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(54) Title: NON-AQUEOUS TREATMENT METHOD

(57) Abstract: The invention provides a method and formulation for the application of at least one substance to a substrate, the method comprising the treatment of the substrate with the formulation which comprises a multiplicity of polymeric particles, the polymeric particles being coated with the at least one substance. Preferably, the substance comprises a dye or a chemical for treatment of the substrate. Most preferably, the substrate comprises a textile fibre. Preferably, each of the polymeric particles is coated with the substance. Typically, the polymeric particles comprise particles of nylon, most preferably in the form of nylon chips. The results obtained are very much in line with those observed when carrying out conventional treatment processes and the method provides the significant advantage that the use of water, with all the attendant drawbacks in terms of cost and environmental considerations, can be avoided.

NON-AQUEOUS TREATMENT METHOD

Field of the Invention

The present invention relates to the treatment of substrates. More specifically, the invention is concerned with a novel method for the treatment of substrates which involves the use of a substantially non-aqueous treatment bath, and thereby eliminates the environmental issues which are associated with aqueous processing. Most particularly, the invention is concerned with the dyeing and post-treatment of textile fibres.

Background to the Invention

Textile dyeing is a major process within the textile industry and traditionally relies on the incorporation of a textile material in a dyebath which comprises an aqueous solution or dispersion of a dye. Indeed, in addition to dyeing operations, many other pre-treatment and finishing processes performed in the textile industry, such as the desizing, scouring, bleaching, mercerising and washing-off of cotton fabrics, are reliant on the use of water, with the consequence that the industry is a major user of water.

However, as the costs and regulations associated with the use of water have increased, there has been a greater motivation to move away from the traditional processing methods which have relied so heavily on the use of this material. There has been a growing realisation of the value of water as a limited resource and, as demands on water supplies have grown on a global basis, so the costs of supply have increased. Furthermore, the problem of waste and effluent production associated with the industrial use of water has resulted in increased environmental concerns, with the consequence that stricter legislation relating to the disposal of these waste materials is now in place on a worldwide basis so that, inevitably, costs have also increased in this regard. In addition, the energy costs associated with the use of aqueous-based processes can often be prohibitive.

Thus, the textile industry, both in terms of its duty to the environment as a major worldwide industry, and with regard to basic economic considerations, has increasingly sought to reduce its dependence on the traditional aqueous processes on which it has always depended. The widespread use of water-based processes has been primarily attributable to the solvent powers of this material, and attention has, therefore, focused on alternative means by which these properties might be replicated, and which could, as a consequence, lead to equally successful results.

Specifically, with regard to textile dyeing processes, several so-called "waterless" processes have previously been developed. Whilst these processes are referred to as "waterless", they include processes which rely on the use of reduced amounts of water as well as those which are completely non-aqueous.

Thus, for example, processes are available which employ alternative solvents, these processes being particularly appropriate for the application of disperse dyes, which are typically applied to hydrophobic fibres as aqueous dispersions, but may be applied from solutions in other solvents. Such processes may either be totally non-aqueous, or may include significantly reduced amounts of water. By way of example, the use of liquid ammonia containing certain inorganic salts as a solvent medium for the dyeing of cellulose has been known for some time and, amongst alternative solvents which have found commercial usage, there may be mentioned:

- A liquid ammonia system containing ammonium thiocyanate; a typical composition (by weight) would comprise 72.1% ammonium thiocyanate, 26.5% ammonia and 14% water;
- Dimethylacetamide containing 10% lithium chloride, which gives highly stable solutions of cellulose;
- Certain cyclic tertiary amine oxides, such as N-methylmorpholine-N-oxide, which has been used in the production of dyed Tencel; and
- N,N-dimethylformamide (DMF) including 15% dinitrogen tetroxide has been used as a solvent in the dyeing of cellulose.

Clearly, however, whilst the use of these alternative solvents can reduce the cost and environmental disadvantages associated with the use of water, there are similar problems to be addressed in relation to the solvents themselves. Thus, whilst volumes may be reduced, often significantly, when compared with aqueous systems, the solvents are frequently highly toxic and very expensive.

A particularly favoured alternative dyeing medium has proved to be supercritical carbon dioxide, which has been successfully employed as a solvent for the dyeing of polyester, polyamide and polypropylene fibres with disperse dyes. The solubility of the dyes in supercritical CO2 is found to increase markedly with increased pressure and a typical dyeing procedure could be as follows:

1. Set-up bath with goods and a charge of a pure disperse dye;
2. Run in supercritical CO_2;
3. Raise temperature and pressure to 130°C and 300 bar, respectively;
4. Gradually reduce pressure in order to reduce the solubility of the disperse dye in the supercritical fluid; and
5. Recover CO_2.

The procedure lasts about 40-45 minutes, and the levelness of dyeing is controlled by the pressure reduction programme; virtually 100% dye uptake is obtained and the requirement for reduction clearing is eliminated. However, the requirement for the use of high pressures is a clear disadvantage, since it presents an inherent safety risk, thereby lessening the attractiveness of this procedure.

A means by which the volume of water associated with the process may be significantly reduced is the technique of foam dyeing, wherein a large percentage of the water (~50-95%) that is normally used to apply the dye to the substrate is replaced by a gas, typically air. In fact, practically all the chemicals that are used for the conventional treatment of textiles can be applied to textiles in a foam medium provided that suitable foam can be produced. The chemical formulation is mixed

with air in a foam generator to create foam, usually having very fine bubble size. Incorporation of air into the formulation usually creates a large volume, which can be spread on the textile fabric more uniformly than can the un-foamed liquid. Generation of the foam is generally achieved by dispersing air in an aqueous solution by means of air injection or mechanical agitation, alternatively, a gas may be chemically generated, or some combination of these techniques may be employed.

Foam dyeing can result in improved dye yield, dyeing can be carried out successfully even without auxiliaries and steaming times can be reduced. In addition, the requirement for wash-off processes can be reduced, and even eliminated in the case of light shades. It is also possible to reduce the amount of dye liquor utilised. The method has found particular application in carpet coloration. However, its usefulness is limited by the high costs which are associated with the foam generation process.

A process which was commercially exploited nearly 50 years ago was the Thermosol process, which is based on the diffusion of disperse dyes into polyester at temperatures of 200-220°C, and has found application in respect of woven polyester/cotton blend fabrics. The process essentially comprises the steps of:

1. Padding the dye liquor onto the fabric;
2. Drying down to a low moisture content to prevent migration;
3. Final drying; and
4. Fixing the colour by treatment at around 200-220°C for 30-60 seconds.

However, the process can be difficult to carry out since, before dyeing, the textile must be carefully prepared in order to avoid uneven dyeing. Furthermore, the disperse dyes must have very fine, uniform particles, excellent dispersion and high sublimation fastness. In addition, whilst it has found application in continuous processes, the process is not suited to small scale batchwise dye application. The use of the process has also been limited by the high associated costs.

Other means of reducing water usage in dye application procedures have essentially relied on improved housekeeping procedures, for example by the introduction of water management plans, or equipment optimisation, generally relying on the development of new and improved dyeing machinery, designed to provide savings in energy, dyes, chemicals, water, space, time and labour. However, such approaches still rely on the use of significant quantities of water, whilst the increased costs associated with, for example, the installation of new equipment, can more than offset any savings that may be made in terms of usage of water.

In the light of the inadequacies associated with the previous attempts to reduce or eliminate the use of water in textile dyeing processes, the present inventors have attempted to devise a new and inventive approach to the problem, which allows the deficiencies demonstrated by methods of the prior art to be overcome.

Hence, the present invention seeks to provide a process for the treatment of substrates, particularly for the treatment of textile fibres, and most specifically for the dyeing of textile fibres, which substantially eliminates the requirement for the use of water in the treatment bath but is still capable of providing treated materials showing excellent post-treatment properties, whilst also yielding additional economic and environmental benefits. With particular reference to the textile industry, the inventors are seeking to provide such benefits within the context of a process which allows for the production of dyed fibres showing a high degree of levelness and colour fastness.

Statements of Invention

Thus, according to a first aspect of the present invention, there is provided a method for the application of at least one substance to a substrate, said method comprising the treatment of the substrate with a formulation comprising a multiplicity of polymeric particles, said polymeric particles being coated with said at least one substance.

Said substrate may comprise any of a wide range of substrates, including, for example, plastics materials, leather, paper, cardboard, metal, glass or wood. Preferably, however, said substrate comprises a textile fibre, which may be either a natural or a synthetic textile fibre.

Preferably, said substance comprises a dye, a pigment or a chemical for treatment of the substrate. Any class of dye or pigment may be used for the purpose. Examples of suitable chemicals include chemicals used in the post-dyeing treatment of textile fibres, as well as textile finishing agents, scouring agents, bleaches, detergents, perfumes and fragrances. Preferably, each of said polymeric particles is coated with said at least one substance.

Said polymeric particles may comprise any of a wide range of different polymers. Specifically, there may be mentioned polyalkenes such as polyethylene and polypropylene, polyesters and polyurethanes. Preferably, however, said polymeric particles comprise polyamide particles, most particularly particles of nylon, most preferably in the form of nylon chips. Optionally, copolymers of the above polymeric materials may be employed.

Various nylon homo- or co-polymers may be used, including Nylon 6 and Nylon 6.6. Preferably, the nylon comprises Nylon 66 homopolymer having a molecular weight in the region of from 5000 to 30000 Daltons, preferably from 10000 to 20000 Daltons, most preferably from 15000 to 16000 Daltons.

The polymeric particles or chips are of such a shape and size as to allow for good flowability and intimate contact with the textile fibre. Preferred shapes of particles include spheres and cubes, but the preferred particle shape is cylindrical. Particles are preferably of such a size as to have an average weight in the region of 20-50 mg, preferably from 30-40 mg. In the case of the most preferred cylindrically shaped chips, the preferred average particle diameter is in the region of from 1.5-4.0 mm, most preferably from 2.0-3.0 mm, and the length of the cylindrical chips is preferably

in the range from 2.0-6.0 mm, more preferably from 3.0-5.0 mm, and is most preferably in the region of 4.0 mm.

Preferably, the method of the invention additionally comprises a pre-treatment step, wherein said substrate is subjected to an aqueous wetting treatment. Typically, said aqueous wetting treatment involves applying water to said substrate, for example by dipping said substrate in water. However, it is not intended, neither is it desirable, that significant amounts of aqueous liquor should be retained by the fibre for the purposes of the method of the invention, so the pre-treatment also provides for the removal of excess aqueous liquor from the substrate prior to treatment of the substrate with the formulation comprising a multiplicity of polymeric particles. Said excess may be removed by any convenient means, such as shaking, squeezing, wringing, or the like. In any event, the method of the invention requires that the water content of the substrate should not exceed 2% w/w during the treatment of the substrate with the formulation comprising a multiplicity of polymeric particles, and said water content is more preferably not in excess of 1% w/w, and most preferably does not exceed 0.5% w/w. The method of the invention provides optimum results when said pre-treatment step is incorporated.

The method of the invention may be applied to a wide variety of substrates as previously stated. More specifically, it is applicable across the range of natural and synthetic textile fibres, but it finds particular application in respect of nylon 6.6, polyester and cotton fabrics. The method of the invention is particularly suited to the application of dyes, pigments and chemicals used for the post-treatment of fabrics. Classes of dyes which may be applied by means of the method of the invention include direct dyes, acid dyes, reactive dyes, disperse dyes and sulphur dyes.

According to a second aspect of the present invention, there is provided a formulation for the application of at least one substance to a substrate, said formulation comprising a multiplicity of polymeric particles, said polymeric particles being coated with said at least one substance.

Preferably, said substance comprises a dye or pigment, or a chemical for treatment of the substrate; particularly suitable chemicals in this regard include chemicals for the post-dyeing treatment of textile fibres. Preferably, each of said polymeric particles is coated with said at least one substance.

The formulation and the method of the present invention may be used for either small or large scale processes of both the batchwise and continuous variety, and are particularly useful in batchwise and continuous dyeing operations. Particularly favourable results are achieved when the method of the invention is carried out in apparatus or containers which encourage Newtonian Flow. Optimum performance frequently results from the use of fluidised beds, and this is particularly the case when the method of the invention is used for carrying out dyeing processes. Amongst other potential applications of the invention may be mentioned spraying and painting processes, for example the painting of cars and other transport vehicles.

Description of the Invention

The method of the invention requires that the polymeric particles should first be coated with the substance, in order to achieve a more level distribution of the substance on the particles and, consequently, on the substrate, as the particles contact the substrate during the treatment process. Typically, the coating process requires that the polymeric particles should be mixed with 0.5%-10%, preferably 1%-5%, most preferably around 2% of the substance, and the resulting mixture held at a temperature of between 30° and 70°C, preferably 40° and 60°C, most preferably in the region of 50°C, for a time of between 15 and 60 minutes, preferably between 20 and 40 minutes, with the most satisfactory results being obtained when the treatment is carried out for approximately 30 minutes.

In the procedure according to the invention, the ratio of coated beads to substrate is based on a nominal "liquor ratio" in terms of a conventional treatment bath, with the preferred ratio being in the range of from 20:1 to 1:1 w/w, preferably in the region of from 10:1 to 2:1 w/w, with particularly favourable results being achieved with a ratio

of around 5:1 w/w. Thus, for example, for the treatment of 5 g of fabric, 25 g of coated polymeric particles would be employed.

As previously noted, the method of the invention finds particular application in the dyeing of textile fibres. In this context, the conditions employed in the dyebath are very much in line with those which apply to the dyeing of textile fibres in conventional aqueous dyebaths and, as a consequence, are generally determined by the nature of the fabric and the class of the dye. Thus, typical dyebath conditions are in accordance with those which are well known to those skilled in the art, as outlined in the following procedures. Naturally, it should be emphasised that the conditions herein disclosed are merely exemplary and that any suitable dyebath conditions which could readily be determined by a skilled person would be appropriate to the method of the invention.

Direct Dyes/Cotton Fabrics

Following entry of the wetted fabric at 30°C, the temperature of the dyebath is increased to 95°C at a rate of 2°C per minute, and then maintained at 95°C for 30 minutes, before being cooled to 80°C at a rate of 2°C per minute, after which the fabric is removed and rinsed.

Disperse Dyes/Polyester Fabrics

Following entry of the wetted fabric at 40°C, the temperature of the dyebath is increased to 130°C at a rate of 1.5°C per minute, and then maintained at 130°C for 45 minutes, before being cooled to 70°C at a rate of 2°C per minute, after which the fabric is removed and rinsed.

Acid Dyes/Nylon 6.6 Fabrics

Following entry of the wetted fabric at 30°C, the temperature of the dyebath is increased to 98°C at a rate of 1°C per minute, and then maintained at 98°C for 40 minutes, before being cooled to 60°C at a rate of 2°C per minute, after which the fabric is removed and rinsed.

Sulphur Dyes/Cotton Fabrics

Following entry of the wetted fabric at 50°C, the temperature of the dyebath is increased to 98°C at a rate of 2°C per minute, and then maintained at 98°C for 45 minutes, before being cooled to 70°C at a rate of 2°C per minute, after which the fabric is removed and rinsed. Subsequently, the fabric is subjected to an oxidation treatment with a suitable commercially available oxidation liquid, such as Diresul® (available from Clariant Limited), at 70°C for 20 minutes, after which the bath is cooled as quickly as possible to 50°C and the fabric is removed and rinsed.

Reactive Dyes/Cotton Fabrics

Following entry of the wetted fabric at 40°C, the temperature of the dyebath is increased to 90-95°C at a rate of 1°C per minute, and then maintained at 90-95°C for 45-60 minutes, before being cooled to 70°C, after which the fabric is removed and rinsed.

Reactive Dyes/Nylon 6.6 Fabrics

Following entry of the wetted fabric at 30°C, the temperature of the dyebath is increased to 98°C at a rate of 1.5°C per minute, and then maintained at 98°C for 30-60 minutes, before being cooled to 70°C, after which the fabric is removed and rinsed.

The dyed fabrics obtained by means of the method of the invention have been seen to have good levelness and colour strength. No problems were observed with polymer particles adhering to the fibres when removing the dyed materials from the dyebaths at the completion of the dyeing process, so easy rinsing of the dyeings was facilitated. Furthermore, wash fastness tests have demonstrated that the dyeings show a level of fastness equivalent to that which is obtained by means of conventional dyeing methods, and favourable results have also been observed in comparative light fastness and rubbing fastness tests.

Additionally, it has been demonstrated that re-utilisation of the polymer particles is possible, and that coated particles can be satisfactorily re-used in the dyeing procedure, although some deterioration in performance is generally observed following three uses of the particles. Optimum results are achieved when the particles are used with the same dye in each dyeing procedure.

The method of the invention has also been successfully applied to the after-treatment of dyed fabrics following the dyeing procedure. Again, the conditions employed in such treatments are essentially in accordance with those which apply to the after-treatment of textile fibres in conventional processes and, therefore, are generally determined by the nature of the fabric and the class of the dye. Thus, typical conditions are in line with those which are well known to those skilled in the art. The ratio of polymer particles to fabric is preferably in accordance with the values defined for the analogous dyeing procedures with polymer particles, with the most advantageous ratio again being in the region of 5:1 w/w (e.g. 5 g of fabric in 25 g of polymer particles). Typical treatments are in accordance with the following guidelines, although it should again be emphasised that the conditions herein disclosed are merely exemplary and that any suitable bath conditions which could readily be determined by a skilled person would be appropriate to the method of the invention.

Direct Dyes/Cotton Fabrics

Treatment of the wetted dyed fabric at 70°C for 30 minutes.

Disperse Dyes/ Polyester Fabrics (Reduction Clearing)

Following entry of the wetted dyed fabric at 40°C, the temperature of the bath is increased to 60°C and then maintained at 60°C for 20 minutes, after which the fabric is removed and rinsed.

Acid Dyes/Nylon 6.6 Fabrics

Treatment of the wetted dyed fabric at 70°C for 30 minutes.

Sulphur Dyes/Cotton Fabrics

Treatment of the wetted dyed fabric at 70°C for 20 minutes.

Reactive Dyes/Cotton Fabrics

Treatment of the wetted dyed fabric at 60°C for 20 minutes.

Reactive Dyes/Nylon 6.6 Fabrics

Treatment of the wetted dyed fabric at 70°C for 30 minutes.

Again, the results obtained in all cases were very much in line with those observed when carrying out conventional after-treatment procedures with dyed fabrics, with loosely bound dye which could otherwise lead to poor fastness properties, especially in respect of wash fastness, being successfully removed from the fabrics. Thus, the method of the invention was again found to be successful in allowing for the treatment of textile fibres to be carried out at the same level of performance as is observed with conventional aqueous processes, but with the significant advantage that the use of water, with all the attendant drawbacks in terms of cost and environmental considerations, was avoided.

The method of the invention will now be exemplified, though without in any way limiting the scope of the invention, by reference to procedures involving specific dyes and fibres:

Examples

Example 1 – Dyeing

Scoured, knitted nylon 6.6 fabric and scoured, knitted polyester fabric employed in the tests was supplied by Du Pont (UK) Limited, and scoured, woven cotton fabric was supplied by Whaleys. Nylon 6.6 having AEG of 45 $meqkg^{-1}$ was used. In all cases the fabric was wetted prior to dyeing.

The polymer particles comprised cylindrical nylon chips comprising Nylon 66 polymer having a molecular weight in the region of 15000-16000 Daltons, with average dimensions of 4 mm in length and 2-3 mm in diameter, and an average particle weight of 30-40 mg.

Dyeing trials were conducted with a range of dyes as detailed in Tables 1 and 2. The conditions employed were in line with those detailed above, except where indicated otherwise. All dye percentages are w/w on the fibre.

Dye Class	Commercial Name	Colour Index Reference	Supplier
Reactive	Drimarine Blue X-3LR	C.I. Reactive Blue 52	Clariant
"	Drimarine Red X-6BN	C.I. Reactive Red 243	"
"	Drimarine Yellow X-4RN	C.I. Reactive Orange 70	"
"	Drimalan Blue F-B		"
"	Drimalan Brilliant Red F-B	C.I. Reactive Red 147	"
"	Drimalan Golden Yellow F-3RL	C.I. Reactive Yellow 125	"
Direct	Indosol Navy SF-BL	C.I. Direct Blue 251	"
"	Indosol Rubinole SF-GRN	C.I. Direct Red 261	"
"	Indosol Yellow SF-GL	C.I. Direct Yellow 98	"
Acid	Nylosan Blue F-L	C.I. Acid Blue 80	"
"	Nylosan Red F-5B	C.I. Acid Red 143	"
"	Nylosan Yellow F-L	C.I. Acid Yellow 236	"
Disperse	Dianix Blue BG-FS 200	C.I. Disperse Blue 73	Dystar
"	Dianix Royal Blue SE-R		"
"	Dianix Red E-FB	C.I. Disperse Red 60	"
"	Dianix Yellow S-6G	C.I. Disperse Yellow 114	"
Sulphur	Diresul Black RDT-LS	C.I. Leuco Sulphur Black 1	Clariant

Table 1. Dyes used in Experimental Trials

Fabric	Temperature	Dye	Colours	% Dye	Amou of Chip
Polyester	98°C	Disperse, Dianix	Blue, Red, Yellow	2%, 4%	25g, 7(
Polyester	110°C, 120°C	Disperse, Dianix	Blue, Red, Yellow	2%	25g
Polyester	130°C	Disperse, Dianix	Blue, Red, Yellow	2%	25g
Cotton	98°C	Direct, Indosol	Blue, Red, Yellow	2%	25g
Nylon 6.6	98°C	Acid, Nylosan	Blue, Red, Yellow	2%	25g
Cotton	98°C	Reactive, Drimarene	Blue, Red, Yellow	2%	25g
Nylon 6.6	98°C	Reactive, Drimalan	Blue, Red, Yellow	2%	25g
Cotton	30°C, 40°C, 60°C, 98°C	Sulphur, Diresul	Black	2%, 4%	25g

Table 2. Dyeing Trials with Nylon Chips

Samples of the fabrics dyed in accordance with the details shown in Table 2 were compared with identical fabric samples dyed in accordance with the methods of the prior art, using aqueous dyebaths. The results were very favourable in terms of visual appearance, with the samples dyed according to the method of the present invention being equivalent in terms of colour strength and levelness. It was observed, however, that deeper shades were obtained with the polyester samples dyed with disperse dyes at higher temperatures according to the method of the present invention, with the samples dyed at 130°C showing the optimum results. Furthermore, it was also apparent that dyeings according to the method of the present invention carried out with 4% dye in the dyebath were not as level as those obtained from dyebaths containing 2% dye.

Quantitative comparisons of colour strength were made in the case of direct dyed cotton in order to more closely evaluate the samples. The results are shown in Table 3, wherein the Fk value represents the colour strength.

Conditions	**Blue (Fk)**	**Red (Fk)**	**Yellow (Fk)**
Normal Dyeing	231.8	132.5	102.8
Coated Chips	121.3	143.7	74.89

Table 3. Colour Strength of Direct Dyed Cotton Samples

Although the value for the blue dye was markedly lower in the case of the blue dye, this did not cause any significant problems in terms of visual effect under the naked eye in view of the inherent strength of the colour.

Evaluations of the wash fastness of both the samples dyed according to the method of the present invention and those dyed by conventional methods was also carried out in order to determine the success of the present method. Wash fastness testing was performed by applying test BS EN ISO 105:C06, and the colour strength of the samples was visually compared thereafter. Again, the samples dyed according to the method of the present invention showed equivalent performance to those processed according to conventional methods.

Again, quantitative comparisons of colour strength were made in the case of direct dyed cotton, and the results are shown in Table 4, wherein the Fk value once again represents the colour strength.

Conditions	Normal (Fk)	Coated Chips (Fk)
Blue, Before	231.8	121.3
Blue, After	135.1	100.9
Red, Before	132.5	143.7
Red, After	52.1	65.32
Yellow, Before	102.8	74.89
Yellow, After	8.661	8.875

Table 4. Colour Strength of Direct Dyed Cotton Samples before and after Wash-Fastness Testing

From these results, it is possible to see that the fastness properties of the samples dyed using both the conventional procedure and the method of the present invention were found to be similar.

Example 2 – After-Treatments

In order to evaluate the applicability of the method of the present invention to after-treatment procedures, carried out after dyeing operations, tests were carried out on a series of conventionally dyed fabric samples, dyed with the dyes used in Example 1, as shown in Table 2. Samples of each of the dyeings were subjected to after-treatment procedures either according to the method of the present invention, using nylon chips in accordance with the procedures previously detailed, or by means of conventional after-treatment methods, which are widely documented and will be well known to those skilled in the art. Additional comparative data were acquired by performing after-treatment procedures according to the method of the present invention at a variety of different temperatures, the details of which are shown in the data presentation of Figure 1.

A visual comparison of the samples following the different post-treatment processes showed very little difference in performance between samples afforded the conventional treatments and those subjected to a post-treatment procedure according to the method of the present invention.

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However, quantitative comparisons of differences in colour strength were again made in the case of direct dyed cotton, and the results are illustrated in Figure 1, wherein the Fk value once again represents the colour strength.

10 It can be seen from Figure 1 that the results are very similar for each of the after-treatment methods, with unbound dye being successfully removed in every case. However, the results which were most similar to those of the conventional process were observed when the treatment temperature was the closest to that used by the conventional process.

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Example 3 – Dyeing and After-Treatments

A further set of tests was carried out using Acid Dyes on Nylon 6.6 Fibres, wherein the effects of processing the fibres according to the method of the present invention
20 at either the dyeing or post-treatment stage, or at both those stages, were compared with the performance of fibres processed conventionally at each stage.

For the purposes of this evaluation, the dyes used were Nylanthrene Blue C-GLF (C.I. Acid Blue 281), Nylanthrene Red C-RA, and Nylanthrene Yellow (C.I. Acid
25 Orange 67), all of which are available from Yorkshire Chemicals Plc. Conventional dyeing treatments and post-treatments were carried out in accordance with the instructions of the manufacturer. The method of the present invention was in accordance with the following procedures:

30

Dyeing

The wetted fabric was entered into the dyebath at 40°C and the temperature was maintained at 40°C for 10 minutes, then increased to 98°C at a rate of 2°C per minute, and then maintained at 98°C for 60 minutes, before being cooled to 70°C, whereupon the fabric was removed and rinsed.

After-Treatment

The wetted dyed fabric was entered into the post-treatment bath at 40°C and the temperature was maintained at 40°C for 10 minutes, then increased to 70°C at a rate of 2°C per minute, and then maintained at 70°C for 20 minutes, after which time the fabric was removed and rinsed.

In each case, the tests were carried out using nylon chips as the bath medium, and the ratio of chips to fibre was 5:1 w/w. The following test combinations were used, both with 2% and 4% dye.

1. Normal dyeing and normal after-treatment with syntans – blue/red/yellow dyes;
2. Nylon chips dyeing and normal after-treatment with syntans – blue/red/yellow dyes;
3. Normal dyeing and after-treatment with syntans and nylon chips (replacing water), 20 minutes, 70°C – blue/red/yellow dyes;
4. Normal dyeing and after-treatment with syntans and nylon chips (replacing water), 30 minutes, 70°C – blue/red/yellow dyes;
5. Normal dyeing and after-treatment with syntans and nylon chips (replacing water), 40 minutes, 70°C – blue/red/yellow dyes; and
6. Normal dyeing and after-treatment only with nylon chips.

Comparative data are presented in Figure 2 for the tests carried out with 4% Nylanthrene Blue C-GLF. Again, the Fk value represents the colour strength. The

results which were obtained are representative of those observed with the other dyes as detailed above.

It can be seen from Figure 2 that the samples obtained from dyeing processes using nylon chips are very similar to those dyed via standard procedures. When comparing the after-treatment processes, it was evident from visual observations that dye was removed from the fabric in all cases. In those cases where higher colour strength is shown in Figure 1 following after-treatment, the likely explanation is that the removal of dye from the fabric caused dye to migrate from the inside of the fibre to the surface. It is the case that dye was removed by each of the tested procedures, including that in which only nylon chips were present. It is also apparent from Figure 2 that the wash-fastness of the samples was not good; however, it is seen to have been similar in all cases, irrespective of the procedure which was used.

The results obtained have shown that the treatment of natural and synthetic textile polymers can be successfully carried out by the method of the present invention, thereby eliminating the requirement for the use of large volumes of water in such processes, with the result that environmentally beneficial procedures have been developed for carrying out these treatments, with additional benefits also accruing in terms of reduced costs.

CLAIMS

1. A method for the application of at least one substance to a substrate, said method comprising the treatment of said substrate with a formulation comprising a multiplicity of polymeric particles, said polymeric particles being coated with said at least one substance.

2. A method as claimed in claim 1 wherein said substrate comprises a plastics material, leather, paper, cardboard, metal, glass or wood.

3. A method as claimed in claim 1 wherein said substrate comprises a textile fibre.

4. A method as claimed in claim 3 wherein said textile fibre comprises a natural fibre.

5. A method as claimed in claim 4 wherein said natural fibre comprises cotton.

6. A method as claimed in claim 3 wherein said textile fibre comprises a synthetic fibre.

7. A method as claimed in claim 6 wherein said synthetic fibre comprises nylon 6.6 or a polyester.

8. A method as claimed in any one of claims 1 to 7 wherein said substance comprises a dye.

9. A method as claimed in claim 8 wherein said dye comprises a direct dye, an acid dye, a reactive dye, a disperse dye or a sulphur dye.

10. A method as claimed in any one of claims 1 to 7 wherein said substance comprises a pigment.

11. A method as claimed in any one of claims 1 to 7 wherein said substance comprises a chemical for treatment of the substrate.

12. A method as claimed in claim 11 wherein said chemical comprises a textile finishing agent, a scouring agent, a bleach, a detergent, a perfume or a fragrance.

13. A method as claimed in claim 11 wherein said treatment of the substrate comprises post-dyeing treatment of a textile fabric, and said chemical comprises a chemical for said post-dyeing treatment.

14. A method as claimed in any one of claims 1 to 13 which additionally comprises a pre-treatment step, wherein said substrate is subjected to an aqueous wetting treatment.

15. A method as claimed in claim 14 wherein said aqueous wetting treatment comprises applying water to said substrate.

16. A method as claimed in claim 14 or 15 wherein excess of said aqueous liquor is removed from the substrate prior to treatment of the substrate with the formulation comprising a multiplicity of polymeric particles.

17. A method as claimed in any one of claims 14 to 16 wherein the water content of the substrate does not exceed 2% w/w during the treatment of the substrate with the formulation comprising a multiplicity of polymeric particles.

18. A method as claimed in claim 17 wherein said water content is not in excess of 1% w/w.

19. A method as claimed in claim 18 wherein said water content does not exceed 0.5% w/w.

20. A method as claimed in any one of claims 1 to 19 wherein each of said polymeric particles is coated with said at least one substance.

21. A method as claimed in claim 20 wherein said polymeric particles are coated with said substance by mixing with 0.5%-10% of the substance.

22. A method as claimed in claim 21 wherein said polymeric particles are coated with said substance by mixing with 1%-5% of the substance.

23. A method as claimed in claim 22 wherein said polymeric particles are coated with said substance by mixing with around 2% of the substance.

24. A method as claimed in any one of claims 20 to 23 wherein said polymeric particles are coated with said substance by mixing with said substance and the resulting mixture is held at a temperature of between 30° and 70°C.

25. A method as claimed in claim 24 wherein said temperature is between 40° and 60°C.

26. A method as claimed in claim 25 wherein said temperature is in the region of 50°C.

27. A method as claimed in any one of claims 24 to 26 wherein said polymeric particles are coated with said substance by mixing with said substance at said temperature for a time of between 15 and 60 minutes.

28. A method as claimed in claim 27 wherein said time is between 20 and 40 minutes.

29. A method as claimed in claim 28 wherein said time is approximately 30 minutes.

30. A method as claimed in any one of claims 20 to 29 wherein the ratio of coated particles to textile fibre is in the range of from 20:1 to 1:1 w/w.

31. A method as claimed in claim 30 wherein said ratio is in the region of from 10:1 to 2:1 w/w.

32. A method as claimed in claim 31 wherein said ratio is 5:1 w/w.

33. A method as claimed in any one of claims 1 to 32 wherein said polymeric particles comprise particles of polyalkenes polyesters or polyurethanes, or their copolymers.

34. A method as claimed in anyone of claims 1 to 32 wherein said polymeric particles comprise polyamide particles or their copolymers.

35. A method as claimed in claim 34 wherein said polyamide particles comprise particles of nylon.

36. A method as claimed in claim 35 wherein said particles of nylon comprise nylon chips.

37. A method as claimed in claim 35 or 36 wherein said nylon comprises Nylon 6 or Nylon 6.6.

38. A method as claimed in any one of claims 35 to 37 wherein said nylon comprises Nylon 66 homopolymer.

39. A method as claimed in claim 38 wherein said Nylon 66 homopolymer has a molecular weight in the region of from 5000 to 30000 Daltons.

40. A method as claimed in claim 39 wherein said molecular weight is in the region of from 10000 to 20000 Daltons.

41. A method as claimed in claim 40 wherein said molecular weight is in the region of from 15000 to 16000 Daltons.

42. A method as claimed in any preceding claim wherein said particles or chips are in the shape of spheres or cubes.

43. A method as claimed in any one of claims 1 to 41 wherein said particles or chips are in the shape of cylinders.

44. A method as claimed in claim 43 wherein said cylindrically shaped particles or chips have an average particle diameter in the region of from 1.5 to 4.0 mm.

45. A method as claimed in claim 44 wherein said average particle diameter is in the region of from 2.0 to 3.0 mm.

46. A method as claimed in any one of claims 43 to 45 wherein the length of said cylindrical particles or chips is in the range of from 2.0 to 6.0 mm.

47. A method as claimed in claim 46 wherein said length is in the range of from 3.0 to 5.0 mm.

48. A method as claimed in claim 47 wherein said length is in the region of 4.0 mm.

49. A method as claimed in any preceding claim wherein said particles or chips have an average weight in the region of from 20 to 50 mg.

50. A method as claimed in claim 49 wherein said average weight is in the region of from 30 to 40 mg.

51. A method as claimed in any preceding claim which comprises a batchwise process.

52. A method as claimed in any one of claims 1 to 50 which comprises a continuous process.

53. A method as claimed in any preceding claim wherein said method is carried out in an apparatus or container which encourages Newtonian Flow.

54. A method as claimed in claim 53 wherein said process is carried out in a fluidised bed.

55. A formulation for the application of at least one substance to a substrate, said formulation comprising a multiplicity of polymeric particles, said polymeric particles being coated with said at least one substance.

56. A formulation as claimed in claim 55 wherein said substrate comprises a textile fibre.

57. A formulation as claimed in claim 55 or 56 wherein said substance comprises a dye.

58. A formulation as claimed in claim 55 or 56 wherein said substance comprises a pigment.

59. A formulation as claimed in claim 55 or 56 wherein said substance comprises a chemical for treatment of the substrate.

60. A formulation as claimed in any one of claims 55 to 59 for application to a substrate according to the method as claimed in any one of claims 1 to 54.

61. A treated substrate whenever obtained by a method as claimed in any one of claims 1 to 54.

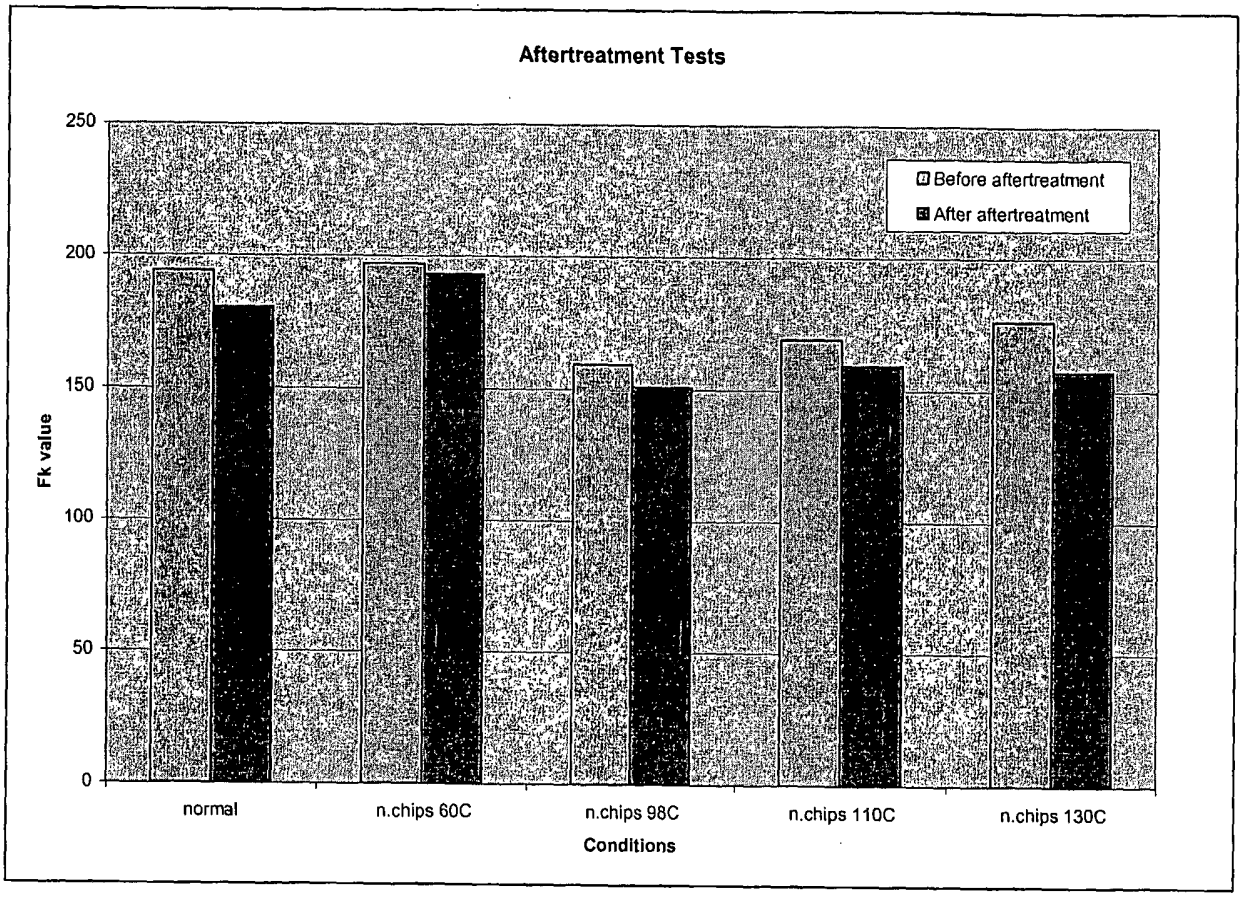

Figure 1. Comparison of Conventional After-Treatment Procedures with Procedures according to the Invention

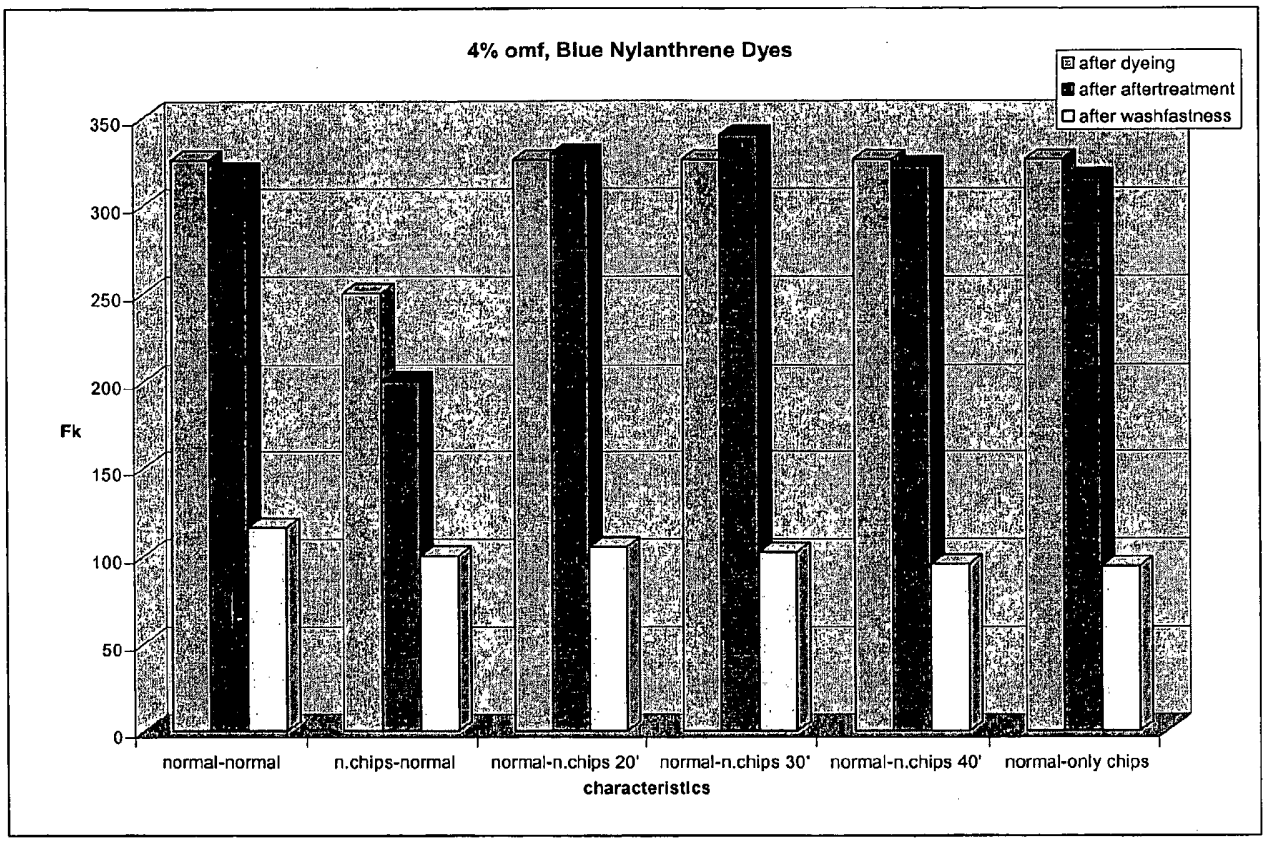

Figure 2. Dyeing and After-Treatment Studies with Nylanthrene Dyes on Nylon 6.6 Fibres

INTERNATIONAL SEARCH REPORT

Inte onal application No
P(GB2005/003906

A. CLASSIFICATION OF SUBJECT MATTER
D06P1/00 D06P5/02 D06M23/08 D21H21/50 C14C11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D06P D06M D21H C14C C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

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X	WO 03/057815 A (CIBA SPECIALTY CHEMICALS HOLDING INC; KVITA, PETR; MENGE, ULLRICH; ROH) 17 July 2003 (2003-07-17) examples ----- -/--	1-7, 11-15, 20-32, 42-56, 59-61

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
27 January 2006	08/02/2006

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