

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO THE DYEING AND/OR FINISHING OF TEXTILES

(71) We, UNITED STATES DEPARTMENT OF COMMERCE, a Department of the United States Government, of Washington, D.C. United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to the dyeing and/or finishing of textile fibres. In the following description parts and percentages are by weight unless otherwise specified.

It is known that many textiles must be dyed either prior to or after formation into utilizable products. For centuries the dyeing of textiles has been carried out in aqueous solutions. Presently, textiles are dyed commercially by agitating the textile in an aqueous dyebath maintained at boiling temperatures for a period of one hour or longer. The operations require large quantities of water, usually 10—50 times the weight of the fabric. The disposal of the resulting spent liquors has created a major pollution problem, and treatment to avoid this increases costs.

Attempts have been made at replacing water with an organic solvent, such as perchloroethylene, which can be recovered easily by distillation. There are, however, several disadvantages inherent in solvent dyeing. First, such solvents are not capable of dissolving polar or ionic dyes used in aqueous systems and adapted for use with particular fibres, e.g., acid dyes conventionally used in wool dyeing are not soluble in such organic solvents. The use of solvent dyeing systems will necessitate the development of appropriate solvent-soluble, non-polar dyes. Since dyes derive much of their affinity for fibres from their polarity, the creation of suitable non-polar dyes becomes even more difficult. Secondly, distillation procedures required for recovery of solvent from spent liquors are

expensive and invariably involve a loss of material, usually to the atmosphere, thus causing pollution problems. 50

The dyeing of polyester fibres or fabrics in water requires the use of a carrier to facilitate the reaction of the fibre with the dye. Generally, for this purpose an arylphenol, such as *o*-phenylphenol, is employed. If the dyeing is carried out at atmospheric pressure, a substantial amount of the carrier, e.g., about 10% or more based on the weight of the fibre, is necessary. The dyeing of the polyester may be carried out at superatmospheric pressure, under which circumstance less carrier is required, but this is expensive. Further, the carriers present a pollution problem and disposal of the spent solutions is difficult. The dyeing of polyester fabric requires about the same amount of time as aqueous dyeing of natural fibres, i.e., about one hour or longer. 55 60 65

According to the present invention there is provided a process of modifying textile fibres, which process comprises contacting the fibres with an anhydrous solution of a dyeing and/or finishing agent in a solvent selected from glycol(s), glycidols and glycerol(s) in the presence of phosphoric acid at a temperature in the range of from 110 to 165°C. The invention also provides a process for rapidly dyeing textile fibres in the absence of water, which comprises: 70 75 80

(a) contacting the fibres with a dyebath at a temperature in the range of from 110 to 165°C., said dyebath containing dye, phosphoric and/or sulphuric acid and a solvent selected from a glycol, a glycidol and a glycerol, 85

(b) continuing said contact until a desired level of dyeing is attained, and

(c) separating the dyed fibres from the dyebath. 90

It is preferred that the solvent be selected from ethylene glycol, glycidol, propylene glycol, glycerol and diethylene glycol, it being especially preferred that the solvent is ethylene glycol. 95

This invention thus provides a means for

obviating the aforementioned problems. The fibres can be dyed in a bath in which the dye is dissolved in ethylene glycol. The primary advantage of the invention is that dyeing can be accomplished in a very short time. As a result, the dyeing time can be reduced from one hour or more to as little as 2 to 10 seconds. Rapid, continuous processing is much less costly than slow, continuous processing or slow, batch processing. The rapid dyeing feature of the invention is totally unexpected. In the instance where other organic solvents have been substituted for water, the time of dyeing did not vary from that in conventional aqueous dyeing. Another advantage is that the solvent used in the invention, especially ethylene glycol, as opposed to other organic solvents, such as hydrocarbon and chlorinated solvents, swells the fibres and permits the dye to penetrate and the dye is applied evenly. A further advantage is that the solvent used in the present invention especially ethylene glycol, readily dissolves dyes which are conventionally used on textiles. Other organic solvents, particularly hydrocarbon and chlorinated solvents, dissolve very few dyes unless the dyes are chemically modified to render them soluble. Another advantage of the invention is that polyesters can be dyed without the use of carriers and high pressures. Another advantage is that the textile fabrics may be dyed without impairing the desirable properties of the textile, e.g., hand, elasticity, porosity, resilience, strength and wear-resistance. Another advantage is that the dyed fabric can retain its colour even after repeated launderings. In conventional dyeing, prolonged boiling or other severe conditions must be used to obtain washing fastness. Under such conditions the fibre is readily susceptible to damage. A further advantage of the invention is that the dyebath can be reused after regeneration with additional dye, and the glycol can be recovered. Any residual solvent containing spent dyes can be disposed of readily without danger to the environment. Another advantage is that it may be practised, with only slight modification, using dyeing equipment to be found in any textile-treating plant. Also, the invention can be applied to textiles which consist entirely of proteinaceous fibres (e.g., wool, mohair, silk, camel or other animal hair; regenerated protein fibres such as those prepared from casein, soybeans, peanut protein, zein, gluten, egg albumin, collagen, or keratins such as feathers, animal hoof or horn. The invention can also be applied to textiles which contain synthetic or non-proteinaceous natural fibres, such as cotton, linen, hemp, jute, ramie, sisal, cellulose acetate, cellulose acetatebutyrate, saponified acetate rayons, viscose rayons, cuprammonium rayons, ethyl cellulose, polyurethane, polyacrylonitrile, polyesters such as polyethylene terephthalate, polyamides such as polyhexamethylene adipamide, polycaprolactam, polyolefins such as polypropylene and polyvinylchloride. Mixtures of proteinaceous and other fibres such as synthetic and non-proteinaceous fibers, can also be used. The textile may be in the form of bulk fibers, yarns, sliver, roving, top, webbing, tape, or woven or knitted fabrics, garments, garment parts, or nonwoven fiber assemblies, e.g., felt. A most important feature of the invention is that other chemical treatment, i.e., the application of finishing agents, of the textile may be carried out concomitantly with the dyeing operation. The following types of finishing agents may be used by way of illustration: shrinkproofing, shrink-resist, flameproofing, flame-resist, mothproofing, soil-resist, soil-release, waterproofing, oil-repellants, anti-static, softening odorants, durable press, wrinkle-resist, etc. Such treatments also are accomplished more rapidly in ethylene glycol than in conventional solvents. Application of finishing agents may be carried out in ethylene glycol in the absence of any dye. This procedure also offers the unexpected advantages of rapid treatment and durability. Another advantage is that two different fibres can be dyed simultaneously, i.e., cross-dyed, in the same dyebath. The two fibres must differ in their reactivity toward the dyes employed, each being reactive to only one of the dyes. The dyed fibres retain their colour intensity even after repeated aqueous launderings. In dyeing in accordance with the invention, one proceeds in part as in conventional dyeing operations with certain exceptions. A different temperature of the dyebath is employed. However, the particular dye and adjuvants and the amounts thereof are selected in accordance with the usual principles of dyeing and thus may be varied over a wide range, but the dyeing time is less. The most important departure from conventional practice is that the process is preferably conducted continuously rather than batchwise because of the very short period of time required to achieve good dyeing of the textile fabric, and much more fabric can be processed in a shorter period of time than in conventional methods.

In a preferred embodiment of the invention, the following steps are applied:

I. A dyebath is prepared by dissolving the appropriate type and amount of dye in ethylene glycol. If any dyeing adjuvants such as sodium sulphate, sodium chloride, sulphuric acid, phosphoric acid, and wetting agents are used, they are incorporated into the solution at this time. Any finishing agents should be added to the dyebath accordingly. Where it is desired only to apply a finishing agent, the dyes are not employed; only the appropriate chemical reagent is added to the ethylene glycol along with any needed or desired adjuvants such as acids or wetting agents.

The total amount of the dyebath will generally be from 10 to 500 parts of solvent, preferably ethylene glycol, per part of fibrous material. The amount of solvent must be sufficient to wet out the fibre. The amount of dye will vary with such factors as the nature of the dye, the fibre, and the level of dyeing desired. In many cases, one uses from 0.01 to 5% of active dye, on a weight/volume basis. For example, for light dyeing from 0.01 to 0.05% is used; for medium dyeing, from 0.05 to 0.1%; for heavy dyeing, from 0.1 to 1.0% or more. In any case, enough dye should be employed to obtain a 0.1 to 10% uptake thereof by the fibre (based on the weight of fibre).

II. Having established the proper dyebath, the temperature thereof is raised to between 110 to 165°C. and maintained thereat during the dyeing. The textile material to be dyed is then immersed in the dyebath. It is necessary to maintain intimate contact between the fibres and the dyeing solution for a period long enough to attain the desired level of colouration, e.g., from 2 seconds to 10 minutes. A shorter time is required the higher the temperature of the dyebath.

The process of the invention may be carried out continuously and the textile fibre or fabric is passed through the dyeing solution for a period of time required to achieve the desired colouration. The fibre, such as top, or fabric may be attached to two rollers, one of which is driven, to pull the fibre or fabric through the dyebath, although obvious continuous methods such as on a screen, or belt, or perforated drum can be used. Additional dye must be added to the dyeing solution at various times during the course of continuous operation to maintain dye concentration.

Some textiles require more intimate contact with the dyeing solution. Thus, the dyebath may be stirred, rocked, tumbled, and the like, or the fibrous material may be moved about in the bath. Preferably, one can circulate the bath through the mass of fibrous material. For example, high-

pressure jets of dyebath solution can be applied to one side of the immersed fabric so that complete dyeing may take place, although other methods can be used.

III. After completion of the dyeing, the fabric is removed from the dyebath and treated to remove excess liquid therefrom, e.g., the fabric can be passed through squeeze rollers. The excess dyeing solution so removed can be recycled or treated to recover ethylene glycol. The textile is then dried in conventional manner.

In an alternate method, the fabric may be passed through squeeze-rollers and then extracted with an organic solvent, such as methanol, to remove excess ethylene glycol and unreacted dye. The fabric is then dried in a conventional manner. The extracted liquor can be distilled to separate the methanol from the dyeing solution, which can be recycled.

In the alternative, the textile may be rinsed with water, either before or after passing it through squeeze-rollers, to remove residual dyeing solution. The wet fabric is squeezed to remove excess water and dried. This method is less preferred in large-scale operations because recovery of the ethylene glycol, etc., from the aqueous medium is difficult.

Although the use of ethylene glycol as the dyebath solvent has been emphasized, the invention encompasses the use of glycidol, propylene glycol, glycerol or diethylene glycol as a solvent.

EXAMPLES

The proportion of various ingredients is expressed as the percentage based on the weight of ingredient to the volume of ethylene glycol, this being abbreviated as "w/v".

Some samples were subjected to aqueous laundering in a reversing, agitator-type, household washing machine, using a 3-lb. load, a water temperature of 105°F., and a low sudsing detergent in a concentration of 0.1 percent in the wash liquor. The wash cycle itself was for 15 minutes, followed by rinses and spin-drying. In most cases this was repeated. The damp material was then tumble-dried in a household-type clothes dryer.

Example 1

Dyeing of Loose Wool Fibres

A dyebath was prepared containing 0.2% (w/v) Fast Light Red (Colour Index Acid Red 37) and 0.6% (w/v) phosphoric acid in 10 ml. of ethylene glycol. The temperature of the bath was raised to and maintained at 150°C. A sample of loose, clean wool fibres (1 g.) was immersed in the dye solution for 30 seconds, removed and rinsed immediately with water, and dried.

The above experiment was repeated with the following dyes:

	Commercial Dye	Colour Index Designation	Chemical Type
5	Alizarine Direct Blue	CI Acid Blue 41	Anthraquinone
	Alizarine Sky Blue	CI Acid Blue 232	Anthraquinone
	Nylosan Green	CI Acid Green 25	Anthraquinone
	Lanasol Blue 3G	CI Reactive Blue 69	Anthraquinone
	Lanasol Red G	CI Reactive Red 37	Monoazo
	Lanasol Yellow	CI Reactive Yellow 39	Azo
10	Fast Light Red	CI Acid Red 37	Azo
	Fast Light Yellow	CI Acid Yellow 17	Azo
	Lanasyn Brilliant Yellow	CI Acid Yellow 127	Azo
	Supralan Blue	CI Acid Blue 179	Monoazo 1:2 metal complex

15 An examination of cross sections of the so-dyed fibres revealed that the dye had achieved more thorough penetration than in samples dyed according to present commercial processes in an aqueous dyeing medium. 65

Example 2

Dyeing of Wool Fabric

An undyed wool fabric sample (2 g.) was cut (approximately 2 in. in diameter) to fit a sintered glass Buchner funnel. The funnel was heated to 150°C. and attached to a filter flask (1 l.), which in turn was attached to a water aspirator. 70

25 A dyebath (100 ml.), containing Fast Light Red, was prepared as in Example 1. The wool sample was placed in the funnel and water aspiration vacuum was applied. The hot (150°C) dyeing solution was poured over the wool disc continuously for 30 seconds. The sample was washed with water and dried. 75

The dyeing was repeated with the dyes outlined in Example 1.

40 A cross section of fibres from each sample was obtained, using a Hardy microtome. Examination of the fibres showed that, in each sample, dyeing was even and thorough. 85

Example 3

Dyeing of Nylon Fibres

45 A dyebath was prepared containing 0.2% (w/v) Alizarine Direct Blue ARS (an acid milling dye) and 0.6% (w/v) phosphoric acid in 250 ml. of ethylene glycol. The temperature was raised to and maintained at 150°C. A one-gram sample of undyed Nylon (3 denier) was immersed for 10 seconds and another sample for 30 seconds. The samples were removed from the bath rinsed with water, and dried in air. Dye penetration was thorough. 95

Example 4

Cross-dyeing of Wool and Acrylic Fibres

50 A dyebath was prepared by dissolving 1.5 g. of "Sevron" Red (cationic dye from

Dupont Co.) and 1.5 g. of Lanasol Blue (reactive dye from Ciba-Geigy Co.) in 750 ml. of ethylene glycol. To this was added 3 ml. of phosphoric acid. The temperature conditions were as in Example 3. 65

A one-gram sample of wool top (loose fibre) and a one-gram sample of acrylic (Orlon) staple fibre were immersed for 30 sec., withdrawn, rinsed in water, and dried in air. 70

The wool was dyed a deep blue colour, whereas the Orlon was dyed deep red. Dye penetration was complete and the colours retained their intensity after 20 aqueous launderings. 75

Example 5

Cross-dyeing of Wool and Polyester Fibers

The procedure outlined in Example 4 was followed. The dyes used were 0.5% (w/v) "Latyl" yellow (disperse dye for polyesters from Dupont Co.) and 0.5% (w/v) Lanasol Blue fibre reactive dye from Ciba-Geigy Co.). The samples dyed were 1 g. of wool top (loose fibres) and 1 g. of polyester (Dacron) staple fibre (3 denier). 80

The wool was dyed a deep blue colour; the Dacron, a deep yellow. Dye penetration was complete and the colours were wash-fast after 20 aqueous launderings. 85

Example 6

Dyeing of Wool in Glycerol

A dyebath was prepared containing 0.7 g. of Lanasol Scarlet 2R (CI Reactive Red 78) and 3 ml. of phosphoric acid in 750 ml. of glycerol. The temperature was raised to and maintained at 160°C. A sample (2 g.) of loose wool fibres was immersed in the solution for 20 seconds, withdrawn, rinsed in water, and dried. 95

The sample was dyed a deep red colour and the dye was evenly distributed throughout. 100

Example 7

A dyebath was prepared containing 0.6% (w/v) Alizarin Direct Blue ARA (an acid levelling dye) and 0.6% (w/v) phosphoric

acid in 500 ml. of ethylene glycol. The temperature of the bath was raised to and maintained at 145°C. A sample of loose, clean wool fibre (1 g.) was immersed in the dye solution for 10 seconds, removed therefrom, rinsed immediately with water, and dried.

The above experiment was repeated with the following dyes:

10 Nylosan Green 3FGL (an acid levelling dye)
Supralan Yellow NR (neutral pre-metallized dye)
Lansol Red 5B (fibre reactive dye)

15 For purposes of comparison, the above dyeing experiments were repeated with all parameters the same except that the phosphoric acid was omitted.

20 In all cases, the samples dyed in accordance with the process of the present invention (in the presence of acid) exhibited a much deeper shade of colour than those samples dyed in the absence of acid.

25 An examination of cross sections of the fibres dyed in the presence of acid reveals that the dye had achieved complete and thorough penetration. On the other hand, samples dyed in the absence of acid exhibited uneven and non-thorough application of the dye when examined as above. The dye was confined almost exclusively to the surface of the fibres.

WHAT WE CLAIM IS:—

35 1. A process of modifying textile fibres, which process comprises contacting the fibres with an anhydrous solution of a dyeing and/or finishing agent in a solvent selected from glycol(s), glycidol(s) and/or glycerol(s) in the presence of phosphoric acid at a temperature in the range of from 110 to 165°C.

40 2. A process according to Claim 1, wherein the solvent is selected from ethylene glycol, glycidol, propylene glycol, glycerol and diethylene glycol.

45 3. A process according to Claim 1, wherein the solvent is ethylene glycol.

50 4. A process according to Claim 1, 2 or 3, wherein the textile fibres are proteinaceous fibres.

55 5. A process according to Claim 4, wherein the proteinaceous fibres are wool fibres.

60 6. A process according to Claim 5, wherein the wool fibres are blended with other textile fibres.

65 7. A process according to Claim 4, wherein the proteinaceous fibres are blended with other textile fibres.

8. A process according to any one of the preceding claims, wherein the modifying agent is a dye.

9. A process according to any one of

Claims 1 to 7, wherein the modifying agent is a finishing agent.

10. A process for rapidly dyeing textile fibres in the absence of water, which comprises:

(a) contacting the fibres with a dyebath at a temperature in the range of from 110 to 165°C., said dyebath containing dye, phosphoric and/or sulphuric acid and a solvent selected from glycol(s), glycidol(s), and/or glycerol(s),

(b) continuing said contact until a desired level of dyeing is attained, and

(c) separating the dyed fibres from the dyebath.

11. A process according to Claim 10, wherein the solvent is selected from ethylene glycol, glycidol, propylene glycol, glycerol and diethylene glycol.

12. A process according to Claim 10, wherein the solvent is ethylene glycol.

13. A process according to Claim 10, 11 or 12, wherein the textile fibres are proteinaceous fibres.

14. A process according to Claim 13, wherein the proteinaceous fibres are wool fibres.

15. A process according to Claim 14, wherein the wool fibres are blended with other textile fibres.

16. A process according to Claim 13, wherein the proteinaceous fibres are blended with other textile fibres.

17. A process according to any one of Claims 10 to 16, wherein the contact in Step (a) is attained by continuously passing the fibres through the dyebath.

18. A process according to any one of Claims 10 to 17, wherein the contact in Step (b) is maintained for from 2 seconds to 10 minutes.

19. A process according to any one of Claims 10 to 18, wherein the dyebath in Step (a) further contains a finishing agent.

20. A process according to any one of Claims 10 to 19, wherein the concentration of acid in Step (a) is 0.6% based on the weight of acid to the volume of the solvent.

21. A process according to any one of Claims 10 to 20, wherein the acid in Step (a) is phosphoric acid.

22. A process according to any one of Claims 10 to 20, wherein the acid in Step (a) is sulphuric acid.

23. A process according to any one of Claims 10 to 22, wherein the dyebath is rejuvenated with fresh dye at appropriate times to maintain the desired level of colouration of the fibres.

24. A process of dyeing and/or finishing textile fibres, substantially as described in foregoing Example 1.

25. A process of dyeing and/or finishing textile fibres, substantially as described in foregoing Example 2.

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26. A process of dyeing and/or finishing textile fibres, substantially as described in foregoing Example 3.

27. A process of dyeing and/or finishing 5 textile fibres, substantially as described in foregoing Example 4.

28. A process of dyeing and/or finishing textile fibres, substantially as described in foregoing Example 5.

10 29. A process of dyeing and/or finishing textile fibres, substantially as described in foregoing Example 6.

30. A process of dyeing and/or finishing 15 textile fibres, substantially as described in foregoing Example 7.

31. Fibres whenever dyed and/or finished

by the process of any one of the preceding claims.

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