

TITLE

Wool Dyeing Utilizing Controlled Dye Addition

BACKGROUND OF THE INVENTION

The present invention relates to the dyeing of
 5 fibrous articles containing wool with anionic dyes.

Anionic dyes such as acid dyes and pre-metallized
 dyes are widely used for the dyeing of wool. In
 conventional dyeing processes using such dyes, articles
 containing wool are immersed in an aqueous bath containing
 10 a solution of the dye after any pre-treatment processes
 such as scouring. While a wide variety of dyeing
 equipment is used, it is typical for all of the dye to be
 used in the process to be present in the bath initially.
 The bath containing the dye and the article to be dyed is
 15 also usually at a very low initial temperature, e.g., 80-
 120°F (26.7-48.9°C) and the temperature is increased
 gradually to an elevated temperature often as high as the
 boiling point as the dyeing progresses. "Metallizing"
 treatments with, e.g., with potassium dichromate, are
 20 often performed subsequently to dyeing to increase dye
 light and/or wash fastness.

While high quality dyeing can be achieved using
 the conventional dyeing process for some acid dyes such as
 small molecule "levelling" dyes, dye cycles to achieve
 25 levelling with such anionic dyes are sometimes extremely
 long and are therefore costly. In addition, long dye
 cycles are undesirable since the maintenance of the bath
 at a high dyeing temperature for a long period of time can
 decrease the strength of wool. It is very common to dye
 30 wool using large molecule acid and pre-metallized dyes
 which are desirable for applications requiring good light
 and/or wash fastness. However, undesirable dyeings can
 result with conventional dyeing processes using large
 molecule acid and pre-metallized dyes since individual
 35 wool fibers may not dye uniformly. Often, one end of a
 fiber will dye readily while the other end will absorb
 little dye resulting in an "skittery" dyeing in the
 article, i.e., noticeable localized dark/light areas.

REPLACED SHEETS SG

- ☒ Description : paged to paged
☒ Claim(s) : paged to paged
☒ Drawing(s) : paged to paged
☒ Abstract : paged to paged

1

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SUBSTITUTE SHEET

Large molecule acid and pre-metallized dyes are often referred to as "structure sensitive" dyes since non-uniform dyeing can result from minor variations in the fiber physical structure. While dye-levelling and/or
5 retarding agents can be added to the dye bath to improve dyeing uniformity with structure sensitive dyes, such agents sometimes provide only limited increases in dye uniformity and usually have disadvantages including increased initial expense and higher cost to treat the
10 spent dyeing bath. In addition, because of their retarding effect, such chemical agents can sometimes increase dyeing cycles or make it difficult to obtain deep colors or dark shades. Also, dye yields from anionic dyes, i.e., the strength of color produced from a given
15 quantity of dye on the fiber, are sometimes not as high as desired.

SUMMARY OF THE INVENTION

The invention provides an improved process for the dyeing of a fibrous article containing wool with at least
20 one anionic dye and dyed products made by the process. A process in accordance with the invention includes immersing the article in a dyeing bath of a liquid solvent for the anionic dye. The liquid solvent and the article are heated to a temperature at least equal to the dyeing transition temperature. The anionic dye is added to the
25 dyeing bath as a miscible liquid concentrate at a controlled dye addition rate during a dye addition period. At least a portion of the dye is added while the bath and article are at temperature at least equal to the dyeing transition temperature. Stirring of the bath during the
30 dye addition period and while the solvent and article are up to the dyeing transition temperature is done to mix the dye concentrate with the solvent in the bath to form a dilute dye solution and to provide a flow of the dilute
35 dye solution relative to the article to cause the dye to be transported to the article. The stirring also provides, on the average, essentially uniform dye transport of the anionic dye to the article. In



accordance with the process, the dye rate is adjusted at least while the solvent and article are at a temperature at least equal to the dyeing transition temperature so that the dye addition rate is the primary control over the
5 rate of dye uptake by the article.

In accordance with a preferred form of the invention, the conditions in the liquid solvent are maintained so that the anionic dye transfers less than about 10%.

10 In accordance with another preferred form of the invention, the process is performed in a dyeing machine in which the stirring provides a number of repetitive machine cycles and the dye addition rate is adjusted so that an amount of dye between about 0.5% and about 7% of the total
15 dye is added to the dyeing bath during a machine cycle, most preferably between about 0.5% and about 3%.

In accordance with another preferred form of the invention, at least about 33% of the dye is added to the bath while said solvent and said article are at a
20 temperature at least equal to the dyeing transition temperature, most preferably at least about 50% of the dye is added at this time.

In accordance with another preferred form of the invention, the dye addition rate is adjusted so that the
25 concentration of dye at location of lowest concentration in the bath is not greater than about 100 times, most preferably not greater than 50 times, the final equilibrium concentration for any substantial period of time while the solvent and the article are at a
30 temperature at least equal to the dyeing transition temperature.

In accordance with another preferred form of the invention, the rate of dye addition is adjusted so that the concentration of dye in the solvent as measured at the
35 point of lowest concentration in the bath is at least about 2.5 times, preferably at least about 3.5 times, the final equilibrium concentration for a sustained period of time while the solvent and the article are at a



temperature at least equal to the dyeing transition temperature. Preferably, the sustained period of time comprises at least about 10% of the time when the solvent and the article are at a temperature at least equal to the
5 dyeing transition temperature.

The invention is useful in a wide variety of wool dyeing processes using anionic dyes. Surprisingly, it has been found that when used under conditions such that the dyes transfer less than 10%, anionic dyes are utilized
10 more effectively which can provide either better dye yields or the achievement of deep colors or dark shades which were otherwise difficult to obtain or were unobtainable. Also, dye cycles for all types of dyes can be substantially shortened which can decrease cost and
15 decrease the strength loss which is known to occur in wool dyeings. Moreover, the improvements in dyeing are often achievable without the use of or by using lower concentrations of chemical levelling or other chemical agents which, in significant concentrations, can
20 complicate treatment of spent dyeing bath liquids.

DETAILED DESCRIPTION

There are a wide variety of fibrous articles containing wool which can be dyed using the process of the invention including, for example, yarns, fabric, carpets
25 and garments. Wool as stock can also be an article dyed by this process. Fabrics include the usual textile forms including woven, knitted, and non-woven varieties. The wool can be present in the article together with any of a variety of other synthetic or natural fibers. Typical of
30 such articles are yarns made from a "blend" of wool with other fibers and fabrics and garments made from such yarns. The other fibers in such articles may or may not undergo dyeing as the wool is dyed in the process. In addition, the wool to be dyed may already contain the same
35 or a different dye. For example, the process of the invention may be used for a dye "add" to get to "shade" with the fiber already containing most of the dye before the process is used.



The dyes used in the practice of the present invention are anionic dyes and dyeing of the wool is accomplished by uptake of the dyes through the association of the dye molecules with nitrogen-containing groups on the wool fiber. Most anionic dyes are members of the well-known class of "acid" dyes. Another type of anionic dyes is the type referred to as "pre-metallized" dyes which are the reaction products of, for example, chromium or cobalt and selected dyes. As will become apparent hereinafter, mixtures of two or more dyes are often used to achieve a desired shade. In this application, the word "dye" may be used to refer to a single dye or multiple dyes as in a mixture of dyes used in a dyeing process or on a dyed article. In processes using more than one dye such as in dye mixtures to achieve compound shades, a process is intended to be within the scope of the invention provided that at least one dye of compound shade is applied to an article in accordance with the invention.

In accordance with a preferred process in accordance with the invention, conditions are used in the dye bath so that anionic dyes transfer less than about 10%. Transfer is a measure of the propensity of anionic dyes to migrate from one dye site to another after being absorbed by the fiber. Transfer under a given set of conditions can be measured in a mock dye bath as in the transfer test method described hereinafter.

Providing transfer of less than 10% can easily be accomplished by use of dyes from a preferred class of dyes, the "structure sensitive" anionic dyes. These dyes are usually large molecule acid ("milling") dyes or pre-metallized dyes which are non-levelling, i.e., the dye molecules do not "transfer" significantly and thus migrate very little from one dye site to another after being absorbed by the fiber. Typically, structure sensitive dyes "transfer" less than 10% under normal conditions of use. "Structure sensitive" is the term applied to such dyes since non-uniform dyeing can result from even minor, and otherwise undetected, variations in the fiber physical



structure. Such variations occur naturally in wool. Despite their known difficulties in use, structure sensitive dyes are desirable for many applications due to their washfastness, lightfastness, and both.

5 Without intending to limit this preferred form of the invention to these specific dyes, commonly used structure-sensitive dyes are represented, for example, by the list provided below (C.I. refers to the Color Index, 3rd edition, 1971):

10	C.I. Acid Yellow 220
	C.I. Acid Orange 162
	C.I. Acid Brown 282
	C.I. Acid Brown 283
	C.I. Acid Brown 226
15	C.I. Acid Red 407
	C.I. Acid Red 251
	C.I. Acid Black 60
	C.I. Acid Blue 317
	C.I. Acid Blue 80
20	C.I. Acid Blue 171
	C.I. Acid Blue 336
	C.I. Acid Black 172

For dyes which are normally described as "levelling" dyes since they transfer readily and "level" under the normal conditions of use, transfer of less than about 10% can be accomplished using conditions of low pH, low temperature, or both. In addition, with dyes which are normally strongly levelling, it may be necessary to perform the dyeing rapidly even though the conditions in the dyeing bath are such that the dye transfers less than about 10%. Otherwise, the dye yield benefits which are otherwise obtainable using the invention may be diminished due to dye transfer which occurs after the dye is on the article.

35 As in conventional dyeing processes, it is desirable to scour the article before dyeing to remove sizing and other materials which may adversely affect the dyeing. The fabrics can be scoured, for example, in an



open width scouring range or in the apparatus to be used for the dyeing, e.g., a beck or paddle dyer. Scouring solutions used conventionally are generally suitable, e.g., water at 180°F (82.2°C) containing a surfactant such as 0.5 gram/liter of MERPOL LFH® (a liquid non-ionic detergent sold by E. I. du Pont de Nemours & Company, Inc. of Wilmington, DE). After scouring, the fabric should be rinsed such as by being immersed in hot water.

In the process of the invention, the article to be dyed is immersed in a dyeing bath containing a liquid solvent for the anionic dye. The dyeing bath can take a wide variety of forms in which the article is totally immersed in the bath throughout the dyeing process or is partially immersed at any one time and is moved in a cyclical or random fashion to provide contact for the entire article with the solvent. Partial immersion is useful for articles such as fabrics where the fabric can be progressively advanced through the bath, either in continuous rope form or by reciprocation of an article having a discrete length, so that the entire article is ultimately dyed. A preferred process employs the bath formed in a beck dyer for fabric in which the fabric is in the form of an endless rope and is moved by the action of the winch-reel. Most preferably, a beck for use in accordance with this invention is modified to include a pump and appropriate piping for external circulation of the solvent. Jet dyers are advantageously used for wool blend fabrics such as wool/polyester blends.

The liquid solvent for the dye is any suitable solvent for the dye which is capable of transporting the dye to the dye sites on the fiber and which is otherwise compatible with the fabric, dye and other aspects of the process, e.g., aqueous liquids and methanol are suitable solvents. Preferably, the liquid solvent is an aqueous liquid which contains less than about 10% by weight of additives for establishing and maintaining the desired pH and for other purposes. Suitable aqueous liquids useful in the process contain additives for providing a buffer

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system. For example, acetic acid on the order of about 1% and ammonium acetate on the order of about 2% by weight can be used to adjust the pH to a suitable level. Other additives can be chemicals such as wetting agents, retarders, and the like which are referred to collectively in the present application as "dyeing auxiliaries". Dyeing auxiliaries can be present in the process of the invention although such agents often are not needed. If dyeing auxiliaries are present in the bath, a much lower concentration is typically used to keep the dye cycle to a reasonably short duration. Dyeing auxiliaries can be useful and may be desirable for compound shades of dyes of differing affinities.

When the bath has low levels of or is substantially free of dyeing auxiliaries, significant advantages are obtained in the treatment or disposal of the spent dye liquors. Moreover, the dyed fiber may be substantially free of residual dyeing auxiliaries or such agents may be present only at much lower levels than in fibers dyed by the conventional process for structure sensitive dyes which typically require high bath concentrations of dyeing auxiliaries. In addition, it is possible in some instances to use the spent dyeing bath for after-treatments such as for improving wetfastness, lightfastness or softness, applying antistats, and for other known after-treatments employing chemical agents. Metallizing can usually be done in the same bath. For such after-treatments, the chemical agent can be added to the hot bath using a technique similar to that used to add the dye in a process in accordance with the invention. In addition, it is also possible to reuse the spent bath in a subsequent dyeing if dyeing auxiliaries are absent or are present in sufficiently low concentration.

The anionic dye is added to the dyeing bath as a miscible liquid concentrate at a controlled dye addition rate during a dye addition period. "Dye addition period" refers to the time period beginning with the first addition of dye and ending with the final amount of dye



being added. The length of the dye addition period will usually range between about 5 minutes and about 4 hours with typical dye addition periods being between about 20 and about 100 minutes. Upon stirring as will be explained
5 in more detail, the miscible liquid dye concentrate is mixed with the solvent in the bath to form a dilute dye solution. "Miscible liquid concentrate" is intended to refer to a solution in which the dye is fully dissolved and which can be added to and mixed with the liquid
10 solvent in the bath to form a dilute liquid solution of the dye in all proportions of such concentrates which would normally be mixed into a dye bath. The solvent for the miscible liquid concentrate can be different from the liquid solvent provided that the introduction of a
15 different solvent does not otherwise adversely affect the dyeing process. When an aqueous dyeing bath is used, the solvent preferably used in the miscible liquid concentrate is water.

As will be explained in more detail hereinafter,
20 the dye addition rate is adjusted depending on the amount of dye to be applied, the characteristics of the article to be dyed, the type of dyeing apparatus, the type of dye and the conditions of the dyeing to achieve the desired results. Preferably, to facilitate control over the
25 process and make the process more easily reproducible, the dye is added continuously and at a constant rate during the dye addition period.

In processes in which the dilute dye solution in the bath is circulated by means of a circulation pump, the
30 liquid dye concentrate is preferably added to the solvent ahead of the circulation pump. A metering pump is advantageously utilized for this purpose. When dyeing wool fabrics such as wool/polyester blend fabrics which can be dyed in a jet dyer, the circulation pump supplies
35 the dilute dye solution to the jet nozzle so that the newly-added dye contacts the fabric first in the jet.

In a process in accordance with the invention, the dye bath containing the solvent and the article in the



dyeing bath are heated to a temperature at least equal to the dyeing transition temperature. For the purposes of this application, dyeing transition temperature refers to the temperature during dyeing with a particular dye at which the wool fiber structure opens up sufficiently to allow a marked increase in the rate of dye uptake. The dyeing transition temperature for a dye/fiber combination may be determined by running a dyeing under the conditions to be used and plotting % dye exhaust with respect to dye bath temperature when increased at 3°C/min. The temperature at 15% exhaust is the dyeing transition temperature. If more than one dye is to be used in a dyeing process, the temperature in the dyeing process is preferably at least equal to the dyeing transition temperature of the dye having the highest dyeing transition temperature (usually also the most structure sensitive). In the preferred form of the invention using a beck dyeing apparatus modified to include a pump for external circulation of the bath liquid, heating can be achieved using a heat exchanger through which liquid from the bath is circulated externally.

In a process in accordance with the invention, at least a portion of the dye is added while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. This part of the dyeing process can be referred to as the "rapid dye uptake phase", i.e., the time period where there is dye in the bath and the solvent and article are at a temperature at least equal to the dyeing transition temperature. In a process where no dye is added to the bath until the solvent and article are at least equal to the dyeing transition temperature, the rapid dye uptake phase will begin when dye is first added to the bath. In a process where dye addition is begun before the bath is up to temperature, the rapid dye uptake phase will begin when the solvent and article reach a temperature at least equal to the dyeing transition temperature. In typical processes, the rapid dye uptake phase will end when the



bath is exhausted toward or at the end of the dyeing process.

During the rapid dye uptake phase in one preferred process in accordance with the invention, the temperature of the bath and the article in the bath is maintained generally constant so that the dyeing process is not affected by temperature changes which may affect the rate of dye uptake by the article. Generally, provided that the temperature remains above the dyeing transition temperature, the temperature should be controlled to within $+10^{\circ}\text{C}$, preferably $+5^{\circ}\text{C}$. Also, in aqueous systems, it is usually preferable for the pH to be maintained generally constant. It has been found that controlling the pH to within about $+0.2$ units is suitable.

In some processes, particularly processes using a dye mixture where one dye is structure sensitive and the other is strongly levelling, it may be desirable to decrease the pH and/or lower the temperature as the dyeing progresses to promote the exhaustion of the levelling dye from the bath. This is usually desirable towards or at the end of the dyeing since the structure sensitive dye may strike too fast and cause an unlevel dyeing if the pH or temperature is too low initially. Decreasing the pH can be done by metering a suitable acid solution such as acetic acid into the bath after the dye addition period or by using an acid donor such as the acid donor sold by Sandoz Chemical Co. under the trademark SANDACID V® which hydrolyzes and lowers pH in a gradual, controlled manner.

In a preferred process of the invention, at least about 33% of the dye is added to the bath when the solvent and the article are at least equal to the dyeing transition temperature, i.e., during the rapid dye uptake phase. Most preferably, at least about 50% of the dye is added during the rapid dye uptake phase. Increasing dye yield benefits will be obtained with increases in the amount of dye added during the rapid dye uptake phase. However, it may be desirable to forgo some of the dye yield increase to take advantage of decreased cycle time



which may be obtained by adding at least some of the dye into the bath before it is up to the dyeing transition temperature.

Stirring of the bath during a dye addition period and the rapid dye uptake phase is done to mix the dye concentrate with the solvent in the bath to form a dilute dye solution and to provide a flow of the dilute dye solution relative to the article to cause the dye to be transported to the article. The term "stirring" is intended to include any means of mixing and imparting relative motion between the article and the solvent in the dyeing bath. The relative motion between the article and the solvent can be imparted by circulating the solvent in the dye bath, moving the article in the solvent, or both moving the article and circulating the liquid. In the preferred process employing a beck dyeing apparatus, both the article is moved and the bath liquid is circulated by action of the rotating winch-reel. For beck dyers, it is desirable to have a pump for external circulation of the bath liquid into which the dye concentrate can be added to facilitate mixing. It is most preferable for the dye concentrate to be added to the bath liquid ahead of the pump.

The stirring also provides, on the average, essentially uniform dye transport of the anionic dye to the article during the dye addition period and rapid dye uptake phase so that a dyeing results which is sufficiently visually level to be useful for the intended purpose. Typically, a visually level fabric has shade variations across the fabric which are less than about 5%. Thus, during a process in which there are a number of repetitive cycles as in the preferred form of the invention in a beck dyer where the fabric rope cycles numerous times, the dye transport to the fabric may not be uniform in any one machine cycle. However, the additive effect of dye transport during all of the cycles is such that a level dyeing results since dye transport "on the average" is essentially uniform. As will become more



apparent hereinafter, it may be desirable to increase the turnover rate, limit the dye addition rate, or both to decrease the percentage of total dye added per cycle and thereby increase uniformity due to the greater averaging effect obtained. To facilitate control over the process and to enable a process to be repeated, it is preferable for stirring to be performed constantly and at a constant rate.

In accordance with the invention, the dye addition rate is adjusted to be the primary control over the rate of dye uptake by the article at least while the solvent and the article are at or above the dyeing transition temperature. The type of adjustment of the dye addition rate necessary to accomplish this may be better understood by reference to Equation I which takes into account factors impacting the dyeing process:

$$L = \frac{D_s}{K \cdot D_f} \times \frac{r}{\delta} \quad \text{I}$$

In Equation I, D_s is the diffusion coefficient of the dye in solution, D_f is the diffusion coefficient of the dye in the fiber, K is the equilibrium distribution coefficient for the dye-fiber system, r is the radius of the fiber, and δ is thickness of the diffusional boundary layer. In a process in accordance with the invention, it has been discovered that adjusting the rate of dye addition into the bath and coordinating the rate with other conditions in the bath so that the rate of dye addition is the primary control over the rate of dye uptake provides low values for L in Equation I. It has further been discovered that the maximum benefits of the invention result when L is very low, preferably approaching zero.

To cause the rate of dye addition to be the primary control over the rate of dye uptake and thereby provide low L values, the rate of dye addition is limited so that the fibrous article, which is readily capable of



accepting dye since it is above the dyeing transition temperature, is capable of accepting more dye than is supplied to it. Under these conditions, the concentration of dye in the bath is very much lower than in a conventional process and the influence of the diffusion coefficient in the fiber, D_f , is therefore substantially less significant than in a conventional process. Also, the value for $D_s/(K \cdot D_f)$ will be smaller than in a conventional process and will lead to lower L values, primarily because the value for K will increase as the concentration of dye in the dye bath decreases. This effect is particularly pronounced in the preferred form of the invention where dyes are used and/or conditions established so that the dyes transfer less than about 10%. In such cases, the value for K is very high and is further increased by the limited concentration of dye in the bath.

Preferably, the dye addition rate is adjusted so that the concentration of dye in the solvent at the location of lowest concentration in the dyer is not greater than about 100 times the final equilibrium concentration for any substantial period of time while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. In a process in accordance with the invention in which the dye is added to the bath before the dyeing transition temperature is reached, a high concentration of dye may temporarily be present in the bath while the bath is at or above the dyeing transition temperature. This time period with high concentration should not be a substantial period of time, i.e., should not be greater than about 10% of the time when the bath is at or above the dyeing transition temperature. For the maximum benefits to be obtained when conditions are used or dyes are selected so that the dyes transfer less than about 10%, it is preferred for the concentration to not be greater than 100 times the final equilibrium concentration for any period of time while the bath is at or above the dyeing transition temperature. Most preferably, the dye addition rate is adjusted so that



the concentration does not exceed about 50 times the final equilibrium concentration.

The "final equilibrium concentration" is the concentration of dye in the dyebath for a particular % dye on the article under the process conditions at which there is essentially no further increase in the depth of dyeing without the addition of new dye. The final equilibrium concentration can be determined with reasonable certainty in the process itself by extrapolation from the concentration measured in the dye bath at the end of the dyeing process. Usually, when the dyeing process is complete in a commercial dyeing, the dye will have been sufficiently exhausted (and will have a uniform concentration in the bath) so that the final concentration before the bath is dropped can be assigned as the final equilibrium concentration. During the dyeing process, the location of lowest concentration in the dyer is usually just ahead of where dye is introduced into the bath. For example, in a process where the solvent is circulated using a pump and the dye is added ahead of the pump, the concentration of the dye in the solvent just ahead of where the dye is added will be the lowest concentration.

In contrast, in a conventional process for dyeing wool, the dye in the bath is initially on the order of 300-500 or more times the equilibrium concentration and remains in this range for a significant time until it is gradually decreased as the temperature is slowly increased to cause the dyeing to progress. If concentrations were to equal the concentrations used in conventional dyeings for a substantial period of time while the fiber contained little dye and was well above the dyeing transition temperature, a visually un-level dyeing likely would result, particularly when conditions are used or dyes are selected so that the dyes transfer less than about 10%.

To more fully realize the decrease in dye cycle times which are achievable in accordance with the present invention, the rate of dye addition is also preferably adjusted so that the concentration of dye in the solvent,



as measured at the location of lowest concentration in the bath, is at least about 2.5 times the final equilibrium concentration for a sustained period of time while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. Preferably, the sustained period of time comprises at least about 10% of the time while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. Preferably, the concentration in the bath at the location of lowest concentration will be at least about 3.5 times the equilibrium concentration.

In commercial processes employing a number of repetitive machine cycles, e.g., turnovers of the fabric in a beck dyer or circulation of the bath in a package dyer, it is preferable to adjust the rate of dye addition so that an amount of dye between about 0.5% and about 7% of the total dye is added in a machine cycle to achieve, on the average, essentially uniform dye transport and a visually level dyeing in accordance with the invention. Most preferably, an amount of dye between about 0.5% and about 3% is added during a machine cycle. Using laboratory dyeing equipment, percentages of total dye per cycle are typically lower since laboratory equipment usually has a high turnover rate which would not be practical for use in large commercial dyeing equipment although excellent results are obtained.

Rates of dye addition based on the fabric weight in commercial beck dyers are usually on the order of about 0.0005 to 0.5% dye/minute. The rates at the lower end of the range are useful for low percent dye-on-fiber dyeings with extremely high affinity dyes to provide a sufficient number of machine cycles for adequate averaging to provide essentially uniform dye transport.

Using the preferred process of the invention in which conditions are used so that the dyes transfer less than 10% in the same equipment used for conventional wool dyeings, articles containing wool can be produced with a higher relative dye strength for the same relative dye



content, i.e., to have a higher relative dye yield, than can be obtained using conventional processes. Depending on the type of dye being used, the temperature and pH conditions in the dyebath can be used to adjust the relative dye yields obtained for a process of the invention in the same type of equipment under the same conditions. For example, with most anionic dyes, decreasing the pH will provide increases in relative dye yields. For dyes which level under conventional conditions, it may be desirable to employ lower temperatures which has the primary effect of decreasing transfer. With increased temperatures above the dye transition temperature, relative dye yields provided by many structure sensitive dyes may increase. However, in general, conditions which produce the maximum benefits in terms of dye yield with structure sensitive dyes may make it more difficult to obtain a visually level dyeing. Accordingly, it may be necessary to select conditions which provide a compromise between relative dye yield increases and still provide a level dyeing without extraordinary care.

The preferred process of the invention using dyes under conditions such that the transfer is less than 10% is capable of minimizing the sensitivity to structural differences in the fibers which can lead to non-uniform dyeing. Provided that the transport of the dye to the article is, on the average, essentially uniform, a more visually level dyeing can be achieved than is normally achieved using a conventional process since individual fibers are dyed more uniformly in a process in accordance with the invention.

It is also possible to adjust the results of the invention by including dyeing auxiliaries in the solvent in the dye bath or including them in the dye concentrate. In general, auxiliaries which decrease the strike rate of the dye will decrease the relative dye yield obtained and the dyeing will be more like a conventional dyeing. In addition, where the dye is added into the bath before the



bath has reached its dyeing transition temperature, the dye which is absorbed by the fiber before the dyeing transition temperature is reached will impart some conventional dyeing characteristics to the fiber in the article.

For setting up a commercial process in accordance with the invention, it is advantageous for the process to be run first in laboratory scale equipment corresponding generally to the chosen process conditions. In the laboratory scale process, a dye addition rate can thereby be determined in advance or a rate based on past experience for the same or similar dyeings can be confirmed. Due to smaller ratios of the weight of the bath to the weight of the goods and particularly the lower turnover rates in larger scale dyers compared to typical laboratory dyers, the dye addition rate or conditions used may have to be further modified for successful larger scale dyeings.

In the preferred form of the invention, it is usually only necessary to carefully control the process during the rapid dye uptake phase and, at most other times during the process, temperature and other bath conditions need not be as carefully controlled. For example, elevating the bath to the desired temperature can be done quickly and pH adjustment prior to dye addition can be done expeditiously and without the degree of care required in the conventional process for dyeing wool. This is particularly advantageous since, with only one critical stage and when constant temperature and pH are employed, the procedure will be easily reproducible and it will be possible to efficiently make repetitive dyeings of the same fabric. Moreover, in the event that it is discovered early in a dyeing process that the conditions in the bath are not as desired, the dye addition can be stopped and the desired conditions established before the dyeing is resumed.

After the dyeing is complete, the dyeing bath is cooled, typically to below about 175°F (79.4°C) and



dropped. The article can be rinsed, dried and subsequently used in a conventional manner.

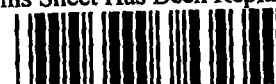
It is believed that improvements in dye yield are due to the distribution of dye in the dyed articles. It is also believed that the wool fiber adjacent to the outside surfaces yarns contain more dye than filaments in the interior of the yarn. In addition, it is believed that the wool fibers are asymmetrically ring-dyed, i.e., the fibers are dyed with more dye being present adjacent to the surface of the fibers than in the interior but the ring-dyeing of at least some of the fibers is asymmetric, i.e., more dye being present on one side or the other. It is also believed that fabrics dyed by the process have more dye on yarns adjacent to the surfaces of the fabric than in the interior of the fabric which is different from the more uniform distribution obtained using conventional processes.

While the dye may be non-uniformly distributed in the fabric, fabrics made using the invention can be visually level and are highly uniform. Although the invention is applicable to other types of fabrics such as non-wovens and tufted fabrics used for carpeting, preferred fabrics in accordance with the invention are selected from the class consisting of knitted and woven fabrics. In addition, it is preferable for the fabric to be dyed with at least one structure sensitive anionic dye.

TEST METHODS

The Dye Transition Temperature is determined for a fiber/dye combination as follows:

A sample of the article is prescoured in a bath containing 800 g water/g of sample with 0.5 g/l of tetrasodiumpyrophosphate and 0.5 g/l of MERPOL HCS® (a liquid non-ionic detergent sold by E.I. du Pont de Nemours & Company). The bath temperature is raised at a rate of about 3°C/min. until the bath temperature is 60°C. The temperature is held for 15 minutes at 60°C, then the fiber is rinsed. (Note that the prescour temperature must not exceed the dye transition temperature of the fiber. If



the dye transition temperature appears to be close to the prescour temperature, the procedure should be repeated at a lower prescour temperature.) The bath (without the article) with a similar quantity of water is adjusted to 30°C and 1% (based on the weight of the article) of the dye to be used and 5 g/l of monobasic sodium phosphate are added. (If more than one dye is to be used in the dyeing process, the dye believed to have the highest Dye Transition Temperature should be used to determine Dye Transition Temperature. Usually, this dye will also be the most structure sensitive.) The pH is adjusted to 5.0 using monobasic sodium phosphate and acetic acid. The article is added and the bath temperature is increased to 95°C at a rate of 3°C/min.

With every 5°C rise in bath temperature a dye liquor sample of ~25 ml is taken from the dye bath. The samples are cooled to room temperature and the absorbance of each sample at a wavelength known to be useful for monitoring the dye is measured on a spectrophotometer such as a Perkin-Elmer C552-000 UV-visible spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT 06856) using a water reference.

The % dye exhaust is calculated and plotted with respect to dyebath temperature. The temperature at 15% exhaust is the dye transition temperature.

% Transfer can be determined using the AATCC Test Method 159-1989 (AATCC Technical Manual/1991, p. 285-286) except with the mock dyebath being at the pH and temperature of the actual process under consideration and a 30 minute time period are used. Percent transfer is calculated in this method by measuring the relative dye strength of the original dyed sample before (control, 100% relative dye strength) and after the transfer procedure. The difference is the % transfer.

Relative Dye Strength is a relative measure of the strength of dye in a fabric determined photometrically for a series of fabrics dyed with the same dye with the sample dyed by the comparative or control procedure being



arbitrarily designated as having 100% relative dye strength.

Relative dye strength for a fabric sample is measured at the wavelength of minimum reflectance using a
5 MACBETH COLOR EYE 1500 PLUS SYSTEM Spectrophotometer, sold by Macbeth Division of Kollmorgen Instrument Corp. of Newburg, N.Y. A scan from 750 to 350 nm can be performed to determine the wavelength of minimum reflectance for the dye. All subsequent samples in a series with the same dye
10 are then measured at the same wavelength. For example, the wavelength of minimum reflectance for C.I. Acid Blue 122 is 640 nm.

The sample produced by the comparative or control procedure is designated the control and assigned a
15 relative dye strength of 100%. The remaining samples are then scaled in relative dye strength by the following:

$$\text{Rel. Dye Strength (\%)} = \frac{\text{K/S sample}}{\text{K/S control}} \times 100,$$

20 and

$$\text{K/S} = \frac{(1 - R)^2}{2R}$$

where: R = reflectance.

Relative Dye Content is a relative measure of dye
25 content determined photometrically for a series of fabrics dyed with the same dye with the sample dyed by the comparative or control procedure being arbitrarily designated as having a 100% relative dye content.

The relative dye content is determined in the
30 following way. First, a sample of the article is cut into small segments and about 0.1 gram is weighed to +0.1 mg accuracy. Typically, a test series of samples of dyed articles is weighed to each have very nearly the same weights. The samples are dissolved in 30 ml of formic
35 acid at ambient temperature. After sample dissolution is complete, centrifugation for 20 minutes is effective for removing titanium dioxide delusterant when present.

A Perkin-Elmer C552-000 UV-visible spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT



06856) is used to record the absorbance of the samples. A scan from 750 to 350 nm is performed and the largest peaks are chosen as analytical wavelengths for the dye tested. All subsequent samples in a series with the same dye are then measured at these wavelengths. Typically, sample sizes around 0.1 gram give absorbance readings in the range of 0.3 AU to 0.8 AU for the dye levels obtained.

A corrected absorbance is calculated for each wavelength measured on every sample in the series. The corrected absorbance is:

$$A \text{ (corrected)} = (S \times 0.1 \text{ gram}) / W$$

where: S = absorbance at a given wavelength; and
W = weight of sample in grams

The sample dyed by the comparative or control procedure is assigned a relative dye content of 100%. The remaining samples are then scaled in relative dye content by the following:

$$\text{Rel. Dye Content (\%)} = (A_s \times 100) / A_1$$

where: A_s = average absorbance of sample; and
 A_1 = average absorbance of the control sample.

This calculation is performed for every analytical wavelength chosen in a given dye series.

Relative Dye Yield is defined as the ratio of the Relative Dye Strength to the Relative Dye Content:

$$\text{Rel. Dye Yield} = \frac{\text{Relative Dye Strength}}{\text{Relative Dye Content}}$$

The invention is illustrated in the following example which is not intended to be limiting. Percentages are by weight unless otherwise indicated.

EXAMPLE 1

Part A

30 grams of a scoured fabric, woven from 100% wool (35 cm x 35 cm), is introduced into a Werner-Mathis Laboratory Dyeing Apparatus, Type JF, sold by Werner-Mathis U.S.A., of Concord, NC. The fabric is placed in



the perforated basket and the see-through door is closed. The dyeing bath is then set with 1800 ml of distilled water at a 60:1 liquor ratio (weight of bath to weight of fabric) at 80° (26.7°C) and then pH is adjusted to 5.0
5 with monosodium phosphate (MSP) and phosphoric acid. 0.15 g (0.5% on weight of sample) of ALBEGAL-B®, a wool leveling agent from Ciba-Geigy Corp., is added to the bath.

The basket device is set into motion by adjusting
10 the rheostat driven motor so that the basket rotates in a clockwise motion for about six seconds; then stops for about five seconds; then reverses to a counter-clockwise motion for six seconds. This sequence of clockwise, pause, and counter-clockwise movements continues
15 automatically throughout the dyeing procedure. This provides adequate movement of the bath liquor and the fabric sample to provide uniform application of dye to the substrate.

The temperature of the dyeing bath is then raised
20 rapidly by 5°F/min. (2.8°/min.) or greater to the dyeing temperature. In this example, the dyeing temperature is held nearly constant at about 200°F (93.3°C) during the dye addition period as the dye is added as described below. (The rapid dye uptake phase of this example begins
25 with the addition of dye during the dye uptake phase, i.e., 100% of the dye is added during the rapid dye uptake phase.)

Separately, 0.6 g of C.I. Acid Blue 336, a pre-metallized acid dye, is dissolved in 200 ml of distilled
30 water to form a dye concentrate. The amount of dye used is calculated to provide 2% dye-on-fiber assuming complete exhaustion of the dye. Using a precision (approx. 1% accuracy) MANOSTAT COMPULAB® liquid metering pump sold by Manostat Corporation of New York, NY, the separately
35 prepared dye solution is metered under the surface of the dyeing bath away from the moving fabric at the rate of 5 ml/minute which is equivalent to 0.05% dye/minute based on the weight of fabric. Under these conditions this dye



transfers less than 10% and there is never any visible build-up of dye in the dyeing bath during the period of dye addition which is complete in 40 minutes. The dyeing bath is then cooled at 5°F/min. (2.8°C/min.) to 170°F (76.6°C), then the fabric is overflow rinsed, removed from the dyeing machine, then air dried.

The result obtained is a level blue dyeing on the woven wool fabric and a visually colorless dyeing bath.

Part B (Comparative)

30 grams of the fabric described above is introduced into the perforated basket in the JF machine as in the previous example. The dyeing bath is again set as in the previous example. Separately, 0.6 grams of C.I. Acid Blue 336, a pre-metallized acid dye, are dissolved in 200 ml of distilled water. All of the dye solution is then added to the dyeing bath in the conventional manner at 80°F (26.7°C). The dyeing bath is raised at 1°F (0.6°C) per minute to 205°F (96.1°C) and held for 45 minutes. The bath is cooled and the fabric rinsed and removed as in the previous example. The result obtained is a level blue dyeing on the woven wool fabric and a visually colorless dye bath.

Assuming the same relative dye content for the fabric dyed by the invention and the comparative example, reflectance measurements show that the relative dye yield is increased 15% in the sample dyed by the process invention compared to the conventional process of the comparative example.

EXAMPLE 2

In this example, 180 grams of a scoured woven wool fabric (30 cm X 90 cm) is dyed in an 8 inch (20 cm) Saucier Beck-dyeing Machine, manufactured by Saucier Stainless Steel Products, Minneapolis, MN. The fabric is placed over the winch of this beck, then sewn at the ends to form an endless "rope." The dyeing bath is then set with 25 liters of distilled water at 139:1 liquor ratio (weight of bath to weight of fabric) at 80°F (26.7°C) and then the pH is adjusted to 5.0 with monosodium phosphate (MSP) and



phosphoric acid. 0.9 g (0.5% on weight of sample) of ALBEGAL-B®, a wool leveling agent from Ciba-Geigy Corp., is added to the bath. The fabric is set in motion by the turning action of the winch-reel. The temperature of the dyeing bath is then raised rapidly by 5°F/min. (2.8°C/min.) to the dyeing temperature. In this example, the dyeing temperature is held nearly constant at about 200°F (93.3°C) during the dye addition period as described below.

Separately 1.8 g of C. I. Acid Blue 336, a pre-metallized acid dye, is dissolved in 1000 ml of distilled water to provide ~1% dye-on-fiber assuming complete exhaustion of the dye. Using a precision (~1% accuracy) MANOSTAT COMPULAB liquid metering pump sold by Manostat Corporation of New York, NY, the separately prepared dye solution is metered under the surface of the dyeing bath away from the moving fabric at the rate of 25 ml/minute which is equivalent to 0.025% dye/minute based on the weight of the fabric. Under these conditions the dye transfers less than 10% and there is never any visible build-up of dye in the dyeing bath during the dye addition period which is complete in 40 minutes. Concentrations determined spectrophotometrically show that the concentration of dye in the bath at the after the dye addition has been in progress for 5 minutes ranges between about 5 and about 20 times the final equilibrium concentration which is reached after the dye addition is complete.

The dyeing bath is then cooled at 5°F/min. (2.8°C/min.) to 170°F (76.7°C), then the fabric is overflow rinsed, removed from the dyeing machine, then air dried.

The result obtained is a level blue dyeing on the wool fabric and a visually colorless dyeing bath.

**CLAIMS:**

1. A process for dyeing a fibrous article containing wool with at least one anionic dye comprising:
immersing said article in a dyeing bath of a
5 liquid solvent for said anionic dye;

heating said liquid solvent and said article in said dyeing bath to a temperature at least equal to the
(dyeing transition temperature) of said wool with said dye;

adding said anionic dye to said dyeing bath as a
10 miscible liquid concentrate at a dye addition rate during a dye addition period, at least a portion of said dye being added while said solvent and said article are at a temperature at least equal to said dyeing transition temperature; and

15 stirring said bath during said dye addition period and while said solvent and said article are at a temperature at least equal to said dyeing transition temperature to mix said dye concentrate with said solvent in said bath to form a dilute dye solution and to provide
20 a flow of said dilute dye solution relative to said article (to cause said dye to be transported to said article, said stirring further providing, (on the average, (essentially) uniform dye transport of said anionic dye to said article);

25 said dye addition rate being adjusted to be the primary control over the rate of uptake of said dye by said article at least while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

30 2. The process of claim 1 further comprising maintaining conditions in said liquid solvent so that said anionic dye transfers less than about 10%.

3. The process of claim 1 wherein said process is performed in a dyeing machine in which said stirring
35 provides repetitive machine cycles and said dye addition rate is adjusted so that an amount of dye between about 0.5% and about 7% of the total dye is added to said dyeing bath during a machine cycle.





4. The process of claim 3 wherein said dye addition rate is adjusted so that an amount of dye between about 0.5% and 3% is added during a machine cycle.

5. The process of claim 1 wherein said dye is added continuously and at a constant rate during said dye addition period.

6. The process of claim 1 wherein at least about 33% of said dye is added while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

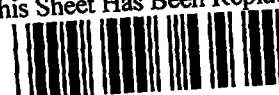
7. The process of claim 1 wherein at least about 50% of said dye is added while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

8. The process of claim 1 wherein said dye addition rate is adjusted so that the concentration of dye as measured at the location of lowest concentration in said bath is not greater than about 100 times the final equilibrium concentration for any substantial period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

9. The process of claim 8 wherein said concentration of dye is not greater than about 50 times the final equilibrium concentration for any substantial period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

10. The process of claim 1 wherein said dye addition rate is adjusted so that the concentration of dye in said solvent as measured at the location of lowest concentration in said bath is at least about 2.5 times the final equilibrium concentration for a sustained period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

11. The process of claim 10 wherein said concentration of dye in said solvent is at least about 3.5





times the final equilibrium concentration for a sustained period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

5 12. The process of claim 10 wherein said sustained period of time comprises at least about 10% of the time when said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

10 13. The process of claim 1 wherein said liquid solvent is an aqueous liquid.

 14. The process of claim 1 wherein said anionic dye is a structure sensitive anionic dye.

15 15. The process of claim 1 wherein at least some of said stirring is provided by a pump which circulates solvent in said bath.

 16. The process of claim 15 wherein said liquid dye concentrate is added into said solvent ahead of said pump to form said dilute dye solution.

20 17. The process of claim 16 wherein said liquid dye concentrate is added into said solvent by a metering pump.

 18. An article containing wool dyed by the process of claim 2.

25 19. An article containing wool dyed by the process of claim 14.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : D06P 1/00, 3/16	A1	(11) International Publication Number: WO 93/23604 (43) International Publication Date: 25 November 1993 (25.11.93)
(21) International Application Number: PCT/US93/04357 (22) International Filing Date: 13 May 1993 (13.05.93) (30) Priority data: 07/884,500 15 May 1992 (15.05.92) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: HOLFELD, Winfried, Thomas ; 700 Thornby Road, Wilmington, DE 19803 (US). MANCUSO, Dale, Emmett ; 2403 Berwyn Road, Wilmington, DE 19810 (US). (74) Agents: HENDRICKSON, John S. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: WOOL DYEING UTILIZING CONTROLLED DYE ADDITION		
(57) Abstract A process for the dyeing of a fibrous article containing wool with an anionic dye and products produced thereby. The process includes immersing the article in a dyeing bath of a liquid solvent for the anionic dye. The liquid solvent and the article are heated to a temperature at least equal to the dyeing transition temperature. At least a portion of the dye is added as a miscible liquid concentrate while the solvent and the article are up to temperature. Stirring of the bath during the dye addition period and while the solvent and article are up to temperature is done to mix the dye concentrate with the solvent to form a dilute dye solution and to provide a flow of the dilute dye solution relative to the article to cause, on the average, essentially uniform dye transport of the anionic dye to the article. The dye addition rate is adjusted so that the dye addition rate is the primary control over the rate of dye uptake by the article. This Sheet Has Been Replaced 		

19 FEB 1997

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TITLE

Wool Dyeing Utilizing Controlled Dye Addition

BACKGROUND OF THE INVENTION

The present invention relates to the dyeing of
 5 fibrous articles containing wool with anionic dyes.

Anionic dyes such as acid dyes and pre-metallized
 dyes are widely used for the dyeing of wool. In
 conventional dyeing processes using such dyes, articles
 containing wool are immersed in an aqueous bath containing
 10 a solution of the dye after any pre-treatment processes
 such as scouring. While a wide variety of dyeing
 equipment is used, it is typical for all of the dye to be
 used in the process to be present in the bath initially.
 The bath containing the dye and the article to be dyed is
 15 also usually at a very low initial temperature, e.g., 80-
 120°F (26.7-48.9°C) and the temperature is increased
 gradually to an elevated temperature often as high as the
 boiling point as the dyeing progresses. "Metallizing"
 treatments with, e.g., with potassium dichromate, are
 20 often performed subsequently to dyeing to increase dye
 light and/or wash fastness.

While high quality dyeing can be achieved using
 the conventional dyeing process for some acid dyes such as
 small molecule "levelling" dyes, dye cycles to achieve
 25 levelling with such anionic dyes are sometimes extremely
 long and are therefore costly. In addition, long dye
 cycles are undesirable since the maintenance of the bath
 at a high dyeing temperature for a long period of time can
 decrease the strength of wool. It is very common to dye
 30 wool using large molecule acid and pre-metallized dyes
 which are desirable for applications requiring good light
 and/or wash fastness. However, undesirable dyeings can
 result with conventional dyeing processes using large
 molecule acid and pre-metallized dyes since individual
 35 wool fibers may not dye uniformly. Often, one end of a
 fiber will dye readily while the other end will absorb
 little dye resulting in an "skittery" dyeing in the
 article, i.e., noticeable localized dark/light areas.

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☒ Claim(s) : paged ...24... to paged ...25...
☐ Drawing(s) : paged to paged
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☒ Description : paged ...1... to paged ...25...
☒ Claim(s) : paged ...24... to paged ...25...
☒ Drawing(s) : paged ...1... to paged ...1...
☒ Abstract : paged ...25... to paged ...25...
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Large molecule acid and pre-metallized dyes are often referred to as "structure sensitive" dyes since non-uniform dyeing can result from minor variations in the fiber physical structure. While dye-levelling and/or
5 retarding agents can be added to the dye bath to improve dyeing uniformity with structure sensitive dyes, such agents sometimes provide only limited increases in dye uniformity and usually have disadvantages including increased initial expense and higher cost to treat the
10 spent dyeing bath. In addition, because of their retarding effect, such chemical agents can sometimes increase dyeing cycles or make it difficult to obtain deep colors or dark shades. Also, dye yields from anionic dyes, i.e., the strength of color produced from a given
15 quantity of dye on the fiber, are sometimes not as high as desired.

SUMMARY OF THE INVENTION

The invention provides an improved process for the dyeing of a fibrous article containing wool with at least
20 one anionic dye and dyed products made by the process. A process in accordance with the invention includes immersing the article in a dyeing bath of a liquid solvent for the anionic dye. The liquid solvent and the article are heated to a temperature at least equal to the dyeing
25 transition temperature. The anionic dye is added to the dyeing bath as a miscible liquid concentrate at a controlled dye addition rate during a dye addition period. At least a portion of the dye is added while the bath and article are at temperature at least equal to the dyeing
30 transition temperature. Stirring of the bath during the dye addition period and while the solvent and article are up to the dyeing transition temperature is done to mix the dye concentrate with the solvent in the bath to form a dilute dye solution and to provide a flow of the dilute
35 dye solution relative to the article to cause the dye to be transported to the article. The stirring also provides, on the average, essentially uniform dye transport of the anionic dye to the article. In



accordance with the process, the dye rate is adjusted at least while the solvent and article are at a temperature at least equal to the dyeing transition temperature so that the dye addition rate is the primary control over the
5 rate of dye uptake by the article.

In accordance with a preferred form of the invention, the conditions in the liquid solvent are maintained so that the anionic dye transfers less than about 10%.

10 In accordance with another preferred form of the invention, the process is performed in a dyeing machine in which the stirring provides a number of repetitive machine cycles and the dye addition rate is adjusted so that an amount of dye between about 0.5% and about 7% of the total
15 dye is added to the dyeing bath during a machine cycle, most preferably between about 0.5% and about 3%.

In accordance with another preferred form of the invention, at least about 33% of the dye is added to the bath while said solvent and said article are at a
20 temperature at least equal to the dyeing transition temperature, most preferably at least about 50% of the dye is added at this time.

In accordance with another preferred form of the invention, the dye addition rate is adjusted so that the
25 concentration of dye at location of lowest concentration in the bath is not greater than about 100 times, most preferably not greater than 50 times, the final equilibrium concentration for any substantial period of time while the solvent and the article are at a
30 temperature at least equal to the dyeing transition temperature.

In accordance with another preferred form of the invention, the rate of dye addition is adjusted so that the concentration of dye in the solvent as measured at the
35 point of lowest concentration in the bath is at least about 2.5 times, preferably at least about 3.5 times, the final equilibrium concentration for a sustained period of time while the solvent and the article are at a

REPLACEMENT SHEET

19 FEB 1997

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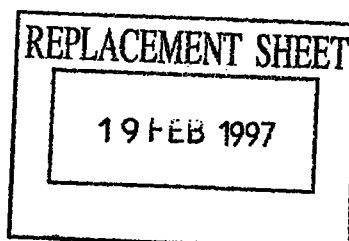


temperature at least equal to the dyeing transition temperature. Preferably, the sustained period of time comprises at least about 10% of the time when the solvent and the article are at a temperature at least equal to the dyeing transition temperature.

The invention is useful in a wide variety of wool dyeing processes using anionic dyes. Surprisingly, it has been found that when used under conditions such that the dyes transfer less than 10%, anionic dyes are utilized more effectively which can provide either better dye yields or the achievement of deep colors or dark shades which were otherwise difficult to obtain or were unobtainable. Also, dye cycles for all types of dyes can be substantially shortened which can decrease cost and decrease the strength loss which is known to occur in wool dyeings. Moreover, the improvements in dyeing are often achievable without the use of or by using lower concentrations of chemical levelling or other chemical agents which, in significant concentrations, can complicate treatment of spent dyeing bath liquids.

DETAILED DESCRIPTION

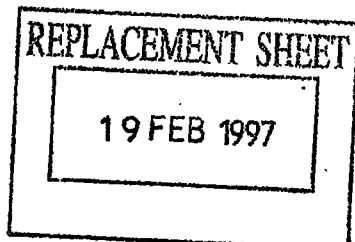
There are a wide variety of fibrous articles containing wool which can be dyed using the process of the invention including, for example, yarns, fabric, carpets and garments. Wool as stock can also be an article dyed by this process. Fabrics include the usual textile forms including woven, knitted, and non-woven varieties. The wool can be present in the article together with any of a variety of other synthetic or natural fibers. Typical of such articles are yarns made from a "blend" of wool with other fibers and fabrics and garments made from such yarns. The other fibers in such articles may or may not undergo dyeing as the wool is dyed in the process. In addition, the wool to be dyed may already contain the same or a different dye. For example, the process of the invention may be used for a dye "add" to get to "shade" with the fiber already containing most of the dye before the process is used.



The dyes used in the practice of the present invention are anionic dyes and dyeing of the wool is accomplished by uptake of the dyes through the association of the dye molecules with nitrogen-containing groups on the wool fiber. Most anionic dyes are members of the well-known class of "acid" dyes. Another type of anionic dyes is the type referred to as "pre-metallized" dyes which are the reaction products of, for example, chromium or cobalt and selected dyes. As will become apparent hereinafter, mixtures of two or more dyes are often used to achieve a desired shade. In this application, the word "dye" may be used to refer to a single dye or multiple dyes as in a mixture of dyes used in a dyeing process or on a dyed article. In processes using more than one dye such as in dye mixtures to achieve compound shades, a process is intended to be within the scope of the invention provided that at least one dye of compound shade is applied to an article in accordance with the invention.

In accordance with a preferred process in accordance with the invention, conditions are used in the dye bath so that anionic dyes transfer less than about 10%. Transfer is a measure of the propensity of anionic dyes to migrate from one dye site to another after being absorbed by the fiber. Transfer under a given set of conditions can be measured in a mock dye bath as in the transfer test method described hereinafter.

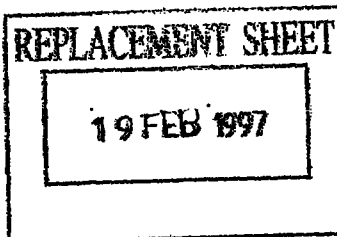
Providing transfer of less than 10% can easily be accomplished by use of dyes from a preferred class of dyes, the "structure sensitive" anionic dyes. These dyes are usually large molecule acid ("milling") dyes or pre-metallized dyes which are non-levelling, i.e., the dye molecules do not "transfer" significantly and thus migrate very little from one dye site to another after being absorbed by the fiber. Typically, structure sensitive dyes "transfer" less than 10% under normal conditions of use. "Structure sensitive" is the term applied to such dyes since non-uniform dyeing can result from even minor, and otherwise undetected, variations in the fiber physical



structure. Such variations occur naturally in wool. Despite their known difficulties in use, structure sensitive dyes are desirable for many applications due to their washfastness, lightfastness, or both.

5 Without intending to limit this preferred form of the invention to these specific dyes, commonly used structure-sensitive dyes are represented, for example, by the list provided below (C.I. refers to the Color Index, 3rd edition, 1971):

10 C.I. Acid Yellow 220
C.I. Acid Orange 162
C.I. Acid Brown 282
C.I. Acid Brown 283
C.I. Acid Brown 226
15 C.I. Acid Red 407
C.I. Acid Red 251
C.I. Acid Black 60
C.I. Acid Blue 317
C.I. Acid Blue 80
20 C.I. Acid Blue 171
C.I. Acid Blue 336
C.I. Acid Black 172



For dyes which are normally described as "levelling" dyes since they transfer readily and "level" under the normal conditions of use, transfer of less than about 10% can be accomplished using conditions of low pH, low temperature, or both. In addition, with dyes which are normally strongly levelling, it may be necessary to perform the dyeing rapidly even though the conditions in the dyeing bath are such that the dye transfers less than about 10%. Otherwise, the dye yield benefits which are otherwise obtainable using the invention may be diminished due to dye transfer which occurs after the dye is on the article.

35 As in conventional dyeing processes, it is desirable to scour the article before dyeing to remove sizing and other materials which may adversely affect the dyeing. The fabrics can be scoured, for example, in an

19 FEB 1997

7

open width scouring range or in the apparatus to be used for the dyeing, e.g., a beck or paddle dyer. Scouring solutions used conventionally are generally suitable, e.g., water at 180°F (82.2°C) containing a surfactant such as 0.5 gram/liter of MERPOL LFH® (a liquid non-ionic detergent sold by E. I. du Pont de Nemours & Company, Inc. of Wilmington, DE). After scouring, the fabric should be rinsed such as by being immersed in hot water.

In the process of the invention, the article to be dyed is immersed in a dyeing bath containing a liquid solvent for the anionic dye. The dyeing bath can take a wide variety of forms in which the article is totally immersed in the bath throughout the dyeing process or is partially immersed at any one time and is moved in a cyclical or random fashion to provide contact for the entire article with the solvent. Partial immersion is useful for articles such as fabrics where the fabric can be progressively advanced through the bath, either in continuous rope form or by reciprocation of an article having a discrete length, so that the entire article is ultimately dyed. A preferred process employs the bath formed in a beck dyer for fabric in which the fabric is in the form of an endless rope and is moved by the action of the winch-reel. Most preferably, a beck for use in accordance with this invention is modified to include a pump and appropriate piping for external circulation of the solvent. Jet dyers are advantageously used for wool blend fabrics such as wool/polyester blends.

The liquid solvent for the dye is any suitable solvent for the dye which is capable of transporting the dye to the dye sites on the fiber and which is otherwise compatible with the fabric, dye and other aspects of the process, e.g., aqueous liquids and methanol are suitable solvents. Preferably, the liquid solvent is an aqueous liquid which contains less than about 10% by weight of additives for establishing and maintaining the desired pH and for other purposes. Suitable aqueous liquids useful in the process contain additives for providing a buffer

19 FEB 1997

system. For example, acetic acid on the order of about 1% and ammonium acetate on the order of about 2% by weight can be used to adjust the pH to a suitable level. Other additives can be chemicals such as wetting agents, retarders, and the like which are referred to collectively in the present application as "dyeing auxiliaries".

Dyeing auxiliaries can be present in the process of the invention although such agents often are not needed. If dyeing auxiliaries are present in the bath, a much lower concentration is typically used to keep the dye cycle to a reasonably short duration. Dyeing auxiliaries can be useful and may be desirable for compound shades of dyes of differing affinities.

When the bath has low levels of or is substantially free of dyeing auxiliaries, significant advantages are obtained in the treatment or disposal of the spent dye liquors. Moreover, the dyed fiber may be substantially free of residual dyeing auxiliaries or such agents may be present only at much lower levels than in fibers dyed by the conventional process for structure sensitive dyes which typically require high bath concentrations of dyeing auxiliaries. In addition, it is possible in some instances to use the spent dyeing bath for after-treatments such as for improving wetfastness, lightfastness or softness, applying antistats, and for other known after-treatments employing chemical agents. Metallizing can usually be done in the same bath. For such after-treatments, the chemical agent can be added to the hot bath using a technique similar to that used to add the dye in a process in accordance with the invention. In addition, it is also possible to reuse the spent bath in a subsequent dyeing if dyeing auxiliaries are absent or are present in sufficiently low concentration.

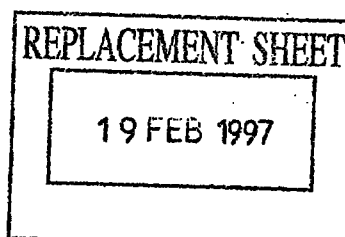
The anionic dye is added to the dyeing bath as a miscible liquid concentrate at a controlled dye addition rate during a dye addition period. "Dye addition period" refers to the time period beginning with the first addition of dye and ending with the final amount of dye

being added. The length of the dye addition period will usually range between about 5 minutes and about 4 hours with typical dye addition periods being between about 20 and about 100 minutes. Upon stirring as will be explained
5 in more detail, the miscible liquid dye concentrate is mixed with the solvent in the bath to form a dilute dye solution. "Miscible liquid concentrate" is intended to refer to a solution in which the dye is fully dissolved and which can be added to and mixed with the liquid
10 solvent in the bath to form a dilute liquid solution of the dye in all proportions of such concentrates which would normally be mixed into a dye bath. The solvent for the miscible liquid concentrate can be different from the liquid solvent provided that the introduction of a
15 different solvent does not otherwise adversely affect the dyeing process. When an aqueous dyeing bath is used, the solvent preferably used in the miscible liquid concentrate is water.

As will be explained in more detail hereinafter,
20 the dye addition rate is adjusted depending on the amount of dye to be applied, the characteristics of the article to be dyed, the type of dyeing apparatus, the type of dye and the conditions of the dyeing to achieve the desired results. Preferably, to facilitate control over the
25 process and make the process more easily reproducible, the dye is added continuously and at a constant rate during the dye addition period.

In processes in which the dilute dye solution in the bath is circulated by means of a circulation pump, the
30 liquid dye concentrate is preferably added to the solvent ahead of the circulation pump. A metering pump is advantageously utilized for this purpose. When dyeing wool fabrics such as wool/polyester blend fabrics which can be dyed in a jet dyer, the circulation pump supplies
35 the dilute dye solution to the jet nozzle so that the newly-added dye contacts the fabric first in the jet.

In a process in accordance with the invention, the dye bath containing the solvent and the article in the



dyeing bath are heated to a temperature at least equal to the dyeing transition temperature. For the purposes of this application, dyeing transition temperature refers to the temperature during dyeing with a particular dye at which the wool fiber structure opens up sufficiently to allow a marked increase in the rate of dye uptake. The dyeing transition temperature for a dye/fiber combination may be determined by running a dyeing under the conditions to be used and plotting % dye exhaust with respect to dye bath temperature when increased at 3°C/min. The temperature at 15% exhaust is the dyeing transition temperature. If more than one dye is to be used in a dyeing process, the temperature in the dyeing process is preferably at least equal to the dyeing transition temperature of the dye having the highest dyeing transition temperature (usually also the most structure sensitive). In the preferred form of the invention using a beck dyeing apparatus modified to include a pump for external circulation of the bath liquid, heating can be achieved using a heat exchanger through which liquid from the bath is circulated externally.

In a process in accordance with the invention, at least a portion of the dye is added while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. This part of the dyeing process can be referred to as the "rapid dye uptake phase", i.e., the time period where there is dye in the bath and the solvent and article are at a temperature at least equal to the dyeing transition temperature. In a process where no dye is added to the bath until the solvent and article are at least equal to the dyeing transition temperature, the rapid dye uptake phase will begin when dye is first added to the bath. In a process where dye addition is begun before the bath is up to temperature, the rapid dye uptake phase will begin when the solvent and article reach a temperature at least equal to the dyeing transition temperature. In typical processes, the rapid dye uptake phase will end when the

REPLACEMENT SHEET

19 FEB 1997

bath is exhausted toward or at the end of the dyeing process.

During the rapid dye uptake phase in one preferred process in accordance with the invention, the temperature of the bath and the article in the bath is maintained generally constant so that the dyeing process is not affected by temperature changes which may affect the rate of dye uptake by the article. Generally, provided that the temperature remains above the dyeing transition temperature, the temperature should be controlled to within $+10^{\circ}\text{C}$, preferably $+5^{\circ}\text{C}$. Also, in aqueous systems, it is usually preferable for the pH to be maintained generally constant. It has been found that controlling the pH to within about $+0.2$ units is suitable.

In some processes, particularly processes using a dye mixture where one dye is structure sensitive and the other is strongly levelling, it may be desirable to decrease the pH and/or lower the temperature as the dyeing progresses to promote the exhaustion of the levelling dye from the bath. This is usually desirable towards or at the end of the dyeing since the structure sensitive dye may strike too fast and cause an unlevel dyeing if the pH or temperature is too low initially. Decreasing the pH can be done by metering a suitable acid solution such as acetic acid into the bath after the dye addition period or by using an acid donor such as the acid donor sold by Sandoz Chemical Co. under the trademark SANDACID V® which hydrolyzes and lowers pH in a gradual, controlled manner.

In a preferred process of the invention, at least about 33% of the dye is added to the bath when the solvent and the article are at least equal to the dyeing transition temperature, i.e., during the rapid dye uptake phase. Most preferably, at least about 50% of the dye is added during the rapid dye uptake phase. Increasing dye yield benefits will be obtained with increases in the amount of dye added during the rapid dye uptake phase. However, it may be desirable to forgo some of the dye yield increase to take advantage of decreased cycle time

REPLACEMENT SHEET

19 FEB 1997

which may be obtained by adding at least some of the dye into the bath before it is up to the dyeing transition temperature.

Stirring of the bath during a dye addition period and the rapid dye uptake phase is done to mix the dye concentrate with the solvent in the bath to form a dilute dye solution and to provide a flow of the dilute dye solution relative to the article to cause the dye to be transported to the article. The term "stirring" is intended to include any means of mixing and imparting relative motion between the article and the solvent in the dyeing bath. The relative motion between the article and the solvent can be imparted by circulating the solvent in the dye bath, moving the article in the solvent, or both moving the article and circulating the liquid. In the preferred process employing a beck dyeing apparatus, both the article is moved and the bath liquid is circulated by action of the rotating winch-reel. For beck dyers, it is desirable to have a pump for external circulation of the bath liquid into which the dye concentrate can be added to facilitate mixing. It is most preferable for the dye concentrate to be added to the bath liquid ahead of the pump.

The stirring also provides, on the average, essentially uniform dye transport of the anionic dye to the article during the dye addition period and rapid dye uptake phase so that a dyeing results which is sufficiently visually level to be useful for the intended purpose. Typically, a visually level fabric has shade variations across the fabric which are less than about 5%. Thus, during a process in which there are a number of repetitive cycles as in the preferred form of the invention in a beck dyer where the fabric rope cycles numerous times, the dye transport to the fabric may not be uniform in any one machine cycle. However, the additive effect of dye transport during all of the cycles is such that a level dyeing results since dye transport "on the average" is essentially uniform. As will become more

REPLACEMENT SHEET

19 FEB 1997

apparent hereinafter, it may be desirable to increase the turnover rate, limit the dye addition rate, or both to decrease the percentage of total dye added per cycle and thereby increase uniformity due to the greater averaging effect obtained. To facilitate control over the process and to enable a process to be repeated, it is preferable for stirring to be performed constantly and at a constant rate.

In accordance with the invention, the dye addition rate is adjusted to be the primary control over the rate of dye uptake by the article at least while the solvent and the article are at or above the dyeing transition temperature. The type of adjustment of the dye addition rate necessary to accomplish this may be better understood by reference to Equation I which takes into account factors impacting the dyeing process:

$$L = \frac{D_s}{K \cdot D_f} \times \frac{r}{\delta} \quad I$$

In Equation I, D_s is the diffusion coefficient of the dye in solution, D_f is the diffusion coefficient of the dye in the fiber, K is the equilibrium distribution coefficient for the dye-fiber system, r is the radius of the fiber, and δ is thickness of the diffusional boundary layer. In a process in accordance with the invention, it has been discovered that adjusting the rate of dye addition into the bath and coordinating the rate with other conditions in the bath so that the rate of dye addition is the primary control over the rate of dye uptake provides low values for L in Equation I. It has further been discovered that the maximum benefits of the invention result when L is very low, preferably approaching zero.

To cause the rate of dye addition to be the primary control over the rate of dye uptake and thereby provide low L values, the rate of dye addition is limited so that the fibrous article, which is readily capable of

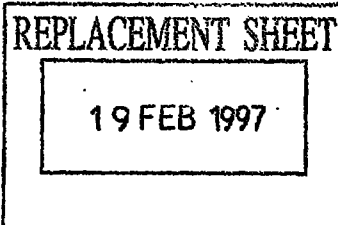
REPLACEMENT SHEET

19 FEB 1997

accepting dye since it is above the dyeing transition temperature, is capable of accepting more dye than is supplied to it. Under these conditions, the concentration of dye in the bath is very much lower than in a conventional process and the influence of the diffusion coefficient in the fiber, D_f , is therefore substantially less significant than in a conventional process. Also, the value for $D_s/(K \cdot D_f)$ will be smaller than in a conventional process and will lead to lower L values, primarily because the value for K will increase as the concentration of dye in the dye bath decreases. This effect is particularly pronounced in the preferred form of the invention where dyes are used and/or conditions established so that the dyes transfer less than about 10%.

In such cases, the value for K is very high and is further increased by the limited concentration of dye in the bath.

Preferably, the dye addition rate is adjusted so that the concentration of dye in the solvent at the location of lowest concentration in the dyer is not greater than about 100 times the final equilibrium concentration for any substantial period of time while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. In a process in accordance with the invention in which the dye is added to the bath before the dyeing transition temperature is reached, a high concentration of dye may temporarily be present in the bath while the bath is at or above the dyeing transition temperature. This time period with high concentration should not be a substantial period of time, i.e., should not be greater than about 10% of the time when the bath is at or above the dyeing transition temperature. For the maximum benefits to be obtained when conditions are used or dyes are selected so that the dyes transfer less than about 10%, it is preferred for the concentration to not be greater than 100 times the final equilibrium concentration for any period of time while the bath is at or above the dyeing transition temperature. Most preferably, the dye addition rate is adjusted so that

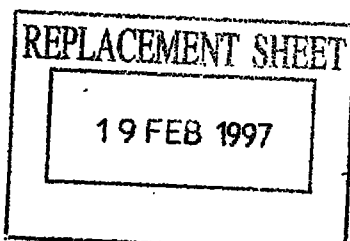


the concentration does not exceed about 50 times the final equilibrium concentration.

The "final equilibrium concentration" is the concentration of dye in the dyebath for a particular dye on the article under the process conditions at which there is essentially no further increase in the depth of dyeing without the addition of new dye. The final equilibrium concentration can be determined with reasonable certainty in the process itself by extrapolation from the concentration measured in the dye bath at the end of the dyeing process. Usually, when the dyeing process is complete in a commercial dyeing, the dye will have been sufficiently exhausted (and will have a uniform concentration in the bath) so that the final concentration before the bath is dropped can be assigned as the final equilibrium concentration. During the dyeing process, the location of lowest concentration in the dyer is usually just ahead of where dye is introduced into the bath. For example, in a process where the solvent is circulated using a pump and the dye is added ahead of the pump, the concentration of the dye in the solvent just ahead of where the dye is added will be the lowest concentration.

In contrast, in a conventional process for dyeing wool, the dye in the bath is initially on the order of 300-500 or more times the equilibrium concentration and remains in this range for a significant time until it is gradually decreased as the temperature is slowly increased to cause the dyeing to progress. If concentrations were to equal the concentrations used in conventional dyeings for a substantial period of time while the fiber contained little dye and was well above the dyeing transition temperature, a visually un-level dyeing likely would result, particularly when conditions are used or dyes are selected so that the dyes transfer less than about 10%.

To more fully realize the decrease in dye cycle times which are achievable in accordance with the present invention, the rate of dye addition is also preferably adjusted so that the concentration of dye in the solvent,

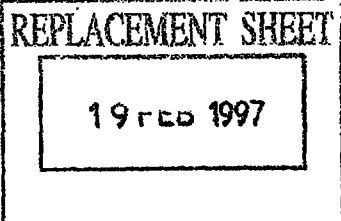


as measured at the location of lowest concentration in the bath, is at least about 2.5 times the final equilibrium concentration for a sustained period of time while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. Preferably, the sustained period of time comprises at least about 10% of the time while the solvent and the article are at a temperature at least equal to the dyeing transition temperature. Preferably, the concentration in the bath at the location of lowest concentration will be at least about 3.5 times the equilibrium concentration.

In commercial processes employing a number of repetitive machine cycles, e.g., turnovers of the fabric in a beck dyer or circulation of the bath in a package dyer, it is preferable to adjust the rate of dye addition so that an amount of dye between about 0.5% and about 7% of the total dye is added in a machine cycle to achieve, on the average, essentially uniform dye transport and a visually level dyeing in accordance with the invention. Most preferably, an amount of dye between about 0.5% and about 3% is added during a machine cycle. Using laboratory dyeing equipment, percentages of total dye per cycle are typically lower since laboratory equipment usually has a high turnover rate which would not be practical for use in large commercial dyeing equipment although excellent results are obtained.

Rates of dye addition based on the fabric weight in commercial beck dyers are usually on the order of about 0.0005 to 0.5% dye/minute. The rates at the lower end of the range are useful for low percent dye-on-fiber dyeings with extremely high affinity dyes to provide a sufficient number of machine cycles for adequate averaging to provide essentially uniform dye transport.

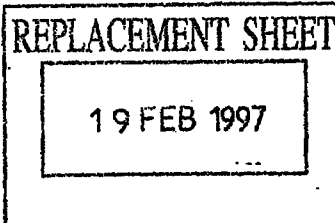
Using the preferred process of the invention in which conditions are used so that the dyes transfer less than 10% in the same equipment used for conventional wool dyeings, articles containing wool can be produced with a higher relative dye strength for the same relative dye



content, i.e., to have a higher relative dye yield, than can be obtained using conventional processes. Depending on the type of dye being used, the temperature and pH conditions in the dyebath can be used to adjust the relative dye yields obtained for a process of the invention in the same type of equipment under the same conditions. For example, with most anionic dyes, decreasing the pH will provide increases in relative dye yields. For dyes which level under conventional conditions, it may be desirable to employ lower temperatures which has the primary effect of decreasing transfer. With increased temperatures above the dye transition temperature, relative dye yields provided by many structure sensitive dyes may increase. However, in general, conditions which produce the maximum benefits in terms of dye yield with structure sensitive dyes may make it more difficult to obtain a visually level dyeing. Accordingly, it may be necessary to select conditions which provide a compromise between relative dye yield increases and still provide a level dyeing without extraordinary care.

The preferred process of the invention using dyes under conditions such that the transfer is less than 10% is capable of minimizing the sensitivity to structural differences in the fibers which can lead to non-uniform dyeing. Provided that the transport of the dye to the article is, on the average, essentially uniform, a more visually level dyeing can be achieved than is normally achieved using a conventional process since individual fibers are dyed more uniformly in a process in accordance with the invention.

It is also possible to adjust the results of the invention by including dyeing auxiliaries in the solvent in the dye bath or including them in the dye concentrate. In general, auxiliaries which decrease the strike rate of the dye will decrease the relative dye yield obtained and the dyeing will be more like a conventional dyeing. In addition, where the dye is added into the bath before the



bath has reached its dyeing transition temperature, the dye which is absorbed by the fiber before the dyeing transition temperature is reached will impart some conventional dyeing characteristics to the fiber in the article.

For setting up a commercial process in accordance with the invention, it is advantageous for the process to be run first in laboratory scale equipment corresponding generally to the chosen process conditions. In the laboratory scale process, a dye addition rate can thereby be determined in advance or a rate based on past experience for the same or similar dyeings can be confirmed. Due to smaller ratios of the weight of the bath to the weight of the goods and particularly the lower turnover rates in larger scale dyers compared to typical laboratory dyers, the dye addition rate or conditions used may have to be further modified for successful larger scale dyeings.

In the preferred form of the invention, it is usually only necessary to carefully control the process during the rapid dye uptake phase and, at most other times during the process, temperature and other bath conditions need not be as carefully controlled. For example, elevating the bath to the desired temperature can be done quickly and pH adjustment prior to dye addition can be done expeditiously and without the degree of care required in the conventional process for dyeing wool. This is particularly advantageous since, with only one critical stage and when constant temperature and pH are employed, the procedure will be easily reproducible and it will be possible to efficiently make repetitive dyeings of the same fabric. Moreover, in the event that it is discovered early in a dyeing process that the conditions in the bath are not as desired, the dye addition can be stopped and the desired conditions established before the dyeing is resumed.

After the dyeing is complete, the dyeing bath is cooled, typically to below about 175°F (79.4°C) and

REPLACEMENT SHEET

19 FEB 1997

dropped. The article can be rinsed, dried and subsequently used in a conventional manner.

It is believed that improvements in dye yield are due to the distribution of dye in the dyed articles. It is also believed that the wool fiber adjacent to the outside surfaces yarns contain more dye than filaments in the interior of the yarn. In addition, it is believed that the wool fibers are asymmetrically ring-dyed, i.e., the fibers are dyed with more dye being present adjacent to the surface of the fibers than in the interior but the ring-dyeing of at least some of the fibers is asymmetric, i.e., more dye being present on one side or the other. It is also believed that fabrics dyed by the process have more dye on yarns adjacent to the surfaces of the fabric than in the interior of the fabric which is different from the more uniform distribution obtained using conventional processes.

While the dye may be non-uniformly distributed in the fabric, fabrics made using the invention can be visually level and are highly uniform. Although the invention is applicable to other types of fabrics such as non-wovens and tufted fabrics used for carpeting, preferred fabrics in accordance with the invention are selected from the class consisting of knitted and woven fabrics. In addition, it is preferable for the fabric to be dyed with at least one structure sensitive anionic dye.

TEST METHODS

The Dye Transition Temperature is determined for a fiber/dye combination as follows:

A sample of the article is prescoured in a bath containing 800 g water/g of sample with 0.5 g/l of tetrasodiumpyrophosphate and 0.5 g/l of MERPOL HCS® (a liquid non-ionic detergent sold by E.I. du Pont de Nemours & Company). The bath temperature is raised at a rate of about 3°C/min. until the bath temperature is 60°C. The temperature is held for 15 minutes at 60°C, then the fiber is rinsed. (Note that the prescour temperature must not exceed the dye transition temperature of the fiber. If

REPLACEMENT SHEET

19 FEB 1997

the dye transition temperature appears to be close to the prescour temperature, the procedure should be repeated at a lower prescour temperature.) The bath (without the article) with a similar quantity of water is adjusted to 30°C and 1% (based on the weight of the article) of the dye to be used and 5 g/l of monobasic sodium phosphate are added. (If more than one dye is to be used in the dyeing process, the dye believed to have the highest Dye Transition Temperature should be used to determine Dye Transition Temperature. Usually, this dye will also be the most structure sensitive.) The pH is adjusted to 5.0 using monobasic sodium phosphate and acetic acid. The article is added and the bath temperature is increased to 95°C at a rate of 3°C/min.

With every 5°C rise in bath temperature a dye liquor sample of ~25 ml is taken from the dye bath. The samples are cooled to room temperature and the absorbance of each sample at a wavelength known to be useful for monitoring the dye is measured on a spectrophotometer such as a Perkin-Elmer C552-000 UV-visible spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT 06856) using a water reference.

The % dye exhaust is calculated and plotted with respect to dyebath temperature. The temperature at 15% exhaust is the dye transition temperature.

% Transfer can be determined using the AATCC Test Method 159-1989 (AATCC Technical Manual/1991, p. 285-286) except with the mock dyebath being at the pH and temperature of the actual process under consideration and a 30 minute time period are used. Percent transfer is calculated in this method by measuring the relative dye strength of the original dyed sample before (control, 100% relative dye strength) and after the transfer procedure. The difference is the % transfer.

Relative Dye Strength is a relative measure of the strength of dye in a fabric determined photometrically for a series of fabrics dyed with the same dye with the sample dyed by the comparative or control procedure being

REPLACEMENT SHEET

19 FEB 1997

arbitrarily designated as having 100% relative dye strength.

Relative dye strength for a fabric sample is measured at the wavelength of minimum reflectance using a
5 MACBETH COLOR EYE 1500 PLUS SYSTEM Spectrophotometer, sold by Macbeth Division of Kollmorgen Instrument Corp. of Newburg, N.Y. A scan from 750 to 350 nm can be performed to determine the wavelength of minimum reflectance for the dye. All subsequent samples in a series with the same dye
10 are then measured at the same wavelength. For example, the wavelength of minimum reflectance for C.I. Acid Blue 122 is 640 nm.

The sample produced by the comparative or control procedure is designated the control and assigned a
15 relative dye strength of 100%. The remaining samples are then scaled in relative dye strength by the following:

$$\text{Rel. Dye Strength (\%)} = \frac{\text{K/S sample}}{\text{K/S control}} \times 100,$$

20 and

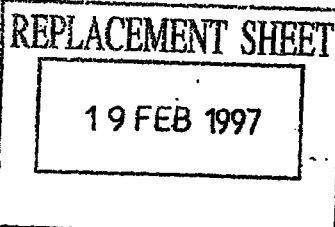
$$K/S = \frac{(1 - R)^2}{2R}$$

where: R = reflectance.

Relative Dye Content is a relative measure of dye
25 content determined photometrically for a series of fabrics dyed with the same dye with the sample dyed by the comparative or control procedure being arbitrarily designated as having a 100% relative dye content.

The relative dye content is determined in the
30 following way. First, a sample of the article is cut into small segments and about 0.1 gram is weighed to +0.1 mg accuracy. Typically, a test series of samples of dyed articles is weighed to each have very nearly the same weights. The samples are dissolved in 30 ml of formic
35 acid at ambient temperature. After sample dissolution is complete, centrifugation for 20 minutes is effective for removing titanium dioxide delusterant when present.

A Perkin-Elmer C552-000 UV-visible spectrophotometer (Perkin-Elmer Instruments, Norwalk, CT



06856) is used to record the absorbance of the samples. A scan from 750 to 350 nm is performed and the largest peaks are chosen as analytical wavelengths for the dye tested. All subsequent samples in a series with the same dye are then measured at these wavelengths. Typically, sample sizes around 0.1 gram give absorbance readings in the range of 0.3 AU to 0.8 AU for the dye levels obtained.

A corrected absorbance is calculated for each wavelength measured on every sample in the series. The corrected absorbance is:

$$A \text{ (corrected)} = (S \times 0.1 \text{ gram}) / W$$

where: S = absorbance at a given wavelength; and
W = weight of sample in grams

The sample dyed by the comparative or control procedure is assigned a relative dye content of 100%. The remaining samples are then scaled in relative dye content by the following:

$$\text{Rel. Dye Content (\%)} = (A_s \times 100) / A_1$$

where: A_s = average absorbance of sample; and
 A_1 = average absorbance of the control sample.

This calculation is performed for every analytical wavelength chosen in a given dye series.

Relative Dye Yield is defined as the ratio of the Relative Dye Strength to the Relative Dye Content:

$$\text{Rel. Dye Yield} = \frac{\text{Relative Dye Strength}}{\text{Relative Dye Content}}$$

The invention is illustrated in the following example which is not intended to be limiting. Percentages are by weight unless otherwise indicated.

EXAMPLE 1

Part A

30 grams of a scoured fabric, woven from 100% wool (35 cm x 35 cm), is introduced into a Werner-Mathis Laboratory Dyeing Apparatus, Type JF, sold by Werner-Mathis U.S.A., of Concord, NC. The fabric is placed in

REPLACEMENT SHEET

19 FEB 1997

the perforated basket and the see-through door is closed. The dyeing bath is then set with 1800 ml. of distilled water at a 60:1 liquor ratio (weight of bath to weight of fabric) at 80° (26.7°C) and then pH is adjusted to 5.0
5 with monosodium phosphate (MSP) and phosphoric acid. 0.15 g (0.5% on weight of sample) of ALBEGAL-B®, a wool leveling agent from Ciba-Geigy Corp., is added to the bath.

The basket device is set into motion by adjusting
10 the rheostat driven motor so that the basket rotates in a clockwise motion for about six seconds; then stops for about five seconds; then reverses to a counter-clockwise motion for six seconds. This sequence of clockwise, pause, and counter-clockwise movements continues
15 automatically throughout the dyeing procedure. This provides adequate movement of the bath liquor and the fabric sample to provide uniform application of dye to the substrate.

The temperature of the dyeing bath is then raised
20 rapidly by 5°F/min. (2.8°/min.) or greater to the dyeing temperature. In this example, the dyeing temperature is held nearly constant at about 200°F (93.3°C) during the dye addition period as the dye is added as described below. (The rapid dye uptake phase of this example begins
25 with the addition of dye during the dye uptake phase, i.e., 100% of the dye is added during the rapid dye uptake phase.)

Separately, 0.6 g of C.I. Acid Blue 336, a pre-metallized acid dye, is dissolved in 200 ml of distilled
30 water to form a dye concentrate. The amount of dye used is calculated to provide 2% dye-on-fiber assuming complete exhaustion of the dye. Using a precision (approx. 1% accuracy) MANOSTAT COMPULAB® liquid metering pump sold by Manostat Corporation of New York, NY, the separately
35 prepared dye solution is metered under the surface of the dyeing bath away from the moving fabric at the rate of 5 ml/minute which is equivalent to 0.05% dye/minute based on the weight of fabric. Under these conditions this dye

REPLACEMENT SHEET

19 FEB 1997

transfers less than 10% and there is never any visible build-up of dye in the dyeing bath during the period of dye addition which is complete in 40 minutes. The dyeing bath is then cooled at 5°F/min. (2.8°C/min.) to 170°F (76.6°C), then the fabric is overflow rinsed, removed from the dyeing machine, then air dried.

The result obtained is a level blue dyeing on the woven wool fabric and a visually colorless dyeing bath.

Part B (Comparative)

30 grams of the fabric described above is introduced into the perforated basket in the JF machine as in the previous example. The dyeing bath is again set as in the previous example. Separately, 0.6 grams of C.I. Acid Blue 336, a pre-metallized acid dye, are dissolved in 200 ml of distilled water. All of the dye solution is then added to the dyeing bath in the conventional manner at 80°F (26.7°C). The dyeing bath is raised at 1°F (0.6°C) per minute to 205°F (96.1°C) and held for 45 minutes. The bath is cooled and the fabric rinsed and removed as in the previous example. The result obtained is a level blue dyeing on the woven wool fabric and a visually colorless dye bath.

Assuming the same relative dye content for the fabric dyed by the invention and the comparative example, reflectance measurements show that the relative dye yield is increased 15% in the sample dyed by the process invention compared to the conventional process of the comparative example.

EXAMPLE 2

In this example, 180 grams of a scoured woven wool fabric (30 cm X 90 cm) is dyed in an 8 inch (20 cm) Saucier Beck-dyeing Machine, manufactured by Saucier Stainless Steel Products, Minneapolis, MN. The fabric is placed over the winch of this beck, then sewn at the ends to form an endless "rope." The dyeing bath is then set with 25 liters of distilled water at 139:1 liquor ratio (weight of bath to weight of fabric) at 80°F (26.7°C) and then the pH is adjusted to 5.0 with monosodium phosphate (MSP) and

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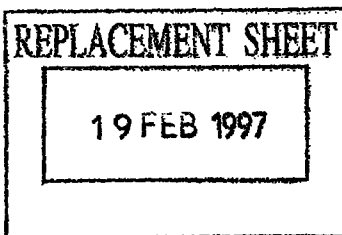
19 FEB 1997

phosphoric acid. 0.9 g (0.5% on weight of sample) of ALBEGAL-B®, a wool leveling agent from Ciba-Geigy Corp., is added to the bath. The fabric is set in motion by the turning action of the winch-reel. The temperature of the dyeing bath is then raised rapidly by 5°F/min. (2.8°C/min.) to the dyeing temperature. In this example, the dyeing temperature is held nearly constant at about 200°F (93.3°C) during the dye addition period as described below.

Separately 1.8 g of C. I. Acid Blue 336, a pre-metallized acid dye, is dissolved in 1000 ml of distilled water to provide ~1% dye-on-fiber assuming complete exhaustion of the dye. Using a precision (~1% accuracy) MANOSTAT COMPULAB liquid metering pump sold by Manostat Corporation of New York, NY, the separately prepared dye solution is metered under the surface of the dyeing bath away from the moving fabric at the rate of 25 ml/minute which is equivalent to 0.025% dye/minute based on the weight of the fabric. Under these conditions the dye transfers less than 10% and there is never any visible build-up of dye in the dyeing bath during the dye addition period which is complete in 40 minutes. Concentrations determined spectrophotometrically show that the concentration of dye in the bath at the after the dye addition has been in progress for 5 minutes ranges between about 5 and about 20 times the final equilibrium concentration which is reached after the dye addition is complete.

The dyeing bath is then cooled at 5°F/min. (2.8°C/min.) to 170°F (76.7°C), then the fabric is overflow rinsed, removed from the dyeing machine, then air dried.

The result obtained is a level blue dyeing on the wool fabric and a visually colorless dyeing bath.



**CLAIMS:**

1. A process for dyeing a fibrous article containing wool with at least one anionic dye comprising:
immersing said article in a dyeing bath of a
5 liquid solvent for said anionic dye;
heating said liquid solvent and said article in said dyeing bath to a temperature at least equal to the dyeing transition temperature of said wool with said dye;
adding said anionic dye to said dyeing bath as a
10 miscible liquid concentrate at a dye addition rate during a dye addition period, at least a portion of said dye being added while said solvent and said article are at a temperature at least equal to said dyeing transition temperature; and
15 stirring said bath during said dye addition period and while said solvent and said article are at a temperature at least equal to said dyeing transition temperature to mix said dye concentrate with said solvent in said bath to form a dilute dye solution and to provide
20 a flow of said dilute dye solution relative to said article to cause said dye to be transported to said article, said stirring further providing, on the average, essentially uniform dye transport of said anionic dye to said article;
25 said dye addition rate being adjusted to be the primary control over the rate of uptake of said dye by said article at least while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.
- 30 2. The process of claim 1 further comprising maintaining conditions in said liquid solvent so that said anionic dye transfers less than about 10%.
- 35 3. The process of claim 1 wherein said process is performed in a dyeing machine in which said stirring provides repetitive machine cycles and said dye addition rate is adjusted so that an amount of dye between about 0.5% and about 7% of the total dye is added to said dyeing bath during a machine cycle.

This Sheet Has Been Replaced



REPLACEMENT SHEET

19 FEB 1997



4. The process of claim 3 wherein said dye addition rate is adjusted so that an amount of dye between about 0.5% and 3% is added during a machine cycle.

5. The process of claim 1 wherein said dye is added continuously and at a constant rate during said dye addition period.

6. The process of claim 1 wherein at least about 33% of said dye is added while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

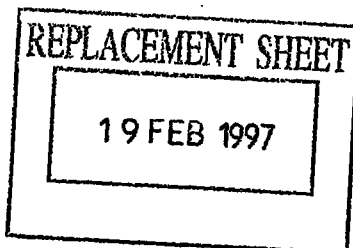
7. The process of claim 1 wherein at least about 50% of said dye is added while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

8. The process of claim 1 wherein said dye addition rate is adjusted so that the concentration of dye as measured at the location of lowest concentration in said bath is not greater than about 100 times the final equilibrium concentration for any substantial period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

9. The process of claim 8 wherein said concentration of dye is not greater than about 50 times the final equilibrium concentration for any substantial period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

10. The process of claim 1 wherein said dye addition rate is adjusted so that the concentration of dye in said solvent as measured at the location of lowest concentration in said bath is at least about 2.5 times the final equilibrium concentration for a sustained period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

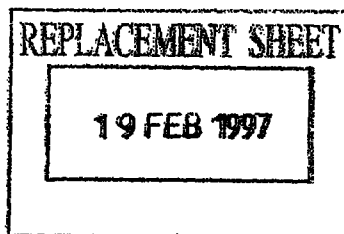
11. The process of claim 10 wherein said concentration of dye in said solvent is at least about 3.5





times the final equilibrium concentration for a sustained period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

- 5 12. The process of claim 10 wherein said sustained period of time comprises at least about 10% of the time when said solvent and said article are at a temperature at least equal to said dyeing transition temperature.
- 10 13. The process of claim 1 wherein said liquid solvent is an aqueous liquid.
14. The process of claim 1 wherein said anionic dye is a structure sensitive anionic dye.
15. The process of claim 1 wherein at least some
15 of said stirring is provided by a pump which circulates solvent in said bath.
16. The process of claim 15 wherein said liquid dye concentrate is added into said solvent ahead of said pump to form said dilute dye solution.
- 20 17. The process of claim 16 wherein said liquid dye concentrate is added into said solvent by a metering pump.
18. An article containing wool dyed by the process of claim 2.
- 25 19. An article containing wool dyed by the process of claim 14.

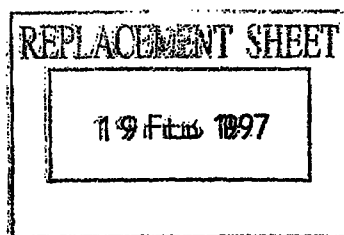


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ABSTRACT
WOOL DYEING UTILIZING CONTROLLED DYE ADDITION

A process for the dyeing of a fibrous article containing wool with an anionic dye and products produced thereby. The process includes immersing the article in a dyeing bath of a liquid solvent for the anionic dye. The liquid solvent and the article are heated to a temperature at least equal to the dyeing transition temperature. At least a portion of the dye is added as a miscible liquid concentrate while the solvent and the article are up to temperature. Stirring of the bath during the dye addition period and while the solvent and article are up to temperature is done to mix the dye concentrate with the solvent to form a dilute dye solution and to provide a flow of the dilute dye solution relative to the article to cause, on the average, essentially uniform dye transport of the anionic dye to the article. The dye addition rate is adjusted so that the dye addition rate is the primary control over the rate of dye uptake by the article.



Large molecule acid and pre-metallized dyes are often referred to as "structure sensitive" dyes since non-uniform dyeing can result from minor variations in the fiber physical structure. While dye-levelling and/or
 5 retarding agents can be added to the dye bath to improve dyeing uniformity with structure sensitive dyes, such agents sometimes provide only limited increases in dye uniformity and usually have disadvantages including increased initial expense and higher cost to treat the
 10 spent dyeing bath. In addition, because of their retarding effect, such chemical agents can sometimes increase dyeing cycles or make it difficult to obtain deep colors or dark shades. Also, dye yields from anionic dyes, i.e., the strength of color produced from a given
 15 quantity of dye on the fiber, are sometimes not as high as desired.

SUMMARY OF THE INVENTION

The invention provides an improved process for the dyeing of a fibrous article containing wool with at least
 20 one anionic dye. A process in accordance with the invention includes the steps as delineated in claim 1, with preferred features as delineated in the dependent claims.

In accordance with a preferred form of the invention, the conditions in the liquid solvent are maintained so that the anionic dye transfers less than about 10%.

In accordance with another preferred form of the invention, the process is performed in a dyeing machine in which the stirring provides a number of repetitive machine cycles and the dye addition rate is adjusted so that an amount of dye between about 0.5% and about 7% of the total dye is added to the dyeing bath during a machine cycle, most preferably between about 0.5% and about 3%.

In accordance with another preferred form of the invention, at least about 33% of the dye is added to the bath while said solvent and said article are at a temperature at least equal to the dyeing transition temperature, most preferably at least about 50% of the dye
 is added at this time.

REPLACEMENT SHEET

21 JAN 1999

REPLACEMENT SHEETS SG

☒ Description : paged 1. to paged 3.
☒ Claim(s) : paged 4. to paged 5.
☐ Drawing(s) : paged 6. to paged 6.
☐ Abstract : paged 7. to paged 7.

DATE OF RECEIPT 21/1/99

In accordance with another preferred form of the invention, the dye addition rate is adjusted so that the concentration of dye at location of lowest concentration in the bath is not greater than about 100 times, most preferably not greater than 50 times, the final equilibrium concentration for any substantial period of time while the solvent and the article are at a temperature at least equal to the dyeing transition temperature.

10 In accordance with another preferred form of the invention, the rate of dye addition is adjusted so that the concentration of dye in the solvent as measured at the point of lowest concentration in the bath is at least about 2.5 times, preferably at least about 3.5 times, the
15 final equilibrium concentration for a sustained period of time while the solvent and the article are at a

REPLACEMENT SHEET

21 JAN 1999

21 JAN 1999



26

CLAIMS:

1. A process for dyeing a fibrous article containing wool with at least one anionic dye comprising:
immersing said article in a dyeing bath of a
5 liquid solvent for said anionic dye;
heating said liquid solvent and said article in said dyeing bath to a temperature at least equal to the dyeing transition temperature of said wool with said dye which is the temperature during dyeing with a particular dye
10 at which the wool opens up sufficiently to allow a marked increase in the rate of dye uptake;
adding said anionic dye to said dyeing bath as a miscible liquid concentrate at a dye addition rate during a dye addition period, at least a portion of said dye
15 being added while said solvent and said article are at a temperature at least equal to said dyeing transition temperature; and
stirring said bath during said dye addition period and while said solvent and said article are at a
20 temperature at least equal to said dyeing transition temperature to mix said dye concentrate with said solvent in said bath to form a dilute dye solution and to provide a flow of said dilute dye solution relative to said article;
25 transporting said dye to said article, said stirring and transporting further providing shade variations across said article when visually level which are less than 5%;
said dye addition rate being adjusted to be the primary control over the rate of uptake of said dye by
30 said article at least while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.
2. The process of claim 1 further comprising maintaining conditions in said liquid solvent so that said
35 anionic dye transfers less than about 10%.
3. The process of claim 1 wherein said process is performed in a dyeing machine in which said stirring provides repetitive machine cycles and said dye addition rate is adjusted so that an amount of dye between about 0.5% and about 7% of the total dye is added to said dyeing bath during a machine cycle.



times the final equilibrium concentration for a sustained period of time while said solvent and said article are at a temperature at least equal to said dyeing transition temperature.

- 5 12. The process of claim 10 wherein said sustained period of time comprises at least about 10% of the time when said solvent and said article are at a temperature at least equal to said dyeing transition temperature.
- 10 13. The process of claim 1 wherein said liquid solvent is an aqueous liquid.
14. The process of claim 1 wherein said anionic dye is a structure sensitive anionic dye.
- 15 15. The process of claim 1 wherein at least some of said stirring is provided by a pump which circulates solvent in said bath.
16. The process of claim 15 wherein said liquid dye concentrate is added into said solvent ahead of said pump to form said dilute dye solution.
- 20 17. The process of claim 16 wherein said liquid dye concentrate is added into said solvent by a metering pump.

