United States Patent Office 3,738,803 Patented June 12, 1973

3,738,803

DYEING OF TEXTILE FIBERS IN A SOLVENT MEDIUM

Remy Blanc, Lyon, Willy Hess, Limas, and Georges Ramier, Villefranche-sur-Saone, France, assignors to S.T.X., Groupement d'Interet Economique, Paris, France

No Drawing. Continuation-in-part of application Ser. No. 33,094, Apr. 29, 1970. This application Dec. 12, 1971, Ser. No. 210,571

Claims priority, application France, Apr. 30, 1969, 6912355; Nov. 26, 1969, 6940684; Mar. 20, 1970, 7011537; Feb. 2, 1971, 7105279

Int. Cl. D06p 1/68

U.S. Cl. 8—93 22 Claims

ABSTRACT OF THE DISCLOSURE

Treatment of textile fibers such as dyeing, sizing, mothproofing, etc. is accomplished by the "exhaustion" method using a bath of a solvent for the treating agent and a diluent in which the treating agent is relatively insoluble, at an elevated temperature, the solvent being progressively removed from the bath in the liquid or vapor phase during the treating operation resulting in a homogeneous and resistant dyeing or other treatment of the textile fibers and a neaarly complete exhaustion of the treating agent.

FIELD OF THE INVENTION

This application is a continuation-in-part application of copending application Ser. No. 33,094 filed Apr. 29, 1970, now abandoned.

The present invention relates to a novel treating process, more particularly a dyeing process, for textile fibers in an anhydrous medium by the "exhaustion" method.

BACKGROUND OF THE INVENTION

Until recently, most dyeing techniques have required the use of aqueous media. The use of aqueous systems, however, have a number of serious disadvantages, foremost of which are the economic consequences of dyestuff lossage and the pollution of streams resulting from discarding the dyestuff laden water after dyeing.

It has been previously proposed to dye textile materials in organic solvents or mixtures of solvents, in order to eliminate the numerous problems caused by such utilization, traditional until recently, of great quantities of water. However, such known procedures involve the use of large classes of chemical compounds—and especially organic solvents—which cannot be satisfactorily used either because of their incompatibility with the required dyeing adjuvants or coloring agents, or because of the hazards they represent (fire, explosion, intoxication) or because solvent recovery conditions are not adequate and, thus, lead to waste and a higher cost compared with classical dyeing in an aqueous bath.

Moreover, it is known that dyeing "by exhaustion" has been suggested in operations in anhydrous baths. However, a good fixing and distribution of coloring agents on the material at the end of the dyeing operation has heretofore not been obtained and these known processes are costly because of the only partial exhaustion of the baths.

SUMMARY

In accordance with the present invention there has now been developed a process for treating textiles using a combination of (1) a solvent for the dye or other treating agent and (2) a non-solvent diluent preferably having a higher boiling point than the solvent, and in which such

combination is especially chosen for its low cost and the safety of use conditions. This new process provides easier solvent and diluent recovery and the homogeneous dyeing and/or other treatment of textiles.

In its most general form, the technique according to the present invention comprises using, as a dyeing or other treatment medium in an "exhaustion" process, a bath containing a minor proportion of at least one organic solvent in which the coloring and/or other agents are soluble, and a major proportion of a diluent in which the agents are only slightly soluble or are insoluble, and continuously removing the organic solvent from the bath during the dyeing or the treating operation. If desired, the dyed or otherwise treated textile material may be rinsed with the diluent.

Among the advantages which ensue from the present invention are reduced cost of dyeing due to saving of dyestuff from the nearly 100% complete exhaustion of the bath with little or no loss of dye; better and deeper dyeing; and the elimination of water pollution along with the recovery of solvent and diluent.

For a better understanding of the invention, a more detailed description by way of possible embodiments will now be described, it being understood that such description is exemplary and not limitative.

DETAILED DESCRIPTION

(A) The material to be dyed

The process according to the invention may be applied to any form of continuous or discontinuous fibers or to fibers disposed in flocks, ribbons, fleeces, cards, etc. It may also be used on woven, knitted or non-woven fabrics, provided that such fabrics be rolled on a perforated beam in order to constitute a kind of reel, dyed by means of a circulation pump. According to a variant, such fabrics may be disposed in bundles either in a circulation machine or in a rotary perforated drum.

Dyeing may also be achieved according to the tank method provided the tanks are tight with regard to the solvents and diluents used and which tanks are provided with feeding devices so that solvent and diluent loss by evaporation when introducing fabrics to be dyed is reduced to a minimum; however, for best results the evolution of bubbles should be avoided.

The process of the present invention can be applied to natural, artificial and synthetic textile materials of all kinds, such as those based on cellulose including regenerated cellulose, and cellulose esters; polyesters including polyester basic dyeables; acrylic polymers and copolymers; polyamides, such as nylon 6, nylon 6—6 and nylon 11, and cyclic polyamides; polyvinyl alcohols; wool; fibers "animalized" by grafting or other processes; and more generally, all the fibers capable of being dyed by coloring agents in any form, such as those known as "acids"; "metal-bearing acids"; basic and plasto-soluble coloring agents, and the like.

(B) The bath

The solvents used may be chosen from among the usual organic compounds capable of dissolving coloring and/or other agents at room temperature, as well as fatty and waxy substances, especially the oiling agents for the fibers although it is preferred that high boiling point polar solvents not be used. The diluents are preferably chosen from among the non-toxic and fire-proof organic compounds, the boiling points of which are higher than that of the solvents used.

According to one form of the invention, there is advantageously used a bath consisting essentially of a mixture of several solvents, along with the diluent. It has, for example, been found that excellent dyeing has resulted

using a mixture of methanol and isopropanol as the solvents and perchloroethylene as the diluent.

According to another form of the process of the invention there is used as solvent at least one compound capable of forming an azeotrope with the diluent. Thus, for example, there may be used a bath comprising an halogenated aliphatic alcohol capable of forming an azeotrope with perchloroethylene. Among such halogenated alcohols are 2-chloro-ethanol, 2-bromo-ethanol, 1-chloro-propanol and 2-chloro-propanol.

The solvent and diluent used in the process can be either polar or non-polar so long as they are separable. It is also possible to use water as a diluent instead of an organic component. It is also possible to use any combination of a solvent and diluent capable of leading to the formation of an azeotrope whose boiling point is preferably below that of the diluent, thus allowing for its separation by means of vaporization.

Among the combinations of dyeing bath components which could be used are

methanol/isopropanol/perchloroethylene;
2-chloroethanol/perchloroethylene;
methanol/perchloroethylene;
methanol/monochlorobenzene;
trichlorotrifluoromethane/trialkylamine perfluoride;
methanol/water;
acetonitrile/water;
methanol/trichloroethylene; etc.

The preferred mixture is methanol/perchloroethylene which gives excellent results and provides economic advantages over other mixtures.

It has further been established that the present process is suitable not only for dyeing by exhaustion, but also for sizing or conditioning treatments of textile fibers and fabrics such as for example optical bluing, treatment with insecticides, etc. In this case, the bath which is used is composed of a solvent for the sizing or conditioning agent and a diluent in which this agent is insoluble or slightly soluble. This treatment may be performed in conjunction with the dyeing or separate therefrom.

The respective proportions of solvent and diluent are not critical and may be selected within broad limits. Solvent proportions may vary advantageously between 20 and 375 parts by volume for 1000 parts of dyeing bath; when a mixture of polar solvents, especially methanol and isopropanol is used, the respective weights of these alcohols may be approximately the same.

Moreover, small quantities of acetic acid may optionally be added to the dyeing bath. Between 0 and 5 parts of acetic acid by volume of the bath may be used. When using an halogenated aliphatic alcohol, as explained hereinabove, the quantity of acetic acid used may be increased up to 10 parts per 1000 parts of bath. As a variant, acetic acid may be replaced wholly or partially by a stronger acid, such as for example, monochloracetic acid.

If the fibers to be dyed contain sufficient water to present the risk of causing the dyeing bath to separate into two liquid phases upon extraction of such water from the fibers, it might be advisable to provide a prior treatment whereby the water is removed from the material to be treated by means of a water absorbent such, as for example, hot perchloroethylene. Moreover, where needed this pre-treatment has the further advantage of simultaneously removing from the fibers impurities and other ingredients, such as oil, which are soluble in the bath.

The coloring agents used are preferably in the form called "not charged," i.e., they contain only a minimal amount of impurities resulting from their preparation and excluding all additives. Thus, in fact, coloring agents directly prepared and at a maximal concentration are used, for which it is not necessary to proceed to purification by means of extraction, or crystallization, or other processes.

The coloring agents used may be selected from among the various types of known coloring agents compatible with the textile material being treated and the solvents and diluents used. In addition to coloring agents with anionic characteristics there may be used those with a cationic nature, the plastosolubles, etc.

(C) Processing, and operating conditions

The dyeing operation may be advantageously achieved according to the following preferred procedure:

In the case of the mixture methanol/isopropanol/perchloroethylene, a pulverulent coloring agent is first dissolved in methanol at room temperature, then isopropanol is added to the solution; the mixture is introduced into perchloroethylene, and then glacial acetic acid may be added when desirable.

Where use is made of a solvent capable of forming an azeotrope with the diluent, a mixture such as that of 2-chloroethanol/perchloroethylene, for example, having the azeotropic composition of about 24.3% by weight of 2-chloroethanol and about 75.7% of perchloroethylene (boiling point 110–111° C. under 760 mm. Hg) was found to be a good solvent for most of the coloring agents. It is easy to use such a mixture as it comes, for example, from the distillation of a previous dyeing bath, in order to dissolve coloring agents, then to add further perchloroethylene in order to reach the preferred proportions and, if desired, organic acid. However, for some coloring agents, the maintenance of a small proportion of methanol, isopropanol or of their mixture, at dissolution stage, may remain necessary, along with the azeotropic composition. Alternatively, it is possible to avoid this addition and, in place thereof, add to the bath the previously mentioned maximum quantities of acetic acid or a stronger acid, this addition being made at the time of bath preparation or gradually after a determined period of dyeing.

When the dyeing bath is prepared, it is introduced in a suitable dyeing apparatus, previously packed with textile, which, except in the case when fabrics with sized warp are concerned, has been submitted to no previous desoiling.

The lengths of treatment are not critical and may be selected within broad limits, according to the nature of the fibers and of the dyes. The maximum temperatures used are a function of the boiling points of the solvents and diluents which may be used, and the textile fibers and fabrics treated.

Dyeing operation begins at room temperature, then the bath is gradually heated for about 15 to 80 minutes up to temperatures ranging from about 40° C. to about 130° C., the selected final temperature being maintained for a period of time which may vary between about 15 and 90 minutes. The dyeing may be achieved under normal pressure or in a suitable vessel under a pressure higher or lower than atmospheric pressure.

The total time is adjusted according to the degree of exhaustion of the bath, evaluated by the coloration of a sample taken from the bath. The same sampling permits adjusting of the optimal time of gradual heating by referring to samples taken systematically during test dyeings, the colorations of which are evaluated with a colorimeter.

The selection of temperatures and times depends mainly upon the boiling points of the selected solvents and diluents. When working with light aliphatic alcohols, for example methanol, together with perchlorethylene, the final temperature is about 70–110° C., the time of gradual heating is preferably between 20 and 30 minutes, and the time of temperature maintenance at maximum temperature is preferably between 10 and 60 minutes. With a bath constituted of 2-chloro-ethanol and perchloroethylene, azeotrope boiling point of 110–111° C., dyeing is achieved at about 100° C. and the time of gradual heating is extended up to 45 or even 60 minutes. Of course, the recommended temperatures may vary in some proportion with regard to pressure conditions.

An essential feature of the process, which has the advantage of greatly improving the exhaustion rate of the coloring agents, comprises the progressive removal of the solvents from the dyeing bath in a continuous manner during treatment; the solvents may be so continuously removed either in vapor or in liquid phase. As a result of this step, coloring agents, after having been uniformly distributed in the material to be dyed, are fixed all the more completely to the fibers due to the combined effects of (1) the gradual elimination of the solvent in which the dye is soluble, thereby progressively leaving an increasing quantity of dye on the fibers, and (2) the heat energy provided. Thus, at the end of the operation, the dye is in the presence only of a diluent in which it is insoluble. This fixing is favored by the fact that the dyeing temperature is not limited by the solvent boiling point and may be higher than when there is no solvent removed.

As soon as the dyeing bath, which operates under a pressure equal to, greater or lower than atmospheric, reaches at least the theoretical boiling temperature of the solvent, under normal pressure, solvent removal may be effected in a continuous manner. The solvent may be removed in vapor phase directly from the dye bath and then easily condensed by any known means and, if desired, partially or wholly recycled to the bath. When dyeing is carried out at atmospheric pressure, the bath is heated to the evaporation temperature of the solvent. The solvent vapors are passed through a condensation device and recovered. When dyeing is carried out at superatmospheric pressure or under a vacuum, the condensation device is preferably maintained at the same pressure as that of the bath.

In a preferred embodiment of the invention, however, a liquid fraction of the bath containing a mixture of solvent and diluent is continuously removed from the bath. The solvent is then separated from this mixture wholly or partially and the remaining liquid fraction is recycled in a continuous way to the dyeing bath. The solvent may be separated according to known techniques. Thus, for example, the liquid fraction taken off from the dyeing bath may be led into a flash-distillation apparatus in which the separation between the solvent and diluent takes place. When the dye bath is at superatmospheric pressure, the solvent can be quickly vaporized by expansion and recovered as heads while the diluent can be recovered at the bottom in the liquid state and then recycled to the dyeing tank.

The removal can be accomplished in the liquid phase even when the dyeing bath is at normal pressure or under vacuum provided it is kept at a temperature below its boiling point. It is evident that the operation of the flash distillation apparatus may be adapted with considerable flexibility to various conditions for the application of the dyeing process according to the invention. The vaporizer could be made to function equally well under atmospheric pressure as at pressures above or below normal. When the pressure prevailing in the dyeing container is the same as or less than that selected for the flash-distillation apparatus, the liquid removed at the outlet of this container may be reheated sufficiently so that its most volatile component can be separated in the flash-distillation apparatus. On the other hand, when the pressure of the dyeing bath is higher than that in the flash-distillation apparatus, the temperature in the dyeing container should be maintained at a sufficiently high level to permit the volatile component of the removed liquid fraction to be then separated by simple expansion. It has also been found possible to substitute any separation of known type which utilizes the differences in the physical properties of the components, such as, crystallization, azeotropic distillation (possibly by means of a third body), selective adsorption (e.g. by the use of molecular sieves), passage across semi-permeable membranes, etc.

According to the present method, the dye bath is progressively depleted of the solvent for the coloring agent, thus allowing the coloring agent—which is insoluble or but slightly soluble in the diluent—to "ascend" preferentially to the fibers in a very homogeneous way. Since the dye bath is of constant volume, the progressive removal of the solvent is compensated by a feeding of a corresponding quantity of the diluent. The extraction speed of the solvent may be made in a manner regulated at will, whatever separation techniques may be used.

The extraction rate of the solvent, whether or not it is reintroduced in part with the recovered diluent, permits regulation of the exhaustion of the bath in coloring agent, that is coloring agent ascent to the fiber to be dyed. In accordance with the invention, it has been noted that there is a proportional relation between the rate of coloring agent on the fibers and the quantity of the solvent extracted. When solvent removal is effected in vapor phase directly from the dye bath, at the beginning of the dyeing operation, the extraction rate is quite weak; then, as the temperature increases regularly according to the preselected thermal conditions, and as soon as the rate of coloring agent adsorbed on the fibers is satisfactory, solvent removal is accelerated until complete.

After completion of dyeing, a rinsing at room temperature may sometimes be necessary for black and dark colors. It is not necessary for light and clear colors in which bath exhaustion is quite total. However, when acetic acid has been used, it is better to conduct a rinsing in order to remove acetic acid odor except for very clear dyeings in which the acid quantity is very small or when acid odor is sufficiently removed during drying. For greater acid quantities two successive rinsings are achieved by adding, if necessary, a small quantity of an organic base, such as triethanolamine, piperidine, morpholine, etc. to the first rinsing bath. According to one form of the invention, rinsing or rinsings are made using the same diluent as was used in the dyeing bath.

After rinsing, the dyed textiles are dried in the usual manner.

The recovery of solvents and diluents used in the process of the invention does not present any particular problem and may be practically complete for the diluents.

(D) Specific examples

The non-limitative examples hereinafter emphasize the different possibilities of the process according to the invention. In particular, the invention may be used not only for dyeing, but also for treating fibers and fabrics, such as mothproofing, sizing, biological treatment, ignifugation, and the like. The baths, in such cases, comprise a solvent for the treating agent and a diluent in which this agent is insoluble or slightly soluble. This treatment may, or may not, be associated with the dyeing operation.

In the examples, percentages are expressed in weight and parts in volume.

EXAMPLE 1

In this example which illustrates the utilization of an azeotropic composition according to the invention, the textile fiber is polyamide 66, 3000 deniers, in the form of reels having a very tight winding, each weighing 1 kg., dyed in a pressure vessel with pump bath circulation, in a bath ratio of between ⅛ and 1/20 according to the quantities to be dyed.

Dyeing with 1% (with regard to fiber weight) of the coloring agent C.I. Acid yellow 61.

Bath composition:

Azeotrope: (24.3% by weight of 2-chloro-ethanol) – (75.7% by weight of perchloroetyhlene)	225 parts
Industrial perchloroethylene	771 parts.
Glacial acetic acid	4 parts.
Dyeing total time	1 hr. 25 min.

Temperature gradual ascent ..... 45 min.
Initial temperature ..... 19° C.
Final temperature ..... 98° C.

Vapor phase removal of the azeotrope solvent was gradually effected. At the end of the dyeing operation, the exhaustion of the bath was about 100%. Only one final perchloroethylene rinsing at 20° C. for 5 minutes.

Examples 2 and 3 relate to an application of the process to the dyeing of polymaide 6—6, 1040 deniers, for carpets, in the form of cylindrical reels, each of them weighing 750 g., and having a very tight winding; they are dyed in a bath ratio of about 1/13. Example 3 concerns wool dyeing under the same conditions. Pressure during dyeing is 3 bars.

EXAMPLE 2

Dyeing with 1% of the coloring agent Acid yellow 61 was accomplished on polyamide fibers previously treated, as explained above.

Bath composition:

Denaturated industrial methanol	parts	100
Industrial perchloroethylene	do	899
Glacial acetic acid	do	1
Initial temperature	° C	19
Final temperature	° C	100

Temperature gradual ascent in 30 min. up to 82° C.

Polar solvent removal (by drawing off a bath liquid phase, separation of methanol and recycling perchloroethylene) was effected from 82° C. on.

The extraction of polar solvent was regulated uniformly in order to remove it completely in 40 minutes.

At the end of the dyeing the perchloroethylene was practically colorless: only one perchloroethylene rinsing at 40° C. during 6 minutes was sufficient. Dyeing time: 1 hour, 10 min.

EXAMPLE 3

Dyeing with 1% Acid red C.I. 57 was accomplished on polyamide fibers with the following conditions:

Bath composition:

Industrial methanol	parts	100
Industrial monochlorobenzene	do	899
Glacial acetic acid	do	1
Initial temperature	° C	20
Final temperature	° C	100

A temperature of 80° was reached in 30 minutes.

Polar solvent removal was accomplished beginning at 80° C. at a uniform speed within 40 min. Dyeing time: 1 hr. 10 min.—Exhaustion of the bath: about 100%.

EXAMPLE 4

Dyeing with 1.2% Acid blue C.I. 129 was accomplished on wool fibers under the following conditions:

Bath composition:

Industrial methanol	parts	100
Isopropanol	do	40
Industrial perchloroethylene	do	857
Glacial acetic acid	do	3
Initial temperature	° C	20
Final temperature	° C	102

Temperature ascent was made gradually in 30 minutes.

Polar solvents removal was achieved from 90° C. at the rate of 25 parts in 27 minutes, the remaining being extracted in 33 minutes. Operation total time: 1 hr. 30 min.—Exhaustion of the bath: 100%.

Later, two successive rinsings were made with perchloroethylene at 22° C. for 10 min.

In all the above examples dyeing was achieved in a satisfactory way as to permanence and tincotorial yield.

EXAMPLE 5

Exhaustion dyeing of 2 lots of 400 g. of jersey (polyamide 6.6) was effected under the following conditions:

0.5% by weight (relative to the jersey) of acid red C.I. 57, and

0.5% by weight (relative to the jersey) of acid yellow C.I. 25.

Composition of the bath:

Methanol	parts by volume	75
Perchloroethylene	do	925
Total volume of bath:	liters	39

For the first lot, dyeing was performed at atmospheric pressure, with an initial temperature of 37° C., raised to 60° C. in one hour, after which the latter temperature was held for 45 minutes, for a total duration of 1 hour, 45 minutes. Removal of a liquid fraction from the bath began 1 hour after the start of dyeing and continued until completion.

This liquid fraction was first passed into a reheater where it was brought to its boiling point, then into a flash-evaporator. The condensed vapors represented a volume of 7.05 liters which contained all of the methanol used. The non-vaporized perchloroethylene was recycled into the dyeing container, with fresh diluent added to keep the bath at a constant volume.

The exhaustion of the coloring agent, evaluated by photocolorimetry, was 24% at the end of 1 hour, i.e. before the start of removal of the liquid, and 100% at the end of the dyeing process.

A highly uniform red color was obtained, resistant to light and washing.

For the second lot, dyeing was conducted under exactly the same conditions as before, with a total dyeing time of 1 hour. 45 min. but without removing a liquid fraction from the bath; the exhaustion of the coloring agent at the end of the dyeing process was only 24%.

EXAMPLE 6

The same textile material as in Example 5 was dyed with the same coloring agents and the same bath, all proportions likewise being identical to those of the preceding example.

Dyeing was performed at a pressure of 4 bars (absolute), with an initial temperature of 30° C., raised to 100° C. in 50 minutes, after which this temperature was maintained for 1 hour.

Removal of a liquid fraction was begun after 1 hr. 10 min. of dyeing, and removal continued until the end of the dyeing step. This liquid fraction was passed directly into a vaporizer which operated at atmospheric pressure; the vapors thus obtained represented (after condensation) a volume of 7.20 liters, containing all the methanol initially introduced.

The exhaustion of the coloring agent was 40% at the end of 1 hour 10 min. and 100% at the end of the dyeing process.

Operating under the same conditions but without removing any liquid from the bath resulted in exhaustion of only 40% at the end of the dyeing process.

EXAMPLE 7

This test illustrates several possibilities for removal of the solvent in the vapor phase. Dyeing was performed using the same textile material as in the previous example, with similar coloring agents and a bath having substantially the same composition.

The bath was initially at 30° C. and at atmospheric pressure.

On the basis of these common data, the following three procedures were followed:

(a) An open system was used, and the bath temperature was raised to 65° C. in 1 hour 15 min. Removal of the vapors then began and was continued until the end of the dyeing process, i.e. for a total of 2 hours, 10 min.

(b) A closed system was used and the bath was heated

to 73° C. after 1 hour 25 min. The pressure was then 1.4 bars (absolute). Removal of the vapors then began and was continued until the end of the dyeing process, i.e. for a total of 1 hour 45 min., while raising the temperature to 90° C.

(c) The bath was gradually raised to 60° C. at the end of 1 hour and a slight vacuum was applied so that the pressure in the dye container was on the order of 600 mm. Hg. Removal of the vapors then began. The total duration of the dyeing process was 2 hours 30 minutes.

In the 3 cases described in this example, the exhaustion of the coloring agent was total at the end of the operation.

EXAMPLE 8

Dyeing of 350 g. of polyester material with 0.5% by weight (relative to the material) of plastosoluble coloring agent, disperse blue C.I. 40 was effected under the following conditions.

Composition of the bath:

2-chloroethanol	parts by volume	25
Trichloroethylene	do	50
Perchloroethylene	do	925
Volume of the bath	liters	100

Dyeing was performed at a pressure of 4.5 bars (absolute) with an initial temperature of 20° C., raised to 130° C. in 55 minutes, then held at this level for 1 hour. Removal of a liquid fraction from the bath began 1 hour 25 min. after the beginning of treatment. This liquid fraction was passed directly into a vaporizer functioning at atmospheric pressure; after condensation, the vapors represented a volume of 40 liters which contained all the trichloroethylene and chloroethanol. The exhaustion of the coloring agent was on the order of 80%.

The fabric was thereafter rinsed with cold perchloroethylene and dried. A uniform medium blue was obtained, resistant to light and washing.

When operating under the same conditions but without removal of liquid from the bath, a 10% exhaustion only of the coloring agent was obtained.

EXAMPLE 9

Dyeing of 900 g. of cloth made of polyacrylonitrile-based fibers (trademark: Crylor), with 1% by weight of cloth of Lyrcamine blue 2 BLL (trademark) was effected under the following conditions.

Composition of the bath:

Methanol	parts by volume	100
Isopropanol	do	10
Glacial acetic acid	do	5
Perchloroethylene	do	885
Total volume of the bath	liters	40.5

Dyeing was performed at a pressure of 4.5 bars (absolute).

Initial temperature: 25° C.

Gradual increase to 110° C. in 30 min.

Total duration of the dyeing: 1 hr. 50 min.

Start of removal of the liquid phase: 1 hr. 15 min. after the start of dyeing. Separation of solvent from the removed fraction was accomplished directly by vaporization at atmospheric pressure.

Amount of liquid recovered by vapor condensation: 4 liters after 10 minutes, 9 liters at the end of the operation.

The exhaustion of the coloring agent was 100%.

The cloth had a uniform medium blue color, resistant to light and washing. By operating under the same conditions but without removal of liquid from the bath a 45% exhaustion only of the coloring agent was achieved.

EXAMPLE 10

Dyeing of 400 g. of cellulose triacetate cloth with 1% by weight of disperse blue C.I. 40 was effected using the following conditions.

Composition of the bath:

Methanol	parts by volume	100
Isopropanol	do	10
Perchloroethylene	do	890
Total volume of bath	liters	40.5

Dyeing was performed at a pressure of 4.5 bars (absolute).

Initial temperature: 40° C.

Gradual increase to 110° C. in 20 min.

Total duration of dyeing: 1 hour, 25 min.

Start of removal in liquid phase: 50 min. after start of dyeing. Separation of solvent from the removed liquid fraction was effected by vaporization at atmospheric pressure.

Amount of liquid recovered by vapor condensation: 2.6 liters after 10 min., 8.3 liters at the end of the process.

The exhaustion of the coloring agent was only 2% before removal of the liquid was begun, while it was 80% at the end of the operation.

EXAMPLE 11

Dyeing of 500 g. of cloth made by cellulose diacetate with 1% (based on cloth weight) of the acid coloring agent acid red C.I. 57 was carried out under the following conditions.

Composition of the bath:

Methanol	parts by volume	100
Isopropanol	do	10
Perchloroethylene	do	890

Total volume of bath: 40.5 liters. Dyeing was performed at a pressure of 3 bars.

Initial temperature: 30° C.

Gradual increase to 52° C. in 35 minutes. This low temperature was selected by reason of the tendency of the treated textile material to be deformed by heat.

Total duration of dyeing: 1 hour, 20 min.

Start of removal of liquid phase: 35 min. after start of dyeing. Separation of solvent was carried out by reheating removed liquid to 80° C., followed by vaporization at normal pressure.

Amount of liquid recovered by vapor condensation: 2.20 liters after 10 min., 4.10 liters after 20 min., 8.80 liters at the end of the operation.

Exhaustion of the coloring agent, which was 24% before removal of the liquid was begun reached 100% at the end of the dyeing process.

The cloth had a bright red color, resistant to washing and light.

In operating under the same conditions but without removing any liquid, exhaustion of the coloring agent on the order of 25% only was achieved.

EXAMPLE 12

Dyeing of two spools of textured polyamide 6.6 thread, with a total weight of 1.5 kg. and 0.8% (by weight of the cloth) was effected with disperse blue C.I. 40, without dilution or addition of dispersing agent, the coloring agent being insoluble in water.

Composition of the bath:

Methanol	parts by volume	375
Ion exchanged water	do	625
Total volume of bath	liters	40

Dyeing was performed at a pressure of 4 bars absolute.

Initial temperature: 22° C.

Gradual increase to 80° C. in 45 minutes.

Total duration of dyeing: 2 hours.

Start of removal in liquid phase: 1 hour after the start of dyeing. Separation of solvent from the removed liquid fraction was accomplished by vaporization at atmospheric pressure.

Amount of liquid recovered by vapor condensation: 3.50 liters after 10 minutes, 8 liters after 30 minutes, 14 liters at the end of the operation.

Exhaustion of coloring agent was total.

EXAMPLE 13

A moth-proofing treatment was given to 2 spools of wool with a total weight of 1.5 kg., treating them under the conditions of the invention with a solution of a moth-proofing product of 3,3',4' - trichloro-(2-sulfo-4-chlorophenoxy)-6-diphenylurea (trademark: Mittin FF) in methanol and isopropanol, diluted with perchloroethylene.

Composition of the bath:

Methanol	parts by volume	100
Isopropanol	do	10
Perchloroethylene	do	890

Volume of the bath: 40.5 liters.

Treatment was performed at a pressure of 4 bars (absolute).

Initial temperature: 40° C.

Gradual rise to 100° C. in 30 min.

Total duration of treatment: 1 hr., 20 min.

Start of removal of liquid phase: 30 minutes after start of treatment. Separation of solvents from a removed liquid fraction was effected by vaporiztion at normal pressure.

Quanity of liquid recovered by vapor condensation: 6.80 liters after 30 min., 9.50 liters at the end of operation.

No precipitation of the insecticide was observed, either in the treatment bath or on the surface of the treated textile material.

The moth-proofing treatment may be performed simultaneously with the dyeing, if desired.

EXAMPLE 14

Dyeing of 100 g. of polyester cloth with 0.3% (based on the weight of cloth) of a plasto-soluble dye of ruby color (Rubis dye) without dilution and without dispersant, the dye being insoluble in water.

Composition of the bath:

Pyridine	parts by volume	100
Water	do	900
Total quantity of bath:	liters	1.5

The dyeing was effected under a pressure of 3 bars.

Initial temperature: 40° C.

Rising gradually up to 110° C. in 30 minutes.

Total duration of the dyeing: 1 hr., 15 min.

Start of removal in liquid phase: 45 min. after commencement of the dyeing. Separation of the solvent from the liquid fraction was effected by vaporation under atmospheric pressure.

Quantity of liquid recovered: 0.30 litre.

Exhaustion of dye was complete.

The cloth had a perfectly uniform and intense ruby color, resistant to light and washing.

It will be obvious to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is described in the specification.

What is claimed is:

1. A process of dyeing textile fibers and fabrics in solvent medium by the exhaustion method comprising effecting said dyeing with a coloring agent utilizing as dyeing medium a bath containing a minor proportion of a solvent in which said coloring agent is soluble and a major proportion of a diluent in which said coloring agent is insoluble or only slightly soluble, at an elevated temperature and continuously removing said solvent from the dyeing bath during said dyeing operation, until substantially all of the coloring agent is fixed on the textile fibers or fabrics.

2. A process according to claim 1, wherein said solvent has a lower boiling point than the boiling point of said diluent.

3. A process according to claim 1 wherein the dyeing operation begins at room temperature, then the temperature is gradually elevated for approximately 15 to 80 minutes to a temperature of at least 40° C., the elevated temperature being then maintained for 15 to 90 minutes.

4. A process according to claim 1 wherein the solvent is removed in vapor phase.

5. A process according to claim 1 wherein a liquid fraction of the bath is removed, said fraction containing a mixture of the solvent and diluent, the solvent is separated from the mixture, and the remaining liquid fraction is recycled to the dyeing bath.

6. A process according to claim 1 wherein after dyeing the textile is rinsed with said diluent.

7. A process according to claim 1 wherein said solvent is selected from the group consisting of methanol and a mixture of methanol and isopropanol, and the diluent is perchloroethylene.

8. A process according to claim 1 wherein said solvent is an halogenated aliphatic alcohol which forms an azeotrope with said diluent.

9. A process according to claim 8 wherein said halogenated aliphatic alcohol is selected from the group consisting of 2-chloroethanol, 2-bromo-ethanol, 1-chloropropanol, and 2-chloro-propanol.

10. A process in accordance with claim 1 wherein 20 to 375 parts of said solvent are used per 1000 parts by volume of dyeing bath.

11. A process according to claim 1 wherein up to 10 parts by volume of acetic acid is added to the dyeing bath per 1000 parts by volume of bath.

12. A process according to claim 3 wherein said solvent removal is started when the temperature of the bath reaches at least the theoretical boiling temperature of said solvent.

13. A process according to claim 1 wherein said solvent is methanol and said non-solvent diluent is water.

14. A process according to claim 5 wherein said solvent is separated from said liquid fraction by flash evaporation.

15. A process according to claim 5 wherein said solvent is separated from said liquid fraction by azeotropic distillation.

16. A process according to claim 5 wherein said solvent is separated from said liquid fraction by crystallization. is separated from said liquid fraction by selective adsorption.

18. A process according to claim 5 wherein said solvent is separated from said liquid fraction by passage across a semi-permeable membrane.

19. A process according to claim 1 wherein mothproofing is accomplished at the same time as said dyeing.

17. A process according to claim 5 wherein said solvent

20. A process of treating textile fibers and fabrics in anhydrous medium by the exhaustion method comprising effecting said treatment with a treating agent in a bath containing a minor proportion of a solvent in which said treating agent is soluble and a major proportion of a diluent in which said treating agent is insoluble or only slightly soluble, at an elevated temperature, and continuously removing said solvent from the bath during said treating operation, until substantially all of the coloring agent is fixed on the textile fibers or fabrics, recovering the diluent and recycling the removed solvent and the recovered diluent to prepare a new dyeing bath for a succeeding dyeing operation.

21. A process according to claim 20 wherein said treating is sizing.

22. A process according to claim 21 wherein said treating is mothproofing.

(References on following page)

13

References Cited

UNITED STATES PATENTS

3,558,267	1/1971	Langenfeld	8—172
3,129,053	4/1964	Castle	8—93
2,182,964	12/1939	Dreyfus et al.	8—35
1,738,978	12/1929	Whitehead	8—175
2,274,751	3/1942	Sowter et al.	8—173
3,510,243	5/1970	Seuret et al.	8—39
2,184,559	12/1939	Mellor et al.	8—175 X

FOREIGN PATENTS

1,507,460	11/1967	France	8—93
1,560,532	2/1969	France	8—93

14

OTHER REFERENCES

Journal of the Society of Dyers and Colourists, vol. 72, 1956, p. 100.

W.A.S. White: Amer. Dyestuff Reporting, July 3, 1967, pp. 18–24.

LEON D. ROSDOL, Primary Examiner

T. J. HERBERT, JR., Assistant Examiner

U.S. Cl. X.R.

8—173, 174