Patented Jan. 2, 1945

2,366,347

UNITED STATES PATENT OFFICE

2,366,347

METHOD OF DYEING

Henry Edmond Millson, Plainfield, N. J., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application July 23, 1942, Serial No. 452,081

6 Claims. (Cl. 8—2)

This invention relates to an improved method of dyeing and drying, more particularly to a method whereby a dye is distributed throughout the fiber in a more uniform manner.

In general the dyeing of different fibers such as wool, cotton, silk, rayon, nylon, cellulose acetate, lanital, jute or any other natural or artificial fibers presents different dye problems depending upon the fibers to be dyed. However, one problem is common to all, namely that of producing a uniform penetration and coloring of the fiber by the dye. This problem must be solved whether the fibers are in the form of yarn, slub, pieces, cut staple, raw stock or in any other physical form in which fibers are dyed or printed since it appears to be the distribution of color in the fiber itself which largely governs the apparent shade of the finished piece.

Broadly speaking the coloring of fibers, whether by dyeing or printing, presents two difficulties. First, in order to produce a uniform shade, the dye or other color must be uniformly distributed throughout the fiber. Secondly, any excess liquid in or on the fiber after the dye-contacting step must be removed. These two requirements are present whether the fibers are contacted with a relatively large body of dye liquor as in piece or yarn dyeing or a relatively small body of color composition as in the printing of cloth.

Thus, failure to secure uniform coloring may be caused not only by a non-uniform penetration of the dye during the color-contacting step but also by upsetting the color distribution during the drying step. The drying of the color-contacted fiber presents an entirely different problem from the simple removal of excess moisture. In drying the dyed fiber, not only must the moisture be removed but it must also be done under conditions which will not disturb the uniformity of color distribution. Since the production of a uniform shade is one of the first prerequisites of successful dyeing, great care is usually taken in attempting to provide a satisfactory solution to both the distribution and the drying problems.

Since, as pointed out, every fiber type presents a different set of dyeing problems, in order to achieve control of the color distribution and therefore to some extent the resultant shade, an attempt is usually made in dyeing operations, for example, to cause the fiber to take up all the color it can from the dye-bath. In other words, when the material is removed from a particular dye-bath it should be in exhaustion equilibrium and incapable of taking up further color from that bath. The amount of available color can then be adjusted so that this will produce the desired shade. In batch dyeing this is carried out by so adjusting the dye-bath that all the dye will be exhausted on or in the material. In continuous dyeing, the dye-exhaustion equilibrium is attempted by regulating the contact time in relation to the dye-bath conditions.

However, these equilibrium conditions are not always easy to achieve, and they are not the only factors to be considered. For example, for a given weight of fibers and a fixed amount of dye, different apparent shades are produced if the color is uniformly distributed in the fibers in one case, and unevenly distributed on the fibers in another case. Consequently many additional controls are used. For example, such expedients as using wetting out agents, adjusting the strength of the dye liquor, adjusting the pH of the dye liquor, adding various salts, controlling the time of contact and using care in handling the material are employed.

Not the least important of these is the control of the temperature during the color contacting step. It was found early in the dyeing art that the color could be exhausted more quickly when the dye-bath was heated. Various means of heating the dye-bath directly or indirectly have therefore become more or less universally used. Careful observation, however, has shown that the speed with which fibers exhaust dye is increased as the temperature is increased but that in ordinary practice, the principal advantage lies in the fact that equally good dyeing can be accomplished much more quickly.

Even after exercising the greatest degree of skill and care in employing these many different expedients and controls, the color distribution may not be absolutely uniform. The dyeing produced may still show unevenness or mottling caused by absorption of different amounts of dye in different portions of the fibers themselves or in different parts of the yarn or piece into which the fibers may have been made. Or a failure to produce an even dyeing of the desired shade may result from having a greater concentration of color at or near the surface of the fibers so that the apparent shade changes as the surface loses color through surface wear or in washing.

After a contact between the fibers and the dye has been made, the problem of removing any excess moisture without disturbing the uniform color distribution still must be solved. Many different drying devices have been used in actual

practice such as lofts, ovens, tenters and the like, all of which have been used in various drying operations.

In order to guard against the difficulties which arise in drying the dyed fabric extreme care must be taken in this step as well. For example, in plant operation any excess dye solution which may be carried by the material must be removed before drying. This necessitates a series of washing and rinsing steps. The material must be passed slowly through the dryer or care taken in some other way to prevent too rapid evaporation from the surface. In spite of the precautions exercised, dyed pieces are often spoiled, so far as their shade is concerned, by color migration during the interval between the color-contacting step and the end of the drying operation. This has brought about the use of fixing agents which are supposed to prevent migration of dye before and during drying. This treatment, which must be in addition to the rinsing and washing steps, increases the cost and reduces production by requiring two or more additional baths.

Where the fibers must be handled in a thick package as in the drying of rayon cakes after the cellulose regeneration step, drying has been carried out by subjecting the annular cake to an electromagnetic field. In that case, however, the only use of the electromagnetic field has been to force the heat through a thick mass of fibers which are held in such a manner that uneven shrinkage is a serious problem when heat is applied to only one surface of the cake. If the fibers which go to make up the mass are individually subjected to any other form of heating, the drying problem as presented, is satisfactorily met. There is no distribution of color problem. Since this type of drying is less efficient from the point of view of energy consumption than other drying methods and since it has no particular advantage so far as single strands or piece goods are concerned it is not an ordinarily used method of heating.

As was pointed out, the drying problem presented in securing a uniform coloring differs from an ordinary drying problem in that not only must the excess liquid be removed but it must be removed without upsetting the color distribution which has been so carefully managed in the dye-contacting step. Drying may cause color distribution difficulty in any of several ways. For example, since the surface becomes dry more rapidly than does the interior the color tends to migrate toward the surface and produce a concentration of color at or near the surface. In some cases this tendency may be so pronounced as to cause highly undesirable bronzing and crocking.

It is, therefore, an object of the present invention to provide a method whereby a dye can be both more uniformly caused to penetrate and dye or color the fiber and be more readily dried without upsetting the color distribution. It is also an object of the present invention to provide a method by which a dyeing and drying rate which would be wholly impractical with previously known methods may be readily maintained.

In general the objects of the present invention are accomplished by first contacting the fibers with a coloring composition of some type and then subjecting the color-contacted fibers to a field of radiant energy such as an alternating electrostatic or electromagnetic field adapted to internally heat the fibers and their accompanying moisture, fillers, dye and the like. Since substantially all electrostatic fields are also to some extent electromagnetic fields and vice versa, the term "electrostatic field" in the present specification and claims may include both.

Since the type of dryers which depend upon external heating and the known types of high frequency dryers are both used with substantially similar efficiency, so far as the removal of moisture is concerned, it would be expected that they would act in the same way when applied to the dye-contacted fibers. Surprisingly enough this is not the result. By using electrostatic heating, whether on single fibers, yarns or woven pieces, the drying function may be achieved without disturbing the uniformity of color distribution. It not only does not upset the color distribution but also carries out the actual drying step more easily and quickly than any of the more conventional methods. A dyeing and drying rate may be easily maintained which is high enough so that if the heat had been externally applied the color distribution would have been completely upset.

One action of the high frequency radiation is apparently to set up an unbalanced electromotive force which either causes or tends to cause current flow within the actual fibers, liquid or other materials in intimate contact with the fibers. Where there is a considerable quantity of moisture or other relatively good conductor present the current flow probably causes eddy currents which are greatest in the best conductor. If all the material is a good dielectric, little current will flow but hysteresis will occur in the non-conductor. In any case, the result is to set up almost instantaneously a uniform, increased temperature throughout the fiber.

This is in direct contrast with other forms of heating in which heat is externally applied and consequently the fiber surface is first raised to a temperature higher than that of the interior of the fiber, thereby forcing heat into the interior. By means of the uniform heating of the present invention, drying occurs uniformly throughout the fiber rather than the surface first drying and the moisture from the inner portion then being forced through a relatively dry outer zone.

In addition to carrying out the drying function in a superior manner, heating the dye-contacted fibers according to the process of the present invention has entirely separate and distinct advantages due to the effect on the fiber itself. In the older processes the dye-contacted fibers are passed to some form of drying apparatus. For example, a tenter or drying oven may be used in which a relatively high temperature is maintained and through which the material is passed. However, except at the exit end of the tenter the temperature of the material is not the average temperature inside the dryer. There are two opposing tendencies. The dryer is attempting to heat up the fibrous material by applying heat to the surface but at the same time evaporation from the surface is tending to keep it cool. As a net result, the surface of the fibers is necessarily at a somewhat higher temperature than the interior. Since, as was pointed out above, color penetration is speeded up by heating and the color migrates to the hottest portion, there is a distinct tendency for dye to pass to, and become concentrated upon the surface of the fibers. As pointed out above, this result is highly undesirable and very slow drying rates have been required to prevent it. This has added to the

processing time, the apparatus required and the floor space occupied, all of which increased the cost of processing.

On the other hand, when the fibers are heated by being subjected to an electrostatic field, as in the present invention, they may be substantially instantaneously heated to a uniform temperature throughout. Then as evaporation tends to cool the surface, the hottest portion will be the interior of the fibers, rather than the exterior. Any migration of color which may occur, will be, therefore, toward the interior of the fiber rather than to the exterior, as in the conventional form of apparatus in which heat is externally applied.

The effect of heat in the drying step should not be confused with heat effects in the dye-contacting step. There temperature gradient is not particularly important because since there is liquid contact and the fibers are in effect quite thin, they come almost intantaneously to the temperature of the dyeing liquid. The inside of the fiber can never be hotter than the outside, however, and there are almost always some fibers which have not been uniformly colored. As pointed out, this is overcome by the present method of heating. It is clear, therefore, that the problem of heat transfer in the color-contacting step is not as important as in the drying step in which the temperature gradient across the diameter of the fibers can be, and usually is, an important factor in either producing or maintaining uniformity of coloring.

Another effect of the electrostatic-heating, as used in the present process, is to produce a uniform swelling of the fibers themselves. This is a distinct advantage of the present invention since it assists in the production of a uniform penetration of color to all parts of the fiber. Conventional methods allow many fibers to remain undyed throughout the entire dyeing operation because their scaly formation prevents swelling when heat is applied externally. When these fibers are processed according to the present invention, swelling of the fiber with the consequent opening of the scaly formation and better penetration of color is insured. This is particularly important in the case of such fibers as wool, fur, casein and the like in which color penetration and equalization has been found to be largely dependent on the extent of fiber swelling.

The action of electrostatic-heating in these ways is a distinct advantage in producing a more uniform shade. It can be made use of in connection with a conventional method, including all the usual rinsing and washing steps, using the electrostatic field only to carry out the drying. In this way advantage can be taken of the property possessed by this type of heating of equalizing the color distribution. It can be used in this way either to serve as an added margin of safety in securing a uniform shade, or to enable the dye-contacting operation to be carried out with less care, and in a shorter time. While these possibilities are important advantages of the present process, they do not take full advantage of the inherent capabilities of this type of heating.

Full advantage can be taken by combining the dye-contacting and drying steps into a single operation. In this way, for example, continuous dyeing can be carried out easily and quickly and with the elimination of many handling steps such as the rinsing and washing which is necessary in conventional practice. It is only necessary to provide a dye-bath and some means for keeping its composition approximately constant. Then the material may be passed through the dye-bath and directly through the electrostatic field omitting the rinsing and washing procedure. Any dye in the liquor carried by the material will be caused to be uniformly distributed through the fibers because of the uniform heating of the present invention. Therefore, not only may a uniform shade be obtained but the shade may be controlled, almost alone, by the rate at which the material is passed through the dye-bath and electrostatic field.

By way of contrast, if a similar piece of the same material was passed through the same dye-bath and then directly to a conventional dryer an entirely different result would be obtained. Regardless of the drying rate in the conventional dryer, it is virtually impossible to obtain any color penetration during drying because the water is evaporated from the dye liquor at the fiber surface only, and the color is deposited there. Since substantially all the color remains on the surface, the resultant shade is visually different. The product has not only been given a different apparent shade, but in many cases a wholly unsatisfactory one, since it is neither permanent nor uniform. In many cases the surface concentration of color is so great as to produce bronzing and crocking. In addition, this surface concentration is usually improperly fixed to the fiber and therefore tends to be readily removed by washing.

It is therefore apparent that by combining the dyeing and drying operation according to the present invention a number of advantages are obtained. A uniform shade is readily obtained. Control of the shade is relatively simple. A number of handling steps are eliminated. The process is very fast as compared to a conventional dyeing and drying. The space required for a conventional dryer is very large and this may be used now for other purposes. And finally a maximum even shade can be obtained at the expense of a minimum amount of dye, since such dye as is present is uniformly distributed and the material does not suffer from that unevenness of coloring which requires a greater amount of actual dye to produce the same appearance.

In carrying out this combined dyeing and drying procedure, another important advantage of the present process becomes apparent. As pointed out, the material passes rapidly through the color-contacting operation and comes out carrying a large amount of liquor which contains enough color to complete the dyeing function. The dyeing is then completed during the drying operation. It should also be noted that in ordinary practice with many dyes, the dye liquor contains a dilute acid to exhaust the dye in and on the fiber and that further acid is added as the dye becomes exhausted. As the dye is exhausted the total dye remaining in the liquor obviously decreases. However, in the present process as the dye is being exhausted the volume of dye liquor is also being decreased and the concentration of both dye and acid is being simultaneously increased due to evaporation. In this way, the most favorable conditions for complete exhaustion of all the dye are maintained.

These conditions can not be equally well maintained by any conventional means. For example, in bath-dyeing it is customary to add increasing amounts of acid to the bath as the dye content decreases. This promotes further dye exhaustion

but is not nearly as effective as it would be if the volume of liquor could be continuously decreased in order to maintain a relatively high concentration of dye. This desirable condition is maintained in the dye liquor carried by the material as it passes through the electrostatic heating zone in the process of the present invention. At the same time, a saving in acid is made since there is no need for further additions. The present process, therefore, not only makes a better dyeing but does so with the use of less acid.

The invention will be described in greater detail in conjunction with the following specific examples, which are meant to be merely illustrative and do not in any way limit the invention.

Example 1

A wool yarn was treated by passing it continuously through a dye bath containing 1% Calcoid Orange Y (C. I.–151), 2% sulfuric acid and 8% Glauber's salt and then directly through an electrostatic field having a frequency of about 25 megacycles at a rate such that final moisture content was approximately 5%. A good dyeing of uniform shade was produced. A similar sample was passed through the same bath and dried with radiant heat from a bank of lamps. An uneven shade which bronzed badly was produced.

Example 2

A cotton yarn was processed by passing it continuously through a dye bath containing 5% Calcosol Blue BLD (C. I.–1114), caustic soda and hydrosulfite concentrate and then, while excluding air currents, passing the yarn through an electrostatic field having a frequency of about 22 megacycles at a rate which produced a residual moisture of about 2.5%. No appreciable oxidation occurred. The sample was then oxidized and developed a full, even shade which indicated excellent penetration of the dye in leuco-form before oxidation. A second sample, dried by external heating as in Example 1, was found to have the major portion of the oxidized dye on the material surface.

Example 3

The procedure of Example 2 was repeated on a sample of rayon (viscose) yarn. An excellent even shade was produced.

Example 4

A cotton yarn was processed in similar manner using a dye bath containing 5% Calcogene Blue 2 RCF (C. I.–959), sodium sulfite and soda ash and the moisture content reduced to 5%. The developed color was well distributed and of an excellent, even shade in the case of the electrostatic dyeing and unevenly deposited, largely on the fiber surfaces in the case of the external heating.

Example 5

A rayon yarn was processed according to Example 4, reducing the hygroscopic moisture to about 2.5%. A good even dyeing was produced on the electrostatically dried sample but very poor results which crocked badly were obtained with radiant heating.

Example 6

Cotton yarn was processed from a bath of 5% Calcodin Yellow 4 GL (C. I.–346) and 10% common salt to a moisture content of about 3% to produce an excellent dyeing. A similar yarn dried by radiant heat as in Example 1 exhibited a very poor shade and uneven dyeing, with a surface deposit removable by rubbing.

Example 7

The procedure of Example 6 was repeated on rayon yarns. The electrostatic drying produced a good shade. Externally heating produced a complete failure as a dyeing operation.

Example 8

Example 7 was repeated on cotton yarn in skeins, drying one skein rapidly with the electrostatic heater. An excellent result was obtained in about 7 minutes' elapsed time. The other yarn was dried very slowly over a period of four hours. The quick-dried skein showed an even dyeing of much better shade.

It is a further advantage of the present invention that it is not necessarily limited to any particular type of dyeing. The fibers and coloring material may be contacted according to any of the existing dye processes now in use. This is true whether the fibers in the particular form in which they are being used are saturated in a bath or treated in a printing process. It applies equally whether a vat dye or some other form of dye is used. An equally uniform shade can be obtained whether the coloring composition is applied cool, heated or at the boil. A little time is saved by applying the coloring material while hot but little difference is to be observed in the final product.

It is also an advantage of the present invention that it is not necessarily limited to an alternating electrostatic or electromagnetic field having a narrow range of frequency. Many existing types of apparatus can be used as a source of high frequency radiation. The process may be carried out effectively using ranges from radio short wave lengths up through the ranges normally used in diathermy treatments and the extreme long wave lengths of the infra-red band. The essential feature is that the chosen frequency be capable of internally heating the material. To be effective in this way, however, the frequency should be below that of the optical range. In the present specification and claims the term "optical range" is intended to include not only the visible portion of the light spectrum but also the shorter infra-red radiations which lie below the visible range and respond similarly with respect to optical laws.

Under different circumstances there may be advantages in using different radiation frequencies. For example, when there is a great deal of moisture present, or when the fibers themselves are for some reason relatively conductive or contain conductive fillers, a frequency of radiation should be chosen that will cause the greatest possible eddy-current losses in the conductive material. This is the most frequently met condition and applies to the present process of combined dyeing and drying. Although the present process is not meant to be so limited, excellent results were obtained with this type of sample using frequencies of from about 20–25 megacycles.

However, as the material becomes more and more thoroughly dyed and dried its conductivity becomes progressively less and less until a point is reached at which heat is more readily developed by way of hysteresis losses than by heating due to current flow in the material. The frequency required to produce the maximum effect will therefore be progressively higher as conductivity decreases. A good non-conductor may re-

quire frequencies as high as several hundred megacycles or more. However, such frequencies are seldom required in carrying out the process of the present invention, since most materials if dried to that extent would not be in a suitable condition for further handling.

Where any type of high frequency generator is available for use, it can usually be used to advantage in producing a better dyeing than by older known methods in which the material is heated from external sources. If a machine of fixed frequency is to be used it should be set at a frequency corresponding to the average condition of the changing conductivity of the material. For the optimum results it would be desirable that generators of frequency be used so that the longer wave lengths are available for the first drying stages and the relatively shorter wave length radiations are available as the material becomes less conductive. Such generators are impractical in general use, however, but such conditions may be approximated by passing the fibers successively through a number of zones in which the frequency becomes progressively higher. This procedure is of particular advantage in processing a running length of material.

Where the material is of a self-supporting nature the problem of passing it through the zone of high frequency radiations is relatively simple. Any winding and reeling apparatus is readily adaptable for the purpose. Where the fibers have not been made into a self-supporting material some carrier device such as an endless belt or screen may be readily adapted as a moving support to carry the material through the treating zone.

Various modifications and refinements of the process and of the apparatus used in handling the material may be used without departing from the scope of the present invention. For example, an automatic control which regulates the time of exposure of a particular sample to the radiant energy may be useful. It may be desirable to have a certain residual moisture remaining in the fibers. Controls for this purpose can be readily developed. With certain fibers the degree of tension during dyeing and drying may require control. The essential features of the present process are the steps of contacting the fibers and dyeing composition and the continuous passing of the fibers through a field of high frequency radiations capable of internally heating the fibers, the dye, the fillers and any other material which may be present.

I claim:

1. A method of securing uniform dyeing and drying of fibers which comprises contacting the fibers with a color-containing composition adapted to penetrate the fibers and passing the color-contacted fibers through an alternating electrostatic field having a frequency below the optical range and down to the frequency of radio short-wave lengths adapted to produce internal heating of the fibers whereby the dyeing and drying is completed and the excess liquid is removed without upsetting the uniformity of color distribution.

2. A method of securing uniform dyeing and drying of fibers which comprises contacting the fibers with a color-contacting composition adapted to penetrate the fibers and continuously passing the color-contacted fibers through an alternating electrostatic field having a frequency below the optical range and down to the frequency of radio short-wave lengths adapted to produce internal heating of the fibers whereby the dyeing is completed and the excess liquid is removed during dyeing without upsetting the uniformity of color distribution.

3. A method as in claim 1 in which the fibers are passed successively through a series of alternating electrostatic fields of progressively increasing frequency.

4. A method according to claim 1 in which an electrostatic field having a frequency between about 20–25 megacycles is used.

5. A method of rapidly dyeing fibers to a uniform shade, making use of dyeing and drying rates sufficiently high to upset the initial uniformity of color distribution when heat is applied from external sources, which comprises passing fibers carrying a dye liquor through an alternating electrostatic field having a frequency below the optical range and down to the frequency of radio short-wave lengths adapted to produce internal heating of the fibers.

6. A method according to claim 5 in which the dye is selected from the group consisting of vat and sulphur dyes in their water-soluble forms and in which air currents are excluded from the fibers during the dyeing and drying operation.

HENRY EDMOND MILLSON.