Patented Dec. 26, 1950

2,535,098

UNITED STATES PATENT OFFICE

2,535,098

GAMMA-VALEROLACTONE AND GAMMA-BUTYROLACTONE AS DYEING ASSISTANTS FOR CELLULOSE ESTER AND ETHER YARNS AND FABRICS

Seth U. Shorey, Oakland, Mo., and George W. Wright, Boston, Mass., assignors to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

No Drawing. Application June 13, 1947, Serial No. 754,602

18 Claims. (Cl. 8—59)

1

This invention relates to methods of dyeing yarns and fabrics, and in particular to an improved method of dyeing yarns and fabrics made of synthetic materials such as cellulose esters and synthetic resins.

Commercial methods of dyeing yarns and fabrics made of synthetic materials such as cellulose acetate are based, in general, upon batch operations or relatively slow continuous operations in which the dyestuff is exhausted from the bath. These methods require bath temperatures ranging approximately from 50° C. to 100° C. The period of immersion of the yarn or fabric in the dyebath ranges from ½ hour to several hours or more at these temperatures. These processes further require the use of specifically adapted dyestuffs, such as the direct-on-acetate dyestuffs, when cellulose acetate yarns or fabrics are dyed. Many dyestuffs such as the acid, basic, vat and mordant dyestuffs, do not give satisfactory results when applied to yarns and fabrics made of cellulose esters or synthetic resins by means of known dyeing processes. This limitation in dyestuffs is a serious one since some of the dyestuffs thus excluded from use, such as the acid dyestuffs, are much more resistant to light and gas fading when applied to fabrics and yarns than are the direct-on-acetate dyestuffs, and are also much more resistant to deterioration in color value resulting from washing or dry cleaning.

In an effort to reduce the time of immersion of synthetic yarns and fabrics in the dyebath, various dye assistants which are also partial solvents for the synthetic material have been proposed. Among those proposed are formic acid, ethyl alcohol, ethylene glycol, mono-ethyl ether, acetone, and certain combinations of these substances. However, even with these assistants, the immersion time is still relatively long in the known processes and with known types of dyebaths. Moreover, the use of most of these assistants or combinations thereof, involves one or more of the hazards of irritating, poisonous, flammable, and explosive vapors.

The results achieved with the various processes in commercial use are not altogether satisfactory. In most of the dyebaths employed at present a relatively large volume of bath liquor is employed and the quantity of dyestuffs incorporated therein is based strictly upon the quantity of fabric or yarn to be dyed. The bath is then utilized with that quantity of dyestuff until the dyestuff is exhausted therefrom. Thereupon, the remaining bath liquor is discarded together

2

with the component assistants. This procedure requires the use of large dyebaths and gives rise to a substantial loss when the exhausted bath containing the dye assistants is discarded. The cost of maintaining the baths at relatively high temperatures is also a factor involving additional expense. Moreover, at the elevated temperatures the hazard involved in the evolution of irritating, poisonous, flammable, and explosive vapors, is materially enhanced. Any attempt to operate at lower temperatures increases the time required for immersion of fabric in the dyebath to such an extent that in continuous operations various means for keeping the fabric in contact with the bath are required, such as the use of a series of rollers to repeatedly immerce the fabric in the dyebath, the use of large volumes of bath liquor, and the use of very slow rates of travel of the fabric through the bath. There is also the very serious factor of deterioration of the quality of the fabric by the dye assistants through prolonged contact of the fabric with the bath liquor at the elevated temperatures.

One of the objects of the present invention is to provide a novel dye liquor for dyeing synthetic fabrics and yarns made of substances such as cellulose derivatives, synthetic resins, or discrete combinations thereof.

Another object is to provide an improved method of dyeing synthetic fabrics and yarns made of substances such as cellulose derivatives, synthetic resins or discrete combinations thereof.

A further object is to provide an improved continuous method of dyeing synthetic fabrics and yarns made of substances such as cellulose derivatives, synthetic resins, or discrete combinations thereof.

A further object is to provide an improved continuous method of applying acid, mordant, mordant acid, vat and pigment dyestuffs to synthetic yarns and fabrics made of substances such as cellulose derivatives, synthetic resins, or discrete combinations thereof.

A particular object is to provide an improved process for continuously and rapidly dyeing cellulose acetate fabrics at substantially room temperature in the presence of certain novel dye assistants, the vapors of which are substantially non-irritating, non-poisonous, non-flammable, and non-explosive. Other objects will become apparent from the following description and examples.

According to the present invention, generally stated, a novel dye liquor for the dyeing of synthetic yarns and fabrics made of vinyl acetate-

containing resins, vinyl chloride-containing resins, vinyl acetal resins, cellulose esters or water-insoluble cellulose ethers is provided by dispersing a dyestuff having an affinity for the synthetic yarns and fabrics in a water solution containing from approximately 2% to approximately 35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone. An organic acid, desirably of aliphatic carboxylic acid type, such as acetic acid, levulinic acid, succinic acid, or citric acid, may be added in addition to the lactone or in place of part of the lactone. With some dyestuffs, a mineral acid such as sulfuric acid may be employed along with the lactone, although with other dyestuffs precipitation of the dyestuff is encountered in the presence of a mineral acid.

Illustrative of the cellulose esters and water-insoluble ethers in the form of fabrics and yarns which may be dyed with the novel dye liquor of the present invention by the improved process hereinafter set forth, are cellulose nitrate, cellulose acetate, cellulose acetate-butyrate, and water-insoluble ethyl cellulose. Illustrative of the synthetic resins in the form of yarns and fabrics which may be dyed in the novel dye liquor of the present invention are vinyl chloride-containing resins, such as polyvinyl chloride, polyvinyl chloride-acetate copolymers, and polyvinyl chloride-vinylidine copolymers; vinyl acetate-containing resins such as polyvinyl acetate and polyvinyl acetate copolymers; vinyl acetal resins such as polyvinyl butyraldehyde acetal, polyvinyl acetaldehyde acetal, and polyvinyl formaldehyde acetal. These acetal resins are prepared by reacting partially hydrolyzed polyvinyl acetate or polyvinyl alcohol with aliphatic aldehyde such as butyraldehyde, acetaldehyde and formaldehyde. These acetal resins may contain varying amounts of vinyl acetate and are acetalized from 33 to 95%, preferably 50 to 78%, for example as described in U. S. Patents 2,120,628, 2,162,678, and Reissue 20,430.

A suitable cationic wetting agent, such as a quaternary ammonium compound of the type represented by cetyl dimethyl benzyl ammonium chloride, various other quaternary ammonium salts and diethyl aminoethyl oleyl amide acetate may be added. The wetting agent is desirably added to the extent of less than approximately 0.1% by weight, since there is a tendency for larger amounts to precipitate part of the dyestuffs in some instances. While other types of wetting agents such as the anionic type, illustrated by the dioctyl ester of sodium sulfo-succinate, sodium lauryl benzene sulfonate, various other alkylated aryl sodium sulfonates and sodium salts of alkylated naphthalene sulfonic acids, and the non-ionic type, illustrated by mannitan mono-oleate, sorbitan mono-oleate, nonyl phenyl polyethylene oxide condensation product, various other condensation products of ethylene oxides and organic acids or phenols, propylene glycol oleate, pentaerythritol mono-laurate and various fatty acid esters of polyhydroxy alcohols can be employed, these wetting agent types merely assist in wetting the fabrics and do not appear to possess the marked synergistic effect in the dyeing of fabrics in the novel dyebath of the present invention which is shown by the cationic type of wetting agent.

The novel dyebath of the present invention possesses the unique characteristic of a narrow temperature range in which the dyeing of cellulose derivative and synthetic resin yarns and fabrics takes place. This range is from approximately 20° C. to approximately 45° C., with a preferred range of 26–30° C. Above or below the over-all range of approximately 20–45° C., the dyeing is unsatisfactory for the immersion period to which the use of the bath is suited.

The dyeing of synthetic yarns and fabrics with the novel dyebath of the present invention at a temperature within the ranges thus specified is substantially instantaneous, although periods of time ranging from 1 second up to 50 seconds may be employed for the purpose of attaining a greater depth of color shade in the yarns or fabrics. The immersion time is desirably correlated with the concentration of the lactone in order to obtain the maximum of desirable characteristics in the dyed yarn or fabric and at the same time to avoid any undesirable effects on the yarn or fabric which may result in certain instances with an unduly prolonged immersion time at a high concentration of the lactone, for example, approaching the upper limit of 50% by volume. This correlation between immersion time and concentration of lactone will be illustrated further in the description and examples hereinafter.

A further unique characteristic of the novel dyebath of the present invention is the fact that the selective absorption between synthetic yarn or fabric of any one of the constituents of the dyebath does not take place to any substantial extent. This means that the dyebath must be replenished with additional volumes of the complete bath formulation. This is contrary to the practice with conventional dyebaths in which the bath is employed until the dyestuff content is exhausted therefrom, although there may, of course, be some entrainment of the bath liquor in the fabric, and the remaining bath fluid is then discarded. The unique characteristic of applicants' dyebath as hereinbefore described is remarkably well adapted to continuous dyeing operations, since by constantly replenishing the dyebath with additional volumes of the complete dyebath formulation, the dyeing operation may be extended for very long periods of time without interruption or shut-down of the dyeing operation required when conventional dyebaths are used.

With the use of the novel dyebath of the present invention, an improved continuous process of dyeing cellulose derivative and synthetic resin yarns and fabrics is provided. This process is characterized by the very short immersion time required, the use of a single pass of the yarn or fabric through the dyebath, and the exposure of relatively short sections of the fabric to the bath during the single pass of the fabric through the bath. The novel process is further characterized by the fact that the volume of dye liquor required is very small in comparison with the large volumes of bath liquor employed with conventional dyebaths, the operating temperature of the dyebath is very close to normal room temperatures and the bath does not evolve irritating, poisonous, flammable or explosive vapors.

The immersion period, which is the length of time during which the yarn or fabric remains in contact with the dyebath, is desirably correlated with the concentration of the lactone in order to obtain the maximum of desirable characteristics in the dyed yarn or fabric and at the same time avoid any undesired effects on the yarn or fabric which may result in certain instances with an unduly prolonged immersion period for a given concentration of the lactone.

For practical purposes, the immersion period is desirably 1 second or less when 30% by volume of the lactone is employed and ranges up to approximately 50 seconds when 2% by volume of the lactone is employed. Immediately upon the attainment of the desired shade of color, and within the limits of the immersion period as hereinbefore described, the yarn or fabric is removed from the dyebath and rinsed in clear water, for example, by immersion in a vessel containing water. Prior to the clear water rinse, particularly when an organic acid is present as a component of the dyebath, it is further desirable to immerse the dyed fabric or yarn in an aqueous neutralizer bath, for example, a 5% sodium carbonate solution in water. Other water-soluble neutralizing agents, such as sodium bicarbonate, potassium carbonate, sodium hydroxide or lithium carbonate may be used in place of sodium carbonate. This procedure serves to remove effectively any residue of acid from the fabric and to prepare the dyed yarn or fabric for any of the drying operations conventionally employed and found suitable for the particular synthetic material of which the yarn or fabric is composed.

In view of the short immersion period required in the improved dyeing process of the present invention, it is not only desirable but quite feasible to employ a single pass of the yarn or fabric through the dyebath and to provide a shallow vat for the dyebath. The depth of the dyebath and the level of the dyebath liquor is desirably determined by the length of the strip or portion of the fabric or yarn which is to travel through the bath during the immersion period. The other factors which are correlated with the immersion period are the rate of travel of the fabric through the dyebath, the concentration, within the limits hereinbefore described, of the lactone, and, if employed, the concentration of the acid; also, the temperature of the dyebath within the limits hereinbefore prescribed. As a factor in this correlation, the length of the strip or portion of the fabric or yarn which is to travel through the dyebath during a prescribed immersion period may be varied, for example, from approximately 2 inches to approximately 6 inches, more or less. When correlated with the rate of travel of the yarn or fabric through the dyebath, the variation in the amount of fabric exposed to the dyebath at any given instant of time will provide a corresponding variation in the immersion time. Various means may be employed for contacting the fabric with the dyebath. For example, the bath may be sprayed upon the fabric and the excess bath removed by passing the fabric through the pressure zone such as that provided by a set of squeeze rolls. A combination of passage through a dyebath plus spraying of the dye liquor upon the fabric may be employed as desired. If a pressure zone is employed subsequent to the application of the dye liquor upon the fabric, the pressure thus exerted upon the fabric may be varied in order to retain varying amounts of the dye liquor upon the fabric until the fabric is immersed in the wash liquor or in the neutralizer liquor. In this manner, the time of contact of the dye liquor with the fabric may be varied over a wide range. For deeper shades of color, it is desirable to retain the dye liquor upon the fabric for a longer period of time than in the case of lighter shades. Thus, a wide variety of combinations is possible in the values of the factors described. Some of these combinations will be illustrated in more detail in the examples provided hereinafter. Other combinations will become apparent to those skilled in the art from the description provided hereinbefore.

In the use of the novel dyebath of the present invention when the improved dyeing process of this invention is employed as a continuous process, it is desirable to maintain the shallow dyebath at a uniform level by continuously feeding into the shallow vat containing the dyebath an additional quantity of the complete dyebath formulation at the rate at which the bath becomes depleted by entrainment of the bath liquor in the yarn or fabric being processed. As described hereinbefore, the level of the dyebath is established or fixed by the length of the strip or portion of the yarn or fabric to be immersed at any given point of time during the continuous dyeing operation. It is further desirable to maintain the surface of the dyebath substantially free of ripples or waves in order to insure as nearly as possible a perfectly level dyeing of the yarn or fabric. The volume of dyebath liquor required for the dyeing of a given quantity of fabric or yarn may be estimated very closely by calculating the volume of dye liquor entrained or picked up by the yarn or fabric in its passage through the dyebath. As stated hereinbefore, only a portion of the dye liquor made up for a given quantity of yarn or fabric to be dyed is placed in the shallow vat under the continuous dyeing apparatus and the balance held in a suitable reservoir is added to the shallow vat at a rate sufficient to maintain the proper level of dye liquor in the vat. Thus, after the dyeing operation is completed for the quantity of fabric or yarn to be processed, little dyebath liquor remains under these circumstances for storage or discard.

In the improved dyeing process of the present invention as applied continuously, the rate of travel of the fabric or yarn through the dyebath is desirably quite high, for example, from approximately 30 yards per minute or lower to approximately 140 yards per minute or higher. The synthetic fabric or yarn actually begins to dye substantially instantaneously when the fabric or yarn comes into contact with the dyebath. The depth of color desired usually requires only approximately 0.1–2 seconds and may require even less time. As as illustration, at a rate of travel of 140 yards per minute and a 2 inch travel of the yarn or fabric through the dyebath, the dyeing operation is accomplished with some dyestuffs in approximately 0.025 second. This may be sufficient for certain dyestuffs or for certain concentrations of dyestuffs. The time of travel of the yarn or fabric through the dyebath may be increased considerably by lengthening the amount of yarn or fabric that comes into contact with the dyebath at any given point of time, for example, from 2 inches of travel through the bath to 6 inches. This does not always require a greater depth of the dyebath, since a substantial increase in the length of yarn or fabric immersed in the dyebath can be obtained through a lateral displacement of the roller under which the fabric or yarn is passed in its passage through the dyebath in conventional dyeing machinery.

One of the many novel features of the dyebath of the present invention resides in the fact that the concentration of dyestuff employed in the dyebath is dependent primarily upon the shade or depth of color desired in the synthetic

yarn or fabric. The dyestuff is not exhausted from the bath by the yarn or fabric as in the cenventional dyebath. The term dye ratio, or the ratio of quantity of dyestuff in the bath to the quantity of fabric to be dyed by the bath, which is customarily employed with conventional dyebaths in which the dyestuff is exhausted from the liquor by a given quantity of fabric has no application in the process of the present invention with the novel dyebath hereinbefore described. The entire dyebath is replenished by the addition of fresh quantities of the complete dyebath formulation. Since the quantity of dyestuff employed in the dyebath of the present invention is determined primarily by the shade or depth of color desired in the fabric, it is difficult, if not impossible, to establish any limits to the amount of dye to be employed in the bath other than the upper limit of the solubility of a given dyestuff in the bath. This in turn varies widely with the various dyestuffs. To illustrate, as little as ½% by weight or less (on the weight of the dyebath) of certain dyestuffs is sufficient to produce satisfactory tints, or even strong colors, depending upon the particular dyestuff employed. On the other hand, from approximately 2% to approximately 15% by weight of certain dyestuff is required for the dyeing of fabrics or yarns designed, for example, for use in fabricating men's suits.

The lactone concentration is essentially a factor of influence on the dyestuff concentration only in those instances in which relatively greater depth of color is required. For example, with certain dyestuffs a larger concentration of the lactone is required in order to dissolve sufficient dyestuff to produce a certain depth of color in the fabric or yarn. The dyestuffs which are suitable for use in the novel dyebath and the improved dyeing process of the present invention are those which have an affinity for synthetic fabrics and yarns made of cellulose derivatives such as cellulose acetate and water-insoluble ethyl cellulose, or of synthetic resins such as vinyl chloride-containing vinyl resins, polyvinyl acetate, or copolymers of these resins. Typical of the dyestuffs which have been found useful for this purpose are the direct-on-acetate dyestuffs, various acid, oil soluble, mordant, mordant acid, and organic pigment dyestuffs, basic dyestuffs and spirit soluble dyestuffs. Certain dyestuffs of the acid, mordant acid, mordant, spirit soluble, and pigment types have been found useful in the novel dyebath and process of the present invention whereas such dyestuffs are not practical for use in many of the conventional processes.

In the dyeing of synthetic fabrics or yarns in the novel process of the present invention, it is desirable to remove the sizing material from the fabric or yarn prior to the dyeing operation. This can be achieved, for example, by means of a soap and water scouring treatment of the conventional type employed with synthetic yarns and fabrics which are thus prepared for dyeing processes. The pre-scouring operation facilitates the penetration of the dyebath into the fabric or yarn and aids in obtaining substantially level dyeing of the fabric or yarn. Subsequent to the dyeing operation, the fabric or yarn may again be sized or finished if desired. It has been found possible to produce variations in the hand of the fabric by varying the lactone content of the dyebath. For example, the higher concentrations of the lactone, approaching 35% by volume, tend to produce a harder hand in the fabric whereas at lower concentrations of the lactone, the hand tends to be somewhat softer.

In the operation of the improved dyeing process of the present invention with the use of the novel dyebath, the employment of approximately 2½% to 40% by volume of an organic acid, such as acetic or citric acid, is found to impart desirable properties as a leveling agent. This practice also tends to improve the resistance to deterioration of the color of the fabric in washing and dry cleaning. It is also possible to decrease the lactone concentration to some extent by replacement of part of the lactone with an organic acid such as acetic acid. For example, very satisfactory results are achieved with a dyebath containing 15% by volume of the lactone and 25% by volume of acetic acid. The results with this bath are comparable and even superior in some respects to a dyebath containing 30% by volume of the lactone and no acid other than that provided by the presence of the tautomeric acid form of the lactone. Moreover, the substitution of part of the lactone in this manner serves to make possible in some instances a longer period of immersion of the yarn or fabric with the production of a softer hand in the fabric or yarn and with less tendency for deterioration of the yarn or fabric from contact with the lactone. The type of organic acid employed in the dyebath may be limited in some instances by the corrosiveness of the particular acid selected on the material of which the vat and other dyeing apparatus is constructed. This can be overcome in most instances by using acid resistant materials such as glass liners, rubber liners, or stainless steel in the construction of the dye vat and other equipment.

While the improved dyeing process with the use of the novel dyebath has been described in connection with continuous operation, the novel dyebath of the present invention may also be employed in batch dyeing operations. This may be desirable in certain instances in which yarns are dyed in the form of hanks. Care must be taken, of course, to avoid over-exposure of the yarn or fabric to the dyebath and the limits of immersion time herein set forth should be observed. In this connection, it is desirable to wash the dyed material as promptly after removal from the dyebath as possible to avoid deterioration of the synthetic yarn which may arise from prolonged contact with the lactone at the particular concentrations employed. The use of an intermediate neutralizer bath between the dyebath and the clear water bath is also desirable, particularly when an organic acid is added to the dyebath. In other respects, the procedure in batch dyeing operations with the novel dyebath of the present invention is substantially the same as that described for continuous operation. The size of the bath in batch operations is desirably larger to accommodate a given quantity of yarn or fabric. In continuous operations, there is no necessity for a large dye vat, although the vat may be as large or small as the occasion requires.

Synthetic yarns of the type described hereinbefore may also be dyed on perforated bobbins or spools by the so-called Franklin process, wherein the dye liquor is forced through the hollow, perforated core of the spool and is dispersed through the yarn on the spool. In using the novel dyebath of the present invention in the Franklin process, it is usually desirable to employ lower concentrations of the lactone and higher concentrations of the dyestuff than would be employed

in a comparable operation based on a continuous travel of the yarn through the dyebath. It is further desirable to employ an organic acid in the dyebath. A suitable dyebath for this purpose is one comprising 2–15% by weight of the dyestuff, 15% by volume of the lactone and 2½–40% by volume of acetic acid, the balance being water. It is also desirable to add a cationic wetting agent to the bath to the extent of approximately 0.1% or less by volume. The flow of dye liquor through the spool of yarn is desirably maintained at a sufficiently high rate such that the dyeing operation can be accomplished in substantially less than 50 seconds, immediately thereafter removing the entrained dye liquor in the yarn by washing, for example, by first passing a 5% sodium carbonate solution through the yarn and thereafter passing clear water through the yarn. In operating under the Franklin process with the use of the novel dyebath of the present invention, it is desirable to accomplish the washing operation by direct displacement of the dye liquor in the yarn with a solid mass of wash liquor in order to provide thorough washing of the yarn and to avoid any channeling which might otherwise give rise to incomplete washing.

The following examples will serve to illustrate the novel dyebath and dyeing process of the present invention. These examples are to be construed as merely illustrative and not as limiting the scope of the invention as described in the appended claims. It is contemplated that in addition to those variations illustrated in the examples, other variations in the dyebath formula and in the dyeing process and alternatives are within the scope of the claims.

Example I

A number of 50 yard lengths of desized 2¼ inch wide white cellulose acetate ribbon were dyed on a conventional continuous dyeing machine set up with a single set of immersion rolls and provided with a shallow dye vat having a depth of approximately 1½ inches. For each 50 yard length of the ribbon, a different dyebath was employed. The basic formulation of the dyebath is represented by the following formula:

Dyestuff	½–15% by weight on the liquid components
Gamma-valerolactone	5–35% by volume
Water	Balance to make 100% by volume on the liquid components

The dyestuff was dissolved in the aqueous lactone solution. The dyestuffs employed in these tests were:

Dyestuff	Type of Dyestuff	Color Index No.
Neolan Yellow G. R. Conc	Acid (Metallized)	[1] 316
Celanthrene Pure Blue B. R. S. Conc.	Direct-on-acetate	[2]
Victoria Blue	Spirit Soluble	729
Methyl Violet	Basic	680
Bismarck Brown G	do	331
Sudan Brown A	Spirit Soluble	81
Bismarck Brown 2G	Basic	
Quinolin Yellow	Acid	801
Rhodamine B	Basic	749

[1] "Prototype Number" adopted by the American Association of Textile Chemists and Colorists.
[2] Manufactured by E. I. du Pont de Nemours Company.

The shallow dye vat was filled in each instance to within ½ inch of the top of the vat. Additional quantities of the complete dyebath formulation were added to the vat continuously to maintain the level at that point. The immersion rolls were set in the dye vat at a point which provided for the immersion of a 2 inch length of ribbon at any one instant in the dyebath. The ribbon was passed continuously from the dye vat through squeeze rolls into a 5% solution of sodium carbonate and then through squeeze rolls into a clear water bath. Following the washing treatment, the ribbon was dried.

In one series of runs, the temperature of the dyebath was maintained at a point within the range of 26–30° C. In another series, the temperature was maintained at various points in the range of 10–20° C. by external cooling means, and in a third series, the temperature was maintained at various points within the range of 35–45° C. by external heating means. In the series of runs at 26–30° C., the depth of color was at a maximum and this range was adopted for the subsequent runs. Above 45° C. and below 20° C., the dyeing results were unsatisfactory. In these series of runs, the gamma-valerolactone concentration was maintained at 30% by volume and the dyestuff content was maintained at 2% by weight on the liquid components. The rate of travel of the ribbon through the dyebath was 30 yards per minute.

In another series, the concentration of gamma-valerolactone in the dyebath was varied between the limits of 5% and 35% by volume, the concentration of the dyestuff being maintained constant at 2% by weight. The ribbon dyed in this series varied in hand from a slightly softer hand when processed at the lower concentration of the lactone to a somewhat harder hand at the higher concentrations of the lactone. In all other respects the quality of the dye work was substantially the same throughout the series, with the depth of color varying from light at the lower concentrations of lactone to deep at the higher concentrations of the lactone. The temperature of the dyebath in this series was maintained in the range of 26–30° C. and the rate of travel of the ribbon through the dyebath was established at 30 yards per minute. It was found that below 5% of the lactone, the dyeing results were not entirely satisfactory. Also, above 35% by volume of the lactone, there was a tendency for the fabric to become tenderized by the lactone at the rate of travel of 30 yards per minute. At the higher rates of travel, for example, 30–140 yards per minute, the lactone concentration can be employed at approximately 35% by volume substantially without resulting in deterioration of the fabric. A series of runs, comparable to that in which the concentration of gamma-valerolactone was varied, was made using gamma-butyrolactone in place of gamma-valerolactone. The results were quite similar to those obtained when gamma-valerolactone was employed and the quality of the dye work was satisfactory in each instance.

A series of runs was made with the dyebath at a temperature in the range of 26–30° C. and a variation in the ratio of travel in the ribbon through the dyebath ranging from 5 yards per minute to 140 yards per minute. The concentration of gamma-valerolactone for this series was maintained at 30% by volume and the length of fabric immersed in the dyebath at any one instance was maintained at 1½ inches. The ribbon dyed at the higher ratio of travel possessed a slightly softer hand than those dyed at the lower rates. The depth of color in the fabric was substantially the same in each instance.

The quality of the dye work and the fastness of the dyes were satisfactory.

The portions of cellulose acetate ribbon dyed in each of the series hereinbefore described were found to possess satisfactory characteristics and the dyeing was quite level. Portions of the ribbon from the various tests were submitted to standard testing laboratories for light and gas fastness tests by standard testing means and were found to meet the standards for the particular dyes employed. The ribbons dyed with acid dyestuffs were found to be more resistant to light and gas fading than were those dyed with direct-on-acetate dyestuffs. Inasmuch as acid dyestuffs can be employed satisfactorily in the process of the present invention, the use of such dyestuffs is to be preferred, since these dyestuffs are inherently far more fast when applied to the synthetic fabric by the present process than are the direct-on-acetate dyestuffs when applied to the synthetic fabrics by any process.

Example II

A number of 50 yard lengths of 2¼ inch wide white cellulose acetate ribbon were dyed continuously in the manner described in Example I, using the following dyebath formula as the basis for the tests:

Dyestuff	½–15% by weight on the liquid components
Gamma-valerolactone	15% by volume
Acetic acid	2–40% by volume
Wetting agent	0.05–0.1% by weight on the liquid components
Water	Balance to make 100% by volume on the liquid components

The dyestuffs employed in this series were the following:

Dyestuff	Type of Dyestuff	Color Index No.
Neolan Yellow G. R. Conc	Acid (Metallized)	[1] 316
Rhodamine B Extra	Basic	749
Methyl Violet	do	680
Acid Fast Violet	Acid	699
Soluble Blue B	do	707
Victoria Green W. B. Base	(Spirit Soluble)	657
Brilliant Azurine	Direct-on-acetate	511
N-nitraniline Orange	Mordant	38
Sudan Brown	Spirit Soluble	81
Fast Red B. T	Acid	87
Alizarin Yellow R	Mordant Acid	40

[1] Prototype.

In one series, runs were made varying the concentration of acetic acid from 2% to 40% by volume. A particularly desirable concentration from the standpoint of quality in the dyed fabric was achieved with 25% acetic acid by volume. Other suitable organic acids, and in particular, various mono and dicarboxylic acids of the aliphatic series such as maleic, levulinic and lactic acids, were used in place of acetic acid at 25% concentration by volume. These acids proved to be satisfactory as substitutes for acetic acid.

A series of runs was made using various types of wetting agents at concentrations ranging from 0.05 to 0.1% by weight. The wetting agents employed were of the cationic, non-ionic, and anionic types. Representative of the cationic types employed were cetyl dimethyl benzyl ammonium chloride, diethyl aminoethyl oleyl amide acetate, and various quaternary ammonium salts. Representative of the non-ionic types employed were mannitan mono-oleate, propylene glycol oleate, pentaerythritol monolaurate, various fatty acid esters of polyhydroxy alcohols, and various condensation products of ethylene oxides and organic acids. Representative of the anionic types employed were the dioctyl ester of sodium sulfosuccinate, various alkylated aryl sodium sulfonates, and sodium salts of alkylated naphthalene sulfonic acids. The acetic acid content of the dyebath was held constant in this series at 25% by volume. The temperature was maintained in the range of 26–30° C. While the various wetting agents employed in this series were found to be satisfactory, the cationic type was outstanding in its leveling effect in the dyebath. It was found desirable not to exceed to any substantial extent the upper limit of 0.1% by weight of the wetting agent on the weight of the liquid components in order to avoid any substantial precipitation of the dyestuff.

In another series, the acetic acid concentration was maintained at 25% by volume and the concentration of gamma-valerolactone was varied over the range of 2–35% by volume. It was found that at approximately 15% by volume of the lactone or higher, the addition of acetic acid has the effect, to a certain extent, of increasing the characteristic of the lactone as a dye assistant and serves as a valuable adjunct to the dyebath in this capacity when relatively slow rates of fabric passage through the dyebath are employed, for example, 5–15 yards per minute. Moreover, the use of acetic acid in conjunction with the lactone was found to enhance the production of deeper colors at the higher rates of travel of the fabric through the dyebath. These results were also found to hold true when gamma-valerolactone was replaced in the dyebath by gamma-butyrolactone.

Example III

A number of skeins of white cellulose acetate yarn were dyed in a batch operation using a dyebath having the following basic formula:

Dyestuff	½–15% by weight on the liquid components
Gamma-butyrolactone	15% by volume
Acetic acid	25% by volume
Dioctyl ester of sodium sulfosuccinate	0.08% by weight on the liquid components
Water	Balance to make 100% by volume on the liquid components

The temperature of the bath was maintained in the range of 26–30° C. The following dyestuffs were employed in the series:

Dyestuff	Type of Dyestuff	Color Index No.
Neolan Yellow G. R. Conc	Acid (Metallized)	[1] 316
Victoria Blue	Spirit Soluble	729
Methyl Violet	Basic	680
Brilliant Azurine	Direct-on-acetate	511
N-nitraniline Orange	Mordant	38
Sudan Brown	Spirit Soluble	81

[1] Prototype.

The yarns were immersed in the dyestuff for a period of 7 seconds and thereafter were transferred to a 5% sodium carbonate bath. Following this the yarns were washed in a clear water bath. The resulting yarns were subsequently dried. The quantity of dyestuff employed in the bath was varied between the range of ½–15%

by weight. The quality of the dye work was excellent.

In another series, specimens of yarns made from fibers of cellulose nitrate, ethyl cellulose, polyvinyl chloride, polyvinyl chloride-acetate vinylidene-polyvinyl chloride copolymer, vinyl acetate-butyraldehyde, and vinyl acetate-acetaldehyde were dyed in a batch operation under the conditions described in the present example relative to acetate yarns. The yarns were found to be dyed satisfactorily and the dye work was excellent.

Example IV

Cellulose acetate yarn wound on a metal spool having a perforated core was dyed by means of a dyebath having the following basic formula:

Neolan Yellow G. R. Conc. (Prototype 316)	5–15% by weight on the liquid components
Gamma-valerolactone	10% by volume
Acetic acid	25% by volume
Condensation product of nonylphenol and polyethylene oxide	0.05% by weight on the liquid components
Water	Balance to make 100% by volume on the liquid components.

The temperature of the dyebath was in the range of 26–30° C. Approximately 100 c. c. of the dyebath was forced through the preforated core and thence through the yarn in approximately 10 seconds. The dye liquor was thereafter immediately displaced with approximately 550 c. c. of a 5% sodium carbonate solution. Thereafter clear water was passed through the yarn until residual sodium carbonate solution was removed. The yarn was thereafter dried. The yarn was found to be dyed satisfactorily.

Example V

A series of 100 yard lengths of 40 inch wide white cellulose acetate were dyed continuously, using the following dye liquor formula:

Dyestuff	½–15% by weight on the liquid components
Gamma-butyrolactone	15% by volume
Acetic acid	25% by volume
Dioctyl ester of sodium sulfosuccinate	0.08% by weight on the liquid components
Water	Balance to make 100% by volume on the liquid components

The dyestuffs employed in the series were the following:

Dyestuff	Type of Dyestuff	Color Index No.
Neolan Yellow G. R. Conc.	Acid (Metallized)	[1] 316
Wool Blue Dye	Acid	

[1] Prototype.

The temperature of the dyebath was maintained in the range of 26–30° C. The rate of travel of the fabric was approximately 50 yards per minute. The dye liquor was applied to the fabric from below by transfer from a pick-up roll, the roll being partially immersed in the dye liquor. The dye liquor was sprayed on the top side of the fabric. After contact with the dye liquor, the fabric was then squeezed to express the excess dye liquor from the fabric. The fabric was thereafter passed through a 5% sodium carbonate bath and thereafter washed in clear water as hereinbefore described. The fabric was then dried. The dyeing results indicated satisfactory level dyeing with the attainment of satisfactory shades of substantially wash-fast colors. The light and gas fading tests were also satisfactory.

We claim:

1. A dye liquor comprising 5–35% by volume of lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, a dyestuff which when applied from said dye liquor has an affinity for a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers, and water.

2. A dye liquor comprising 5–35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, ½–15% of a dyestuff which when applied from said dye liquor has an affinity for a substance selected from the group of cellulose esters, and water-insoluble cellulose ethers, 0.05–0.1% by weight on the liquid components of a wetting agent, 2–40% of an aliphatic carboxylic acid and water.

3. The process of dyeing a synthetic textile in the form of yarns and fabrics made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers comprising contacting said textile with a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said textile, 5–35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., and subsequently washing the textile substantially free from residual dye liquor, the period of time from the initial contact of said textile with said dye liquor until the washing of said textile being less than 50 seconds.

4. The process of dyeing a synthetic textile in the form of yarns and fabrics made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers comprising contacting said textile with a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said textile, 5–35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., subsequently washing the textile in an alkaline neutralizer bath and subsequently washing the textile substantially free from residual lactone, the period of time from the initial contact of said textile with said dye liquor until the washing of said textile being less than 50 seconds.

5. In the art of dyeing a synthetic textile in the form of yarns and fabrics made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers, an improved continuous process comprising continuously contacting said textile at a rate in the range of 5–140 yards per minute with a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said textile, 5–35% by volume of a lactone selected from the group consisting of gamma-valerolactone and

gamma-butyrolactone, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., thereafter continuously neutralizing the residual liquor on said dyed textile, and subsequently continuously washing said dyed textile until residual dye liquor is removed from said textile.

6. In the art of dyeing a synthetic textile in the form of yarns and fabric made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers, an improved continuous process comprising continuously contacting said textile at a rate in the range of 30–140 yards per minute with a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said textile, 5–35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, an organic acid, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., thereafter continuously neutralizing the residual liquor on said dyed textile, and subsequently continuously washing said dyed textile, and subsequently continuously washing said dyed textile until residual dye liquor is removed from said textile.

7. In the art of dyeing a synthetic textile in the form of yarns and fabrics made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers, an improved continuous process comprising contacting said textile at a rate in the range of 5–140 yards per minute with a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said textile, 15–30% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, 2–40% of an aliphatic carboxylic acid, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., thereafter continuously neutralizing said dyed textile and subsequently continuously washing said textile until residual lactone is removed therefrom.

8. In the art of dyeing a synthetic yarn made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers, the improved process comprising winding said yarn on a spool having a perforated hollow core and forcing through said hollow core and thence through said yarn a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said yarn, 5–30% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, 2–40% of an aliphatic carboxylic acid, less than 0.1% of a wetting agent and water, said dye liquor having a temperature in the range of 20–45° C., displacing said dye liquor in said yarn with an aqueous neutralizer solution and thereafter displacing said neutralizer solution with water, the period of time from the contact of the dye liquor with the yarn until the neutralizer solution is applied being less than 50 seconds.

9. In the art of dyeing a synthetic textile in the form of yarns and fabrics made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers, an improved continuous process comprising contacting said textile at a rate in the range of 5-140 yards per minute with a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said textile, 15–30% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, 2–40% of acetic acid, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., thereafter continuously neutralizing said dyed textile and subsequently continuously washing said textile until residual lactone is removed therefrom.

10. A dye liquor comprising 5–35% by volume of lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, an acid dyestuff and water.

11. A dye liquor comprising 5–35% by volume of lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, an acid dyestuff, an organic acid and water.

12. A dye liquor comprising 5–35% by volume of lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, a direct-on-acetate dyestuff and water.

13. In the art of dyeing a synthetic textile in the form of yarns and fabrics made of cellulose acetate, an improved continuous process comprising continuously contacting said textile at a rate in the range of 5–140 yards per minute with a dye liquor comprising an acid dyestuff, 5–35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., and thereafter continuously neutralizing the residual liquor in said dyed textile, and subsequently continuously washing said dyed textile until residual dye liquor is removed from said textile.

14. In the art of dyeing a synthetic textile in the form of yarns and fabrics made of cellulose acetate, an improved continuous process comprising continuously contacting said textile at a rate in the range of 5–140 yards per minute with a dye liquor comprising a direct-on-acetate dyestuff, 5–35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., and thereafter continuously neutralizing the residual liquor in said dyed textile, and subsequently continuously washing said dyed textile until residual dye liquor is removed from said textile.

15. A dye liquor comprising 5 to 35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, an organic acid, water and a dyestuff capable of dyeing a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers when applied from said dye liquor.

16. The process of dyeing synthetic textiles in the form of yarns and fabric made of a substance selected from the group consisting of cellulose esters and water-insoluble cellulose ethers comprising mechanically impregnating said textile with a dye liquor comprising 5 to 35% by volume of a lactone selected from the group consisting of gamma-valerolactone and gamma-butyrolactone, an organic acid, water and a dyestuff capable of dyeing said textile when applied from said dye liquor, said dye liquor being maintained at a temperature in the range of 20 to 45° C., and subsequently washing the textile substantially free from residual dye liquor, the period of time from the initial contact of said textile with said dye liquor until the washing of said textile being less than 50 seconds.

17. A dye liquor comprising 5–35% by volume of gamma-valerolactone, a dyestuff which when

applied from said dye liquor has an affinity for cellulose acetate, and water.

18. The process of dyeing a synthetic textile in the form of yarns and fabrics made of cellulose acetate comprising contacting said textile with a dye liquor comprising a dyestuff which when applied from said dye liquor has an affinity for said textile, 5–35% by volume of gamma-valerolactone, and water, said dye liquor being maintained at a temperature in the range of 20–45° C., and subsequently washing the textile substantially free from residual dye liquor, the period of time from the initial contact of said textile with said dye liquor until the washing of said textile being less than 50 seconds.

SETH U. SHOREY
GEORGE W. WRIGHT.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,249,607	Galatioto	July 15, 1941
2,347,508	Rugeley	Apr. 25, 1944
2,428,834	Croft	Oct. 14, 1947

OTHER REFERENCES

Advertisement in India Rubber World for November 1944, page 221. Available in Scientific Library of Patent Office.

Certificate of Correction

Patent No. 2,535,098 December 26, 1950

SETH U. SHOREY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 16, for "immerce" read *immerse*; column 6, line 52, for the words "As as" read *As an*; column 15, lines 23 and 24, strike out "and subsequently continuously washing said dyed textile,";

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of February, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

Certificate of Correction

Patent No. 2,535,098 December 26, 1950

SETH U. SHOREY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 16, for "immerce" read *immerse*; column 6, line 52, for the words "As as" read *As an*; column 15, lines 23 and 24, strike out "and subsequently continuously washing said dyed textile,";

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of February, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.