is caused to be contacted on alternate sides with the heated rollers although the rollers could be arranged so that the same side of the web material is contacted with the multiplicity of rollers shown. Employment of apparatus as shown in FIG. 12, however, eliminates the need for guide rollers since the zigzag path taken by the web material 110 provides sufficient contact and tension so as to enable the heat of the rollers to effect the necessary chemical or physical change.

After contacting the last of the heated rollers the web material may be passed into fixation unit 125, wherein fixation of the dye or similar material can be carried out in a well-

known manner as previously described with the product taken up upon takeup roll 126.

As was the case with the previous embodiment of the present invention described above, the rollers 171, 172 and 173 employed in accordance with this embodiment of the present invention, can comprise heated, plain or pattern-carrying rollers depending upon the effect desired through the migration or similar process. Here again, it is pointed out that the effect produced by contacting alternate sides of the web material with the heated roll is essentially the same as discussed above with respect to other embodiments of the present invention.

As indicated previously in connection with the description of the present invention the minimum contact time of the web material with the heated roller or dye may be as little as one-fifth of a second or even slightly less, depending upon the speed of the web, chemical and physical nature of the hot roller surface (i.e., metal, ceramic, knurled, smooth, patterned, etc.) tension, chemical and physical nature of the material being treated, temperature of the roller, degree of wetness or moisture in the material being treated, etc. The contact time is usually from 1/2 to 5 seconds. In addition, below about 30 percent moisture content (wet pickup) there appears to be very little migration of dye or similar material to the hot surface. In addition, for example, a knurled surface enables the use of higher temperature, i.e., temperatures within the upper range specified previously whereas a polished surface generally requires the use of temperatures below the very upper limits of the specified temperature range. Thus, in accordance with the present invention by the suitable regulation of contact time dependent in some respects upon the easily regulated parameters above, it is possible to obtain differences in color values or intensity between contacted and uncontacted areas as high as 10:1.

In accordance with the present invention the rollers employed are preferably composed of stainless steel, which rollers appear cherry red at a temperature of approximately 1,000° F. Such a material is preferably employed since in the temperatures utilized in accordance with the present invention it is resistant to deterioration, oxidation, softening, and flaking. Of course, other heat-resistant metals and ceramic materials can be conveniently utilized in accordance with the process of the present invention. It is also to be noted in accordance with the present invention that, while suitable retraction means has been discussed primarily with respect to FIG. 1, such suitable retraction means can be applied to any and all of the embodiments described above. In this regard, suitable retraction means are generally required so as to withdraw the material a substantial distance from the hot surface during emergency or planned stops, such distance being that sufficient to prevent scorching by radiation, convection, etc. from prolonged contact of the web material with the heated surface.

In addition to the retraction means illustrated primarily in connection with the description of FIG. 1, the apparatus described above may contain a simple fan for cooling, not shown, such fan being located to cool the space between the heated roller and web material upon emergency or planned stops of the apparatus and upon retraction of the web material from contact with the heated rollers.

With respect to each of the embodiments described above and hereafter, it is again pointed out that the same is not dependent upon the use of any particular type of dye or pigment, the only requirement being that such dye or pigment, as such or in a fluid medium, be one which is capable of being migrated in the flexible substrate by the application of heat. Thus, any such conventional dye or pigment can be conveniently employed in accordance with the process of the present invention, representative examples of which include:

Direct or substantive dyes or acid dyes—metallized and unmetallized azos, anthraquinones, etc.

Azoics including naphthols, rapidogens, etc.

Reactive dyes

Vat colors—anthraquinones, hydrons, indigos, indigoids, thioindigoids, brominated indigoids, etc.

Sulfur dyes

Water-soluble leuco ester salts of vat dyes—e.g., Algosols, etc.

Pigments—phthalocyanines, etc.

Any and all dyes from the above and other groups can be conveniently employed in accordance with the present invention.

While the above description of the figures has been given primarily with respect to the migration of dyes in accordance with one embodiment of the novel process of the present invention, it is to be clearly understood that such apparatus is similarly applicable in the other processes to be discussed hereinafter.

The apparatus described in FIGS. 1 through 12 as particularly applicable in effecting the migration of dyes to produce an esthetic tone-on-tone effect on textile fabrics is similarly applicable with respect to heat fixation of dyes, destroying or discharging of dyes, curing of synthetic resins, drying, etc., as will be discussed hereinbelow.

#### HEAT FIXATION

As indicated previously, conventional heat fixation processes have generally involved the use of ovens, agers, hot rollers, radiant heaters, or steamers or combinations of the same, to thermally fix colors on synthetic thermoplastic textile fibers and fabrics or to develop colors by diffusion techniques associated with heat fixation. Generally, the previous techniques for heat fixation have involved aging, steaming or curing for times much greater than that of the present invention in view of the use of low operating temperature. Such times, of course, have been substantially reduced to a fraction of a minute or second in accordance with the improved process of the present invention.

In accordance with the present invention, the term "heat fixation" is meant to embrace any and all conventional processes by which a dyestuff is securely fixed to a textile fiber or fabric by the application of heat. Thus, heat fixation as employed in accordance with the improved process of the present invention can include simultaneous diffusion and fixation of the dyestuff into the textile fiber or fabric, simultaneous development and diffusion of a dyestuff or any other chemical process by which the heating of the textile fabric in some manner alters the state of the dyestuff applied thereto, so that the same becomes securely attached to the textile material.

Thus, the process of the present invention is applicable to any and all conventional dyestuffs generally fixed by the application of heat. Such dyestuffs include, for example, those types listed above under "MIGRATION." More specific operative vat dyes include as representative examples:

Vat Yellow 13, C.I. 65425

Vat Orange 15, C.I. 69025

Vat Brown 3, C.I. 69015

Vat Red 31, 2,5 bis(1-amino-2-anthraquinonyl)-1, 3, 4-oxadiazole

Vat Red 1, C.I. 73360

Vat Violet 2, C.I. 73385

Vat Violet 1, C.I. 60010

Vat Blue 6, C.I. 69825

Vat Green 1, C.I. 59830

Vat Green 26, reaction of 3- $\alpha$ -anthraquinonyl aminobenzanthroneanthraquinoneacridine and aluminum chloride with m-nitrobenzene sulfonate and sodium chloride

Vat Black 16, C.I. 59855

Of course, a vat dyestuff dispersion employed in accordance with the process of the present invention may, if desired, be thickened with any thickener, for example, starch and modified starches, modified celluloses, such as methyl and carboxymethyl cellulose, dextrin, locus bean gums or al-

ginates, any of these materials being those conventionally used in previously employed prior art processes.

In addition, vat dyestuffs generally are fixed in the presence of an alkali, the alkali generally being carbonates and hydroxides of sodium and potassium. Similarly, conventional catalysts employed in the fixation of vat dyestuffs can be employed in accordance with the process of the present invention. In addition, the process of the present invention can be carried out in both aqueous and thickened solutions unlike previous methods requiring working with thickened pastes. Here again, the improvement of the present invention does not reside in the particular materials employed, but resides in contacting the fabric containing the necessary materials for a short period with a heated roller at a temperature from about 500° to 1,500° F.

Similarly, in lieu of vat dyestuffs the process of the present invention can be conducted with conventional reactive dyestuffs, that is, a water-soluble dyestuff which contains a reactive group, i.e., a halogen atom or other substituent capable of reacting with the fiber so that the remainder of the dyestuff becomes attached to the fiber through a covalent bond. Such dyestuffs fall into many classes, for example, those of the nitro series, azo series, anthraquinone and phthalocyanine series, either metal free or in the form of a metal complex. Exemplary dyestuffs of these groups include, for example:

- Genafix dyes
- Procion dyes
- Remazol dyes
- etc.

Printing pastes and padding solutions containing the reactive dyestuffs can in accordance with the present invention contain the usual adjuvants used generally in dyeing textiles with these materials. Thus, for example, printing pastes and padding solutions which contain the reactive dyestuffs may contain, for example, alkaline catalysts, urea, wetting agents such as alkylated naphthalene sulfonates and condensates of ethylene oxide with alkylated phenols, fatty alcohols or fatty amines, mild oxidizing agents such as sodium m-nitrobenzenesulfonate and thickeners such as sodium aginates and oil-in-water or water-in-oil emulsions.

In a similar manner conventional dispersed dyes which are generally heat fixed by conventional techniques can be employed in accordance with the improved process of the present invention. Exemplary dispersed dyes include, for example:

- Genacrons
- Cellitons
- etc.

In a similar manner, any and all conventional dyestuffs generally heat fixed or developed by the application of heat can be employed in accordance with the process of the present invention. Thus, other exemplary groups or dyestuffs which are suitably employed include, for example:

- Hydrons
- Indocarbons
- Sulfur colors

as well as similar materials well known in the art.

Thus, in accordance with this embodiment of the present invention an improved heat fixation process is conducted by contacting the fabric containing the necessary reagents with the heated roller maintained at a temperature of 500° to 1,500° F., such contact time being within the order of a fraction of a minute under a tension sufficient to allow adequate contact of a textile material and a heated surface.

Thus, in accordance with this embodiment of the present invention, flash diffusion or flash heat fixation is carried out in a controlled manner, utilizing apparatus such as shown in FIGS. 1 through 12, described in detail with respect to the migration of dyes as discussed above. Thus, with respect to all of these embodiments of the present invention, the apparatus utilized to achieve the localized or overall chemical change and/or physical effect, that is, the heated roller remains substantially

the same, the system being modified only to the extent of providing for the necessary and conventional apparatus for applying the necessary reagents to the textile fiber or fabric or other flexible substrate and treating the textile fiber or fabric after it has been contacted with the heated roller. Since such apparatus, however, is conventional in the art it has not been fully represented in accordance with the present invention, it being again remembered that the present invention comprises an improvement in conventional processes for effecting chemical reactions and physical changes, the improvement relating primarily to conducting such processes in a more economical and a more efficient manner by contacting the substrate containing the necessary reagents or other materials with the heated roller maintained at a temperature of 500° to 1,500° F., the period of contact being conducted under sufficient tension to allow proper contact of substrate and heated roller.

The heat fixation process in accordance with the present invention is particularly adapted to the use of an apparatus such as described previously in connection with FIG. 12. In this regard, it is advantageous in accordance with the present invention to provide a process wherein heat fixation is achieved as the last step of a process which is conducted by contacting a web material with a sequence of heated rollers, i.e., two or more. In this regard, for example, a first roller can be employed to contact the padded web material so as to migrate the dye padded thereon to produce a pattern effect upon the textile material. While some slight degree of fixation may take place during this initial migration of the dye the same is not appreciable when compared to the final heat fixation produced through contact with subsequent heated rollers. Thus, with respect to apparatus such as illustrated in FIG. 12, the second or intermediate heated roller contacting the opposite side of the web material can be utilized to effect a drying of the padded and migrated fabric while the third or last heated roller can be employed to heat fix the migrate dye at an elevated temperature.

FIG. 12 illustrates only the employment of three heated rollers. It is, of course, obvious that any number of heat rollers, i.e., one, two, five, seven, or more can be employed in accordance with the present invention, it only being necessary to regulate the time of contact and moisture contact, etc., so that the desired result is achieved when the web leaves the last heated roller.

Here again, it is pointed out that the process of the present invention is not predicated upon the use of any particular materials but relates to an improvement associated with an elimination of certain disadvantages of previously employed processes by contacting a flexible material, e.g., textile material with a roller heated to a temperature of 500° to 1,500° F. for substantially shortened period of time.

## DEVELOPMENT

A development process as employed in accordance with the present invention differs from heat fixation as discussed above, in that in development chemical reactions take place by the application of heat to a flexible substrate, e.g. textile fiber or fabric, containing the necessary reactants. Thus, included within the scope of this embodiment of the present invention, are the development of dyes, pigments, chemicals or resinous components; that is, any and all materials which when applied to a textile fiber or fabric, can be caused to react by the application of heat. In accordance with the process of the present invention, conventional development processes are substantially improved by contacting the fiber or fabric containing the necessary reactants with a heated die or roller at a temperature of from 500° to 1,500° F., preferably 525°-550° to 1,500° F., the period of contact being merely a fraction of a second or minute, the tension applied being that necessary to afford adequate contact of the fiber or fabric to the heated rollers.



Here again, the dyes, pigments, chemicals or resinous components which can be employed in accordance with the process of the present invention are those which are conventionally employed in development processes, wherein reactants contained in or on a textile fiber or fabric are developed through the application of heat. Thus, representative materials applicably employed in accordance with this embodiment of the present invention include, for example:

Any and all dyes and pigments  
catalysts  
chemical compounds capable of development by heat  
hydrosulfites  
sulfides  
chlorates  
borohydrides  
urea  
ammonium hydroxide  
ammonium vanadate  
gluconic acid  
etc.

Thus, in a conventional process for the development of dyes on textile fibers and fabrics, it has generally been the practice to first contact the textile fiber or fabric with a dye or similar material capable of being subsequently developed, and thereafter, pass the fiber or fabric through a solution of developing agent, the fabric then being subjected to an elevated temperature effective to promote the reaction between the dye and the developing agent. Such a conventional process for developing dyes on textile fibers and fabrics has been improved in accordance with the process of the present invention, wherein the necessary reaction is achieved by a contact of the textile fiber or fabric with a heated roller maintained at a temperature of over 500° to 1,500° F. Here again, by the process of the present invention it is possible to greatly reduce the reaction time to a fraction of a minute.

As indicated previously with respect to the heat fixation process, while the apparatus employed in accordance with the present invention has been discussed primarily with respect to the embodiment of migration of dyes, the same apparatus is similarly applicable to the development of dyes and similar materials as described here. Thus, again, the apparatus need only to be modified to the extent of allowing for apparatus effective to print or impregnate the textile fiber or fabric with the necessary reagents to conduct the chemical development process. Thus, with respect to the developments of dyes, for example, it is necessary that the apparatus include in addition to the heated roller, at least one bath prior to such roller, to impregnate the textile fiber or fabric with the desired dye and reactants. Preferably at least two baths are used, one to impregnate the textile fiber or fabric with the desired dye and one to impregnate the textile fiber or fabric with the necessary developing agents.

### CURING

Synthetic resins are commonly employed in conjunction with a dyestuff or pigment, etc., so that when the synthetic resin is cured through the application of heat the dyestuff or pigment will be permanently fixed to the fabric, substrate, e.g. and subsequent washings, etc., will not remove the dyestuff or pigment from the fabric to which it is fixed.

For this purpose, any and all of the dyestuff or pigments discussed above can be applicably employed since the process of the present invention does not depend upon the use of any particular material for this purpose. In addition, the synthetic resin employed in accordance with this embodiment of the present invention can be any of those conventionally employed in the prior art, whether thermosetting or thermoplastic. Here again, the process of the present invention is not dependent upon the use of any particular materials, it being noted that the improvement of the present invention lies in effecting the curing of a synthetic resin in a more efficient and economical manner by contacting the textile fiber or

fabric with a heated roller at a temperature from 500° to 1,500° F.

Exemplary groups of resins which are conventionally employed in conjunction with flexible substrates, e.g., textile fibers or fabrics, to permanently fix a dyestuff or pigment to such fiber or fabric include, for example:

Synthetic rubber latices, including for example, polybutadiene, styrene-butadiene, acrylonitrile-butadiene, styrene-acrylonitrile-butadiene, polyisoprene, isobutylene-butadiene, polychloroprene, etc.; acrylic resins such as the homopolymers and copolymers of acrylic and methacrylic acid and their lower alkyl esters, including for example, homopolymers of acrylic acid, methylacrylate, methacrylic acid, methylmethacrylate and copolymers thereof with such monomers as vinyl acetate, vinyl propionate, vinyl butyrate, etc. In addition, di-functional monomeric materials and homopolymers and copolymers thereof, including for example such monomers as the glycol polymethacrylates can be suitably employed. Other resinous systems including polyvinyl chloride and copolymers of vinyl chloride and vinylidene chloride as well as polyolefins, e.g. polyethylene, polypropylene, etc., can be suitably employed in accordance with the present invention. Here again, it is pointed out that such resins are those which are conventionally employed to fix dyestuffs and pigments to textile fibers and fabrics.

In addition, with respect to the production of permanent press fabrics, it is conventional to apply a synthetic resin and cure the same so as to provide a permanent set on the textile material. Accordingly, this embodiment of the present invention relating to the curing of resins also encompasses the use of such resins conventionally employed in the production of permanent press fabric, e.g. thermoset resins. Such resins include, for example such as phenol-formaldehyde condensates, resorsinol-formaldehyde condensates, urea-formaldehyde condensates, as well as other resins produced from the condensation of alcohols or phenols and aldehydes.

Again, as with respect to the other embodiments of the present invention discussed above, the apparatus or system for effecting this embodiment of the present invention is the same as discussed with respect to the migration of dyestuffs to produce a tone-on-tone effect. Here again, such apparatus or system need only be modified to the extent of including within the system apparatus to effectively incorporate the synthetic resin within the textile fiber or fabric. In this regard, the heated roller effective in accelerating the curing of the synthetic resin by the brief contact of the fabric with the roller at the elevated temperature of the present invention remains essentially as described above.

### DISCHARGING OR DESTROYING DYES

Discharge printing comprises a process for the destructive removal of dye or dye components from selective areas of textiles containing the dye or dye components, such destructive removal being accomplished by the use of a discharge formula or paste accompanied by the application of heat. As indicated previously, in white discharge printing, the selected areas are left as white on a colored background, while in colored or illuminated discharge printing the selected areas lose their original color and are dyed a different color by a dye incorporated in the discharge composition. In either event, however, the essence of the discharge printing process involves a destruction or removal of dye or dye components by the use of a discharge composition accompanied by the application of heat.

In order to effectively promote the discharge or destruction of the dye, the active components of the discharge composition must be able to penetrate into the flexible substrate, e.g., textile fabric while, of course, not injuring the fibers themselves. In addition, the substances left in the fibers after discharge must be capable of being taken out of the fibers in subsequent washing or soaping operations, and the discharge composition must not be so fluid as to migrate from the

selected areas and discharge areas not intended to be discharged in accordance with the present invention. For this reason, discharge pastes normally containing a thickener or swelling agent are conventionally employed in discharge printing processes. Thus, in conventional prior art processes of discharge printing a discharge formula or composition is generally applied with an engraved roller by a process in which the discharge paste is removed from all except the engraved part of the roller by a doctor blade. After printing, the fabric is dried and passed through a steamer or ager in which the chemical reaction takes place in a period of from about 5 to 30 minutes. The lengthy time in the steamer is necessitated by the fact that the steamer operates only within the limited temperature range of 200° to 250° F., and because there is a limited amount of controlled moisture that can be obtained at such operating temperatures.

Such a conventional prior art process for conducting discharge printing is improved in accordance with the process of the present invention by which the textile fabric carrying the necessary moisture and chemicals, that is, the necessary dye and discharge composition is contacted at a temperature within the range of 500° to 1,500° F., or higher by a roller heated to such temperature, the points of contact of the fabric and the high-temperature roller creating steam at the points of contact, thus resulting in a reduction of the time of the discharge process from 5 to 30 minutes as in conventional processes to a fraction of a minute in accordance with the present invention.

It can be seen from the above, therefore, that the process of the present invention provides an improvement in the procedural aspects with respect to discharge printing, the process of the present invention having available all of the conventional materials generally employed in previously known discharge printing processes. Thus, while the process of the present invention is applicable to any type of dye conventionally employed in discharge printing, the process of the present invention is particularly applicable to azodyes. It is, of course, obvious that any class of substance capable of being discharged can be employed in accordance with the process of the present invention, such classes of substances being well known in the art.

Again, the discharge printing composition employed in accordance with the present invention may contain those conventional thickeners or swelling agents generally employed in conjunction with discharge printing compositions. Thus, a more complete discussion of the applicable materials employed in a conventional discharge printing composition can be found, for example, in U.S. Pat. No. 3,103,404, the subject matter of which is incorporated herein by reference.

#### DRYING

This embodiment of the present invention relates to an improved process for the drying of wet and moist flexible fabrics. Thus, while conventional drying processes have involved the use of drying ovens, drying cans, radiant heaters, or a similar apparatus to effect a slow, steady drying of the wet or moist material, it has been found that in accordance with the present invention such a process can be greatly improved by employing a heated roller, the improvement relating primarily to a great reduction in the time necessary to effect the desired drying. Thus, in accordance with the process of the present invention, it has been discovered that the drying of wet fabrics can be achieved by contacting the wet fabric for a fraction of a minute with one or more cylinders or rollers with a smooth or knurled surface. The temperature of the surfaces and the contact time are regulated so as to allow the necessary drying without damage to the fabric. Generally, the cylinder or cylinders are heated to a temperature of 500° to 1,500° F., or higher when desired for particular purposes. In addition, the fiber or fabric to be dried in accordance with this embodiment of the present invention may or may not contain addition chemicals or dyes in addition to the moisture or water present.

In this regard, it has been discovered in accordance with the present invention that unfixed dye does not transfer from the wet cloth and build up on the heated cylinders when cloth or fabric is contacted with the cylinders at the temperature specified above and for the limited contact period described.

Here again, as with the previous embodiments of the present invention described above, the apparatus necessary for effecting the drying by flash evaporation is essentially the same as described in connection with the migration of dyes to produce a tone-on-tone effect. Thus, the heated roller employed in accordance with this embodiment of the present invention need not be modified from that employed with respect to those embodiments previously described. In this regard, the process of this embodiment of the present invention can be utilized in conjunction with any of the other embodiments described above, wherein subsequent to effecting the chemical reaction or physical change by the application of heat through contact of the fiber or fabric with the heated dies or rollers, it is necessary to further dry the fabric in the manner described above.

The present invention will now be described by reference to the following specific examples. It is to be recognized that such examples are presented for purposes of illustrating the process of the present invention and the apparatus used therein and such examples are in no way to be deemed as limitative of the invention as described in the appended claims. All parts and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

The following dyestuffs and pigments referred to in the examples have the indicated Color Index numbers:

Dyestuff	C.I. No.
Fastazol Turquoise Blue LG	74180
Fast Red Salt 3GL	37040
Katigen Green BBF High Conc.	53571
Brilliant Indigo 4BV	73065
Indanthrene Golden Yellow RK	59105
Indanthrene Brown BR	70800
Algol Orange RF	73335
Hydron Blue RG	53630
Algol Yellow GC Infra Paste	67300
Indanthrene Blue BCF Infra Double Paste	69825
Celliton Yellow 5GA	12790
Celliton Blue BB Extra Conc.	64500
Rapidogen Red GS	Azoic Red 6
Algol Green IBW	59826
Algol Blue IBC	69826
Heliogen Green N	74260
Indanthrene Olive T3R Infra Paste	69525
Indanthrene Brilliant Green BM Infra Double Paste	59825

#### EXAMPLE I

Using apparatus as shown in FIG. 1, a bleached mercerized cotton twill fabric was passed into a pad box containing a solution of reactive dye as follows:

- 3 oz. per gallon blue dye B of example XIII below
- 12 oz. per gallon urea
- 3 oz. per gallon soda ash

The padding was conducted at a temperature of 110° F., with a moisture retention of the travelling web of bleached mercerized cotton twill being 75 percent.

The textile fabric containing the reactive dye solution passed in contact with a heated roller at a temperature of 600° F., the time of contact of the padded fabric and roller being one-half second. As a result of such contact of the padded fabric with the heated roller, approximately 90 percent of the dye was moved from the back to the face of the material leaving a dye image not migrated where there was no contact and clearly visible and differentiated contrast between the non-contacted and contacted areas. The reverse side of the cotton twill fabric showed the same pattern in negative form, that is the reverse of the pattern shown on the face of the fabric contacted with the heated roller.

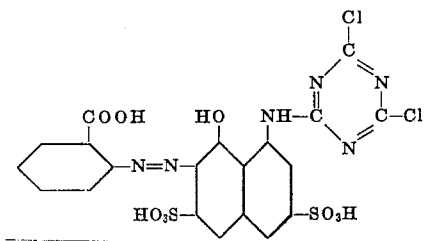
In accordance with this process, when the heated roller carried a pattern comprising parallel raised ridges, the cotton

twill fabric appeared after contact with the heated roller as a turquoise blue background containing lines or stripes of a darker blue and more intense coloration.

#### EXAMPLE II

The process of example I was repeated, except that the bleached mercerized cotton twill fabric was padded with a solution as follows:

- 2 oz. per gallon reactive yellow Dye A of example XIII below
- one-half oz. per gallon of the dyestuff:



one-half oz. per gallon reactive blue Dye B of example XIII below

- 12 oz. per gallon urea
- 3 oz. per gallon soda ash.

The padding was conducted at a temperature of 110° F., with 75 percent moisture retention on the bleached mercerized cotton twill fabric. Here again, the padded fabric was contacted with a roller for a period of time of one-half second at a temperature of 600° F.

An observation of the dyed cotton fabric after such treatment indicated that the background color of the fabric was generally a light brown color, while the areas which were contacted with the hot roller were dark brown. The back or reverse side of the fabric where migration occurred was russet in color. This, therefore, shows the applicability of a mixture of reactive dyes in accordance with the process of the present invention.

#### EXAMPLE III

Example I was again repeated, except that a mercerized cotton twill fabric was padded with a solution of substantive or direct dye in the pad box illustrated in FIG. 1. The mercerized cotton twill fabric was padded with a solution comprising 2 oz. per gallon Fastusol Turquoise Blue LG 50 percent, the padding being conducted at a temperature of 160° C., with the moisture retention on the mercerized cotton twill fabric being 70 percent.

As in example I, the padded fabric was then contacted with a heated roller, in this case, the time of contact with the roller being 5 seconds, the roller being maintained at a temperature of 500° F.

An examination of the dyed fabric after contact with the heated roller showed good contrast between areas on the fabric contacting and not contacting the heated roller.

#### EXAMPLE IV

Following the procedure of example I, a mercerized cotton twill fabric was padded with an azoic dye and contacted with a heated roller at a temperature of 500° F. In this example, a mercerized cotton twill was padded with a solution of 1 oz. per gallon Naphthol AS-SW dissolved in cold water, the padding being conducted at a temperature of 200° F., with a moisture retention of 70 percent. The padded cotton twill fabric was contacted with the roller for a period of time of 5 seconds, the roller being kept at a temperature of 500° F.

After contact of the padded fabric with the heated roller and migration of the dye, the fabric was passed from the roller into a coupling solution comprising 4 oz. per gallon Fast Red

Salt 3GL, with subsequent rinsing and drying of the fabric. Here again, an examination of the fabric after migration and coupling showed good contrast between the areas contacted and not contacted with the heated roller.

#### EXAMPLE V

In a similar manner as described in example I, a mercerized cotton twill fabric was padded with a sulfur dye solution comprising:

- 4oz. per gallon Katigen Green BBF High Conc.
- 4 oz. per gallon sodium sulfide flakes
- 2 oz. per gallon sodium carbonate

the ingredients of the padding solution being dissolved by boiling, the padding of the mercerized cotton twill fabric being conducted to a moisture retention of 70 percent. The padded textile fabric was contacted with a heated roller for a time of 5 seconds, the temperature of the roller being maintained at 500° F.

After migration of the sulfur dye by the contact of the padded textile fabric with the heated roller, the fabric was rinsed, oxidized with sodium dichromate and acetic acid, rinsed and dried. A visual examination of the dyed textile indicated a clear contrast where the dye was migrated to the surface of the fabric contacted with the heated roller.

#### EXAMPLE VI

Similarly, in a manner such as described in connection with example I, a cotton twill fabric was padded with a vat color solution comprising:

- 6 oz. per gallon Brilliant Indigo 4BV
- 8 oz. per gallon glycerine
- 13 oz. per gallon Rongalite CX
- 13 oz. per gallon potash

and the padded fabric was contacted with a heated roller at 600° F. for a contact period of one-half second.

After migration of the dye by contacting the padded fabric with the heated roller, the fabric was aged in neutral steam, oxidized and soaped in a conventional manner. The migration of the dye by contact with the heated roller was clearly observable with the background appearing as a washed-out or faded blue color and the contacted areas as navy blue. Accordingly, a very clear contrast was observed.

#### EXAMPLE VII

Following the procedure of example VI, a similar dyeing was made, except that Indanthrene Golden Yellow RK was employed in lieu of the Brilliant Indigo 4BV.

A clear migration of color was observable with the background appearing as gold and the contacted areas as a light brown color.

#### EXAMPLE VIII

Again repeating the process and conditions of example VI, a fabric was dyed employing the process of the present invention, except that the color Indanthrene Brown BR was substituted for Brilliant Indigo 4BV.

Here again, the color migration was clearly observable with the background appearing as light brown and the contacted areas appearing as a dark brown color.

#### EXAMPLE IX

Example VI was again repeated, except that the color Algol Orange RF was substituted for Brilliant Indigo 4BV. Here again, the contact of the padded fabric with the heated roller produced a migration of the dye clearly observable in the contrasting coloration of the finished fabric. Thus, migration was observable with a background of orange and contacted areas of dark brown color.

#### EXAMPLE X

Example VI was again repeated, except that the color Hydron Blue RG was substituted for Brilliant Indigo 4BV.

Here again, migration of color was clearly observable with the background appearing as purple and the contacted area as navy blue.

In all of the examples above, a clear contrast in color was observed after the padded fabric was contacted for a very short period of time with the heated roller. This establishes that the process of the present invention is effective in producing a phenomenon associated with the migration or movement of the dye to those areas in contact with the heated roll. This produces a very esthetic effect not heretofore possible, except with the use of more expensive and more complicated procedures.

#### EXAMPLE XI

Employing a system such as represented in FIG. 9, a migration process in accordance with the present invention was conducted. A cotton twill fabric was padded with a composition as follows:

- 3 oz. per gallon Algol Yellow GC Infra Paste
- 2 oz. per gallon caustic soda
- 2 oz. per gallon sodium hydrosulfite.

The padded material was squeezed and dried in a dryer where it oxidized to the desired yellow color.

The cotton twill material dyed yellow by the above process was then passed through a second pad box where it was saturated with an unreduced vat dye dispersion comprising a solution of 4 oz. per gallon Indanthrene Blue BCF Infra Double Paste. The products of this second application are not fixed during saturation and subsequent extraction, and thus are susceptible to migration, the first vat color solution being one which fixes as soon as it is applied and thus is not subject to migration. The textile material was then squeezed to retain about 70 percent moisture and brought into contact for one-half second with a heated roller at about 650° F. By this process, only the unreduced vat dispersion moves to produce the design or pattern, leaving the vat coloring applied initially unaffected. An observation of the cotton twill textile dyed in this manner indicates that the areas contacted by the heated roller are greenish-blue or dark green in color whereas the uncontacted areas are light green or greenish-yellow in color.

In order to completely fix the dyes, the material is further treated by conventional reducing agents, comprising 6 oz. per gallon caustic soda and 6 oz. per gallon hydrosulfite, the material being subsequently squeezed and the color developed by a pad steam method with finishing by rinsing, oxidizing, rinsing and soaping in a conventional manner.

Accordingly, the above illustrated the novel process of the present invention, wherein migration of one dye in preference to another is achieved to produce a novel esthetic tone-on-tone effect.

#### EXAMPLE XII

Employing apparatus as shown in FIG. 10, the process of the present invention was carried out as follows. Again, a web of cotton material was saturated in a pad box with an Indanthrene Blue BCF Infra Double Paste and squeezed to a moisture retention of about 70 percent by weight. The padded web of textile material was then contacted with a pattern roller for a contact time of ½ to 1 second at a temperature of 650° F. This produced a pattern on the material at the points of contact of the textile surface with the heated roller.

A ground shade was then produced by passing the textile material from the heated roller into a pad box heated to about 100° F., and containing a reduced vat color comprising:

- 3 oz. per gallon Algol Yellow GC Infra Paste
  - 2 oz. per gallon caustic soda
  - 2 oz. per gallon sodium hydrosulfite.
- From the pad box containing the reduced vat color, the cotton material was passed directly into a unit for further reduction of the vat color and simultaneous reduction of the vat pigment dispersion which was applied to the material initially and then migrated. Thereafter, the material was steamed, rinsed, oxidized, rinsed, soaped and rinsed again as in a conventional dyeing process.

Again, by this process, it is possible to provide a preferential migration of one dye in an initial step of the process so as to produce a finished fabric having an esthetic tone-on-tone effect.

#### EXAMPLE XIII

Again using a system such as shown in FIG. 10, the migration process of the present invention was conducted as follows. A cotton twill fabric was passed through a first pad box containing a fiber-reactive dye solution comprising:

- 3 oz. per gallon Yellow Dye A
- 12 oz. per gallon urea
- 3 oz. per gallon soda ash.

The padded material was dried and passed through a second pad box containing 3 oz. per gallon of blue fiber-reactive Dye B. The fabric padded with a second dye was squeezed to maintain about 75 percent moisture content and passed in contact with a heated roller maintained at a temperature of about 650° F., the period of contact being from ½ to 1 second. After migration, the material was heat cured for 3 minutes at 310° F., rinsed, soaped, rinsed and dried as in a conventional dyeing process. Such a process provided a fabric having green-yellow background effects and a dark green pattern where contacted by the heated roller. Dye A corresponds to the dichlorotriazinyl-containing monoazo pyrazolone dye of example 11 of French Pat. No. 1,178,011. Dye B corresponds to the sulfatoethyl-containing phthalocyanine dye of example 1 of U.S. Pat. No. 3,200,129.

#### EXAMPLE XIV

A. When Example I is repeated except that the fabric was as follows, substantially equivalent results are obtained:

1. a polyester-cotton fabric
2. a polyester (Dacron) fabric
3. a triacetate (Arnel) fabric
4. a rayon fabric
5. a nylon fabric
6. an acrylic fabric
7. a modacrylic fabric
8. a fiber glass fabric

B. When example XI is repeated employing the same fabrics as in (A) above, again substantially equivalent results are obtained.

#### EXAMPLE XV

A dispersed dye was printed on a triacetate (Arnel) fabric in a conventional manner, the dye paste having the following composition:

- 3.00 percent Celliton Yellow 5GA
- 5.00 percent Urea
- 42.00 percent Hot water (160° F.)
- 50.00 percent Keltex S\* (3 percent solution)

Samples of the triacetate fabric printed with the dispersed dye composition were then developed by the conventional aging technique and by the process of the present invention.

A.

A part of the print produced above was passed over a finely knurled cylinder at a temperature of 500° F., at a speed of 7 yards per minute, the full contact distance approximating 8 inches. After such heat treatment, the printed fabric was soaped, rinsed and dried in a conventional manner. The time of contact with the heated cylinder was 0.023 minute.

B.

Employing a conventional aging process, a portion of the print produced as above was cottage steamed for 1 and ½ hours at a pressure of 5 pounds per square inch. The fabric so heat treated was then soaped, rinsed and dried as in A. above.

An examination of the product produced both by the process of the present invention (A.) and that produced employing a conventional steaming of heat-aging process for heat fixation (B.) indicated that the fabrics produced were substantially

\* Keltex S is a sodium alginate product passing through 10 mesh and having a moisture content of about 13 percent. The product is manufactured by the Kelco Co. (Cond. Chem. Dict.—6th) identical. Thus, the continuous, much faster, and more efficient and economical process of the present invention resulted in a heat-fixed product having substantially the same characteristics as that of the prior art.

#### EXAMPIE XVI

Example XV (A.) and XV (B.) were repeated except that the dye used was a 3.00 percent Celliton Blue BB Extra Concentrate. Here again, an examination of the fabric thermally fixed by both the process of the present invention and the slow aging of the prior art indicated substantially the same results even though the time of contact with the heated cylinder in accordance with the process of the present invention was only 0.023 minute.

#### EXAMPLE XVII

Utilizing the process of the present invention and a conventional acid aging process for Rapidogens, prints were produced from the following composition:

- 4.00 percent Rapidogen Red GS
- 2.00 percent caustic soda
- 44.00 percent water
- 50.00 percent Keltex S (3 percent solution)

A sample of the previously printed and dried cotton fabric was saturated with a developing solution comprising:

- 3 percent acetic acid (28 percent)
- 97 percent water

squeezed or extracted and then contacted with a heated roller surface at a temperature of 500° F., for a period of contact of 0.023 minute. The fabric that was produced was bright red in color.

For comparison, another sample of the previously printed and dried fabric as above was acid aged in a conventional manner for 4 minutes at 210° F. An examination of the fabric produced in this conventional manner also showed a bright red color, the fabric being incapable of being distinguished from that produced in accordance with the process of the present invention. The ability to greatly reduce the reaction time, however, showed a great industrial advantage.

#### EXAMPLE XVIII

Using the following composition, Algosol prints were produced both in accordance with the process of the present invention and in accordance with a conventional acid aging process:

- 4.00 percent Algosol Green IBW
- 4.00 percent Glycine A (thiodiglycol)
- 10.00 percent urea
- 22.00 percent water
- 50.00 Poly Gum 260 (Polymer Industries, Springfield Conn.)
- 4.00 percent sodium chlorate (1:3)
- 2.00 percent ammonium hydroxide (28 percent)
- 2.00 percent ammonium vanadate (1-100)
- 2.00 percent gluconic acid

By the process of the present invention, a cotton fabric containing the above was contacted with a heated roller at a temperature of 700° F., the period of contact being 0.011 minute.

For comparison, a similar fabric was treated in a conventional acid-aging procedure for 4 minutes at 210° F. An examination of the fabrics after both treatments indicated that they could not be distinguished, each appearing as an esthetic bright green color.

#### EXAMPIE XIX

Example XVIII was repeated, except that the Algosol print composition contained 4.00 percent Algosol Blue IBC in lieu of the Algosol Green IBW. Here again, by both the process of the present invention and by the conventional acid-aging process a fabric was produced having a esthetic blue color. The process of the present invention while providing a fabric of the same quality as that produced by conventional methods,

has the advantage of allowing the production of such fabric in a continuous, much faster, more efficient and economical manner.

#### EXAMPLE XX

A Heliogen Green N supra paste (pigment) was blended with a resin binder and padded on a mercerized cotton twill, the composition of application being as follows:

- 6.00 ounces Heliogen Green N Supra Paste
- 127.00 ounces of a resin binder consisting of:
  - 43.50 percent Cultex 8 -VX-11 A\*
  - 3.30 percent Acrysol GS\*\*
  - 15.40 percent Carbopol No. 934 (4 percent solution)\*\*\*
  - 25.60 percent Resin Mix\*\*\*\*
  - 12.20 percent XyloI (crude xylene)
  - 100.00 percent

The impregnated mercerized cotton twill was then brought into contact with a knurled and lined roller for a period of ½ to 1 second at a temperature of 600° F. After such contact, the fabric was rinsed and soaped as in a conventional manner. An examination of the fabric after rinsing and soaping revealed that the fabric remained dyed, indicating that the curing of the resin by contact with the heated roller permanently affixed the pigment to the cotton twill fabric.

#### EXAMPLE XXI

An azoic or naphthol Red ground shade was dyed and then discharged to produce white stripes by the following procedure:

- 2.00 oz. per gallon of Naphthol AS-Supra (azoic coupler 2) was dissolved by a conventional cold dissolving process, padded on mercerized cotton twill, dried and coupled with Fast Scarlet Salt GGN (azoic diazo component 3). The dyeing was rinsed, soaped and rinsed in a conventional manner.

\*General Latex \* Chemical Co.—styrene-butadiene latex.

Rohm & Hass—Sodium salt of high-molecular-weight polymer in watersolution—acrylic resin.

B. F. Goodrich Chemical Co. —Carboxy Vinyl polymer of high molecular weight supplied in acid form.

\*\*\*\*Resin Mix: 35.8 percent Cymel 243-3 (American Cyanamid)-urea-formaldehyde resin 35.8 percent Syntex 128 (Jones Dabney)—alkyd resin 14.2 percent Clear T-50-10 percent Ethyl Cellulose T-50 (Hercules Powder) dissolved in XyloI and iso-octyl alcohol. 14.2 Conco Lauryl Sulfate TL (Continental Chemical)

The red or scarlet dyeing was then padded at room temperature with:

- 100 parts Rongalite CX (sodium sulfoxylate-formaldehyde)
- 15 parts Dissolving Salt BA New (sodium benzylsulfanilate)
- 25 parts potash
- 10 parts Anthraquinone Paste 30 percent
- 75 parts Polygum 260
- 275 parts water
- 500 parts total

The dyed material was padded, extracted by squeeze rollers to 70 percent moisture retention and then contacted with a patterned cylinder at a temperature of 600° F., for 0.023 minute (1.38 seconds). Such high temperature contact was followed by conventional rinsing and soaping.

A visual examination of the fabric treated in the above manner showed that the same showed discreet white lines on the red or scarlet background, the pattern of lines corresponding to the pattern of the heated cylinder.

#### EXAMPLE XXII

A cotton fabric which had been dyed with 2.00 percent Phenazo Indigo Blue BR (Direct Blue 120), diazotized and then developed with beta-naphthol was padded at room temperature after drying with the following discharge composition:

- 75 parts Rongalite CX
- 350 parts water

75 parts Polygum 260  
500 Total

After the dyed material was padded with the above composition, excess material was extracted by squeeze rollers to about 70 percent moisture retention. The fabric was then passed over a heated patterned roller as in example XXI. The rollers were heated to 500° F., the distance of contact was 6 inches, and the time of contacts was 0.023 minute (1.38 seconds). At the points of contact with the heated patterned roller, the ground shade was discharged by chemical reaction brought about by the localized heating at elevated temperatures. The part of the dyed fabric not contacted with the heated patterned roller retained the original shade unaffected.

#### EXAMPLE XXIII

A mercerized cotton twill was padded with a dye solution and passed through squeeze rollers at a rate of 40 yards per minute, the wet pickup on the fabric being 56.6 percent by weight. The wet fabric was then contacted with a heated roller or cylinder having a surface temperature of 1,00° F., the distance of contact being approximately 8 inches. With this single contact of the wet fabric, with the heated surface, the moisture content of the fabric was reduced to 42 percent by weight.

A second contact of the moist fabric with another heated roller or cylinder under the same conditions as specified above reduced the moisture content of the fabric to 15.6 percent by weight, while a third contact reduced the moisture to 1.80 percent by weight, based on the total weight of the fabric.

It can be seen from the above that the use of three 6-inch cylinders at 1,000° F., with a combined contact area of 24 inches will accomplish the same degree of drying on the same fabric with the same moisture retention as 20 stainless steel dry cans of 23-inch diameter at 50 pounds steam pressure, the combined contact of 33 yards of fabric. This, of course, is in accordance with Infra employed prior art methods of drying moist or wet fabrics.

#### EXAMPLE XXIV

Referring to the apparatus shown in FIG. 12, an 80+80 desized and bleached cotton fabric was passed through pad bath 142 containing a vat color dispersion made with 2.0 ounces per gallon of Indanthrene Olive T 3R of Paste and 0.2 ounce per gallon of Nekal NF (GAF—sodium alkyl-naphthalene sulfonate wetting agent), squeezed through rollers 133 to a moisture retention of 60 percent and passed at a speed of 40 yards per minute in contact with three 6-inch cylinders 171 to migrate the dyestuff to the upper surface of the fabric. This was accomplished by keeping the middle roller 171 cold or unheated and maintaining the surface temperature of the first and third rollers 171 at a temperature of about 1,000° F. Somewhat similar migration results could be obtained by contact with a single hot roller at a speed of 20 yards per minute. By this treatment, almost 100 percent of the olive dyestuff was transferred to the upper side of the fabric, leaving the lower surface of the fabric slightly off-white.

The fabric was then reversed and padded through a second vat color dispersion made with 2.0 ounces per gallon of Indanthrene Brilliant Green BN Infra Double Paste and 0.2 ounce per gallon of Nekal NF, squeezed to a moisture retention of 60 percent, and passed in contact with rollers 171 at temperatures, speeds and degrees of contact similar to the above but with the initial off-white surface facing up. By this treatment, substantially all the green dye was migrated to the upper surface of the fabric, thereby producing a single-ply fabric dyed a distinct olive shade on one side and a distinct green shade on the other side.

The fabric was then passed through a reducing bath containing, per gallon, 8 ounces of caustic soda and 8 ounces of sodium hydrosulfite, and then developed or fixed in the usual manner by steaming, washing, oxidizing, soaping, rinsing, and drying. A completely novel product was thus produced by the improved, simple, rapid, continuous and economical process

of this invention and not obtainable by any previously known method of printing or dyeing. Any desired variations in results may be obtained by suitable adjustment of the squeeze rollers to other degrees of moisture retention, and/or variations in fabric speed, degree of contact with the hot rollers, temperature of the hot rollers, etc. Obviously, the dyestuffs employed in this example may be replaced by any other desired dyestuffs, pigments and/or chemicals which may or may not require elimination or replacement of the reducing solution by other suitable fixing, developing or other means. Further, although overall effects were obtained in the above-described procedure by use of hot rollers with smooth or uniformly knurled surfaces, any desired pattern effects may obviously be obtained by using suitably patterned hot rollers for contacting one or both surfaces of the fabric. Still further, a product having similar effects on both surfaces can be obtained by suitable use of similar migratable materials in both of the described pad baths.

It can be seen from the above that the present invention comprises an improvement in any and all processes wherein a chemical reaction or physical change is effected on a flexible substrate, e.g. a textile fiber or fabric, wherein such chemical reaction or physical change is effected by the application of heat. Thus, it has been discovered in accordance with the present invention as described above with respect to the various embodiments embraced thereby, that any and all of such processes can be conducted more economically and more efficiently by contacting the fiber or fabric containing the necessary reactants with a roller heated to a temperature within the range of 500° to 1,500° F., preferably 525°–550° to 1,500° and more preferably 700°–1,500° F. As pointed out above, such process of the present invention allows the time of reaction to be reduced from up to several hours or more to a period of a fraction of a minute. Thus, in accordance with the present invention, it is only necessary to contact the fiber or fabric containing the necessary reagents or other liquid materials with the roller heated to the temperature specified above, the tension being applied to the textile fiber or fabric being sufficient to maintain good contact between the fiber or fabric and heated die or roller. Generally, the tension applied to the textile fiber or fabric when conducting the process of the present invention is sufficient to maintain contact with the heated dies or rollers, as was done in all the examples given above.

The present invention is particularly important, for example, with respect to that embodiment of the present invention relating to the production of a tone-on-tone effect through the migration of dyes and the preferential migration of dyes in particular. Thus, in accordance with the present invention, it has been discovered that for the first time it is possible to take advantage of the migration phenomenon associated with the attraction of dye media to heat by locally applying high temperatures to a surface of a textile fiber or fabric, such local application of high temperature being effective to substantially migrate the dye so as to produce the esthetic tone-on-tone effect.

This phenomenon, of course, that is, the phenomenon of migration of dyes is advantageously carried out simultaneously and in conjunction with the fixation of dyes on the textile fiber or fabric. Thus, in accordance with the present invention, it has been discovered that it is possible to simultaneously migrate and fix the dye carried on a textile fabric by employing one or more heated cylinders in addition to that necessary to bring about the migration phenomenon. Thus, with respect to this application of the process of the present invention, a first heated cylinder may produce migration of the dye while a second and/or possibly third or more cylinder may complete the heat fixation process. In this way, it is possible to utilize the process of the present invention in a continuous manner. Of course, as is the case with all of the embodiments of the present invention, the temperature and period of contact of the textile fiber or fabric with the heated surface must be controlled so that the textile fiber or fabric is processed without any damage. The desired migration and possibly some fixation

takes place upon this contact with the first cylinder; the second and/or third cylinder is then used to complete the thermofixation or heat setting in a continuous-type manner.

Accordingly, it is again to be noted that while the present invention has been described with regard to the use of specific materials within the exemplary material, it is to be understood that the improved process of the present invention is in fact applicable to the employment of any and all conventional materials generally employed in processes such as embodied by the instant invention. In this regard again, it is to be noted that the improvement of the present invention, allowing for the more effective and more economic conducting of processes with regard to effecting chemical reactions and physical changes can be accomplished regardless of the materials involved, as long as the textile fiber or fabric containing the necessary reagents is contacted with the heated solid surface at a temperature within the range of 500° to 1,500° F. Thus, as pointed out previously, the process of the present invention has, as additional advantages, the elimination of acid or neutral agers for the development of some types of dyes, the elimination of doctor blades required in conventional roller printing and the elimination of curing ovens for the fixation of certain types of dyes, resins, pigments, etc. In general, it can be said that the process of the present invention allows for a substantial economic improvement with regard to previously employed processes conducted in connection with flexible textile fibers and fabrics.

It should be apparent from the above that the process and apparatus of the present invention, in addition to greatly improving the chemical and physical changes associated with the application of heat to the flexible web or sheet material, e.g., flexible textile fiber or fabric, allow for the production of effects not heretofore possible by previously employed processes and apparatus. This, therefore, affords a great improvement over any and all existing prior art.

Thus for example, as pointed out previously, it is now possible in accordance with a preferred process of the present in-

vention to provide a contrast in coloration as much as 10:1 through the preferential migration of dyes utilizing the heated rollers or dies of the present invention. Such an effect, of course, could not in any way be produced by any known process.

It will be understood that instead of the aqueous media described above, other liquid media, solvents, diluents and/or carriers, organic or inorganic, may be employed herein with commensurate suitable adjustment of the variable factors of time, temperature, etc.

We claim:

1. A process comprising treating a flexible textile fabric to impregnate same with about 30 percent to 125 percent, by weight of the fabric, of a non-film-forming liquid composition comprising a solution or dispersion of a non-film-forming coloring material in a volatile liquid medium, and contacting the resulting impregnated fabric with the surface of a roller maintained at a temperature of about 500° to 1,500° F. for a contact time, within the range of about 1/5 to 5 seconds, sufficient to migrate such liquid composition to the area of the fabric in contact with said roller surface but insufficient to damage the fabric.

2. The process of claim 1 employing an aqueous solution or dispersion of said coloring material.

3. The process of claim 1 wherein said impregnated fabric is under tension sufficient to assure contact with said roller surface.

4. The process of claim 1 wherein the impregnated fabric contacts on the raised portion of said roller having a raised three-dimensional pattern.

5. The process of claim 1 wherein said flexible textile fabric is saturated with said non-film-forming liquid composition and then squeezed to provide a fabric impregnated with about 30 percent to 125 percent of said composition, by weight of the fabric, prior to contacting the impregnated fabric with said roller surface.

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