Europäisches Patentamt European Patent Office

Office européen des brevets



EP 0 945 542 A1 (11)

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication: 29.09.1999 Bulletin 1999/39

(21) Application number: 96938219.1

(22) Date of filing: 13.11.1996

(51) Int. Cl.⁶: **D06L 1/14**, D06P 3/54, D06P 1/667, D06P 1/00

(86) International application number: PCT/ES96/00211

(87) International publication number: WO 98/21395 (22.05.1998 Gazette 1998/20)

(84) Designated Contracting States: BE DE ES FR GB IT NL

(71) Applicant: **CLARIANT INTERNATIONAL LTD.** 4132 Muttenz (CH)

(72) Inventors:

· ESCARRER PIJOAN, Josep E-08640 Olesa de Montserrat (ES) MENDIETA CADENA, Luis E-08340 Vilassar de Mar (ES)

(74) Representative: D'haemer, Jan Constant Clariant International Ltd.. Rothausstrasse 61 4132 Muttenz 1 (CH)

PROCESS FOR SIMULTANEOUSLY DESIZING AND DYEING SYNTHETIC FIBERS AND (54)**MIXTURES THEREOF**

(57)A process for the desizing and simultaneous dyeing of synthetic fibres and their mixtures, in which it is envisaged that these fibres are pure polyesters and polyamides or polyester/viscose or polyamide/polyacrylic mixtures. The invention is based on the development and application of a new detergent/humectant surfactant which has a dispersant effect far higher than those usually employed. This surfactant is made up on the basis of an alcohol with 8 to 14 carbon atoms, with 2 to 10 moles of propylene oxide mixed with an alcohol between 7 and 15 oxyethilated carbon atoms with 1 to 8 moles of ethylene oxide and then phosphated and/or phosphorylated.

The use of this surfactant with other selected products enables desizing and dyeing to be undertaken in processes in succession, with improvements on conventional processes, and savings in time and water are to be stressed.

25

Description

[0001] This invention refers to a process for the simultaneous desizing and dyeing of synthetic fibres and their mixtures, in general, and, more specifically, in polyester fibres and their mixtures with viscose and in polyamide fibres and their mixtures with elastomer fibres.

[0002] The invention develops a dyeing system without having to carry out prior boiling out and desizing, with the resulting savings in material, energy and time compared to conventional methods.

[0003] The invention is based on the development and application of a new detergent/humectant surfactant with a dispersant effect much greater than those known and used at the present time.

[0004] In the current state-of-the-art, it is well known that, prior to dyeing, heat treatments are necessary to ensure the dimensional stability of polyester fibres. These forming and fixing treatments are usually performed with hot air between 180 and 210°C in a Tentering Machine.

[0005] It is also well known that these fibres are deoiled and desized in weakly alkaline media, for example, in a sodium carbonate solution in the presence of non-ionic detergents, operating at temperatures from 80 to 100°C, in the case of pure polyester fibres, and at lower temperatures in certain mixtures with other natural or synthetic fibres.

[0006] Plastosoluble dyes and disperse dyes which are incorporated under pressure at a high temperature (in the order of 130°C) are used for dyeing these fibres, amongst others.

[0007] In the case of blends with viscose, it must be borne in mind that they are desized in the presence of non-ionic detergents at temperatures between 60 and 80°C, in a neutral medium, and direct dyes as well as sulphur or vat dyes or reactive dyes which may form chemical links with cellulose fibres are used for dyeing them.

[0008] Polyamide fibres are desized in strongly alkaline media at 80-100°C. Acid type dyes are used for subsequent dyeing, in the presence of combining agents and at temperatures between 100 and 110°C in circulation machines.

[0009] The use of these fibres in mixtures with other fibres requires specific treatment of the second component. Elastomer fibres are desized in a reducing acid medium, using a non-ionic detergent medium. They are usually boiling dyed with the purpose of increasing dye permeability whilst the medium's acidity is maintained.

[0010] It must be added, in the state-of-the-art, that the desizing process calls for different techniques because of the diverse nature of the sizing products. For example, in viscose fibres, soluble cellulose esters are used, in polyesters, acrylic esters and polyester resins are used, and in polyamides, polyacrylic acids are employed.

[0011] In the same way, two large groups of dyes may be distinguished for dyeing, water soluble and insoluble dyes, using processing technologies in a discontinuous or continuous treatment in machines at atmospheric pressure or low pressure at temperatures over 100°C. In the first case, there are machines with bath circulation or with material circulation and dyeing at high temperature is usually performed in an autoclave working by bath circulation. In other cases, the wet, discontinuous treatment is performed by making the textile fabric continuously circulate in the form of a cord through nozzle or jet staining facilities.

[0012] As stated at the beginning, the process described in this Specification, protection of which is being applied for, refers to a system for simultaneous desizing and dyeing of synthetic fibres and their mixtures.

[0013] Extensive research into dyeing processes in polyester and polyamide fibres and their mixtures with viscose and elastomer fibres respectively have enabled a new surfactant (detergent/humectant) to be discovered. Such agent has a great dispersant effect, much greater than those usually employed.

[0014] The agent is made up on the basis of an alcohol with 8 to 14 carbon atoms with 2 to 10 ethylene oxide moles plus 1 to 7 propylene oxide moles, mixed with an alcohol between 7 and 15 oxyethylenated carbon atoms with 1 to 8 moles of ethylene oxide and then phosphated and/or phosphorylated.

[0015] The combination of this new agent and the selection of other products used, which will be described later, enabled desizing and dyeing to be undertaken in successive processes, both in autoclave processes and in nozzle or jet staining processes.

[0016] The process described as a new invention displays many, major improvements over the conventional processes. Some of these advantages may be cited, without their description representing a limitation on the content of this invention.

40 [0017] Firstly, as a prior desizing and the pertinent washings are not performed, the process time is reduced by over 1 hour, since the prior boiling out used in the conventional process requires an estimated time of 1 hour 50 minutes, and there is also a saving in water estimated at 30 litres/kg of material, since the water used in the process according to this invention is the same as that in the dyeing process.

[0018] Secondly, prior identification of the type of synthetic sizer, for instance, polyester sizers, acrylates, poly (alcohol vinyl) and their mixtures is not necessary.

[0019] Another advantage consists in the reduction in the amount of acid necessary to obtain a suitable pH for dyeing.

[0020] A reduction in differential pressures occurs in autoclave dyeing, as a result of the effect that the surfactant which is the subject of this invention produces on the sizers and other materials or dirt.

[0021] Likewise, filtrates from the sizing agent which

10

15

20

25

are produced at the bottom of the packet (fabric in contact with the material holder) are totally removed.

[0022] Other advantages relate to the improvement in the dispersion of dyes and to the fact of eliminating antireducing treatments on polyester/FIBRANE articles, 5 thus avoiding reducing dyes without the need to undertake any special treatment.

[0023] Finally, it must be pointed out that the process allows the raw fabric to be heat set with no subsequent difficulties involved in removing the sizers.

[0024] To summarize, as a consequence of the advantages listed above, the new process described in this specification represents a reduction in processing time by about 4 hours in comparison with known processes, and a reduction in water consumption by 30 litres of water per Kg. of material treated.

[0025] Some examples of embodiment are described for a clearer presentation. They do not represent any limiting aspect on other possible applications.

EXAMPLE 1

<u>Process for pure polyester (100%) in a nozzle or jet process.</u>

[0026] The apparatus is filled by adding the surfactant at a concentration of 1.5 gm./litre and the textile material is then loaded, heating to 50°C at a heating rate of 2°C/minute, keeping it in circulation for 5 minutes. One percent (1%) of a levelling/dispersant agent is then added, formed by a mixture of an ethoxylated fatty acid with non-ionic surfactants or on the basis of a linear polycondensate in an aqueous solution, 0.3 to 1.0% of a fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate and acetic acid to obtain a pH of 5. After circulating the textile material for 5 minutes at 50°C, a required % of dispersed dye is added and the temperature is raised to 130°C at a rate of 2°C/minute, keeping the system at 130°C for 30-45 minutes and then cooling down to 80°C when the system is emptied, washed and discharged.

EXAMPLE 2

<u>Process for pure polyester (100%) in a nozzle or jet process.</u>

[0027] A variant on Example 1 is to fill the apparatus initially with 1.5 gm/litre of surfactant and 0.3-1% of the fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate. The textile material is loaded, and the temperature is raised up to 50°C by heating at 2°C/minute and keeping it in circulation for 5 minutes, then adding 1% of one of the levelling/dispersant agents described in example 1, adjusting the pH to a value of 5 with acetic acid and circulating the material for another 5 minutes. A suitable percentage of the dispersed dye is added, the temperature is raised up to 130°C by heating

at a rate of 2°C/minute and the system is kept at 130°C for 30-45 minutes, after which it is cooled down to 80°C, emptied, washed and discharged.

EXAMPLE 3

Process for pure polyester (100%) in an autoclave.

[0028] The same stages are followed and means used as described in Example 1.

EXAMPLE 4

Process for pure polyester (100%) in a nozzle or jet process in the presence of acrylic sizers.

[0029] This example is a modification of Example 2, when some types of acrylic sizers are used.

[0030] The apparatus is filled with 1.5 gm/litre of the surfactant, 0.3-1% of the fold/sliding inhibitor agent and 1% of any of the levelling/dispersant agents described in example 1. The pH is adjusted to between 4.5 and 5 with acetic acid and the system circulated for 5 minutes at 50°C. The required percentage of dispersed dye is added, the temperature is raised up to 130°C by heating at a rate of 2°C/minute.

[0031] The system is maintained at 130°C for 30-45 minutes and then cooled to 80°C and 4 gm/litre of sodium carbonate is added and the system circulated for 10 minutes, after which it is emptied, washed and discharged.

EXAMPLE 5

Process for polyester/viscose blends in a nozzle or jet process with dispersed and direct dyes.

[0032] The apparatus is filled with 1.5 gm/litre of the surfactant and loaded with the textile material. The temperature is raised by heating to 40°C at a rate of 2°C/minute and circulating for 5 minutes. One percent (1%) of levelling/dispersant agent on the basis of a mixture of ethoxylated fatty acid with non-ionic surfactants, 0.3 to 1% of the fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate or a levelling/fold inhibitor agent on the basis of a sulphonated fatty acid and acetic acid to fix a pH of 5 are added, and the system is circulated for 5 minutes.

[0033] The required percentages of the dispersed dye and the direct dye are added, then the temperature is raised up to 130°C by heating at 2°C/minute, keeping the system at this temperature for 15 to 40 minutes and then cooling to 60°C, emptying and washing, fixing if necessary and finally discharging.

5

20

25

35

40

45

50

55

EXAMPLE 6

Process for polyester/viscose blends in a nozzle or jet process with disperse and reactive dyes.

[0034] The apparatus is filled by adding 1.5 gm/litre of the surfactant, loading the textile material and heating to 50°C at 2°C/minute. At that temperature, the system is circulated for 5 minutes and 1% of a levelling/dispersant agent on the basis of a blend of ethoxylated fatty acid with non-ionic surfactants and 0.3-1% of a fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate are added and the pH is adjusted to 5 using acetic acid. After 5 minutes, a suitable percentage of the dispersed dye is added, heating to 130°C at 15 2°C/minute, maintaining the system for 30 to 45 minutes after which it is cooled to 80°C, emptied and washed. It is then filled and 50-100 gm/litre of sodium chloride or sulphate are added at 40°C. It is circulated for 5 minutes and then 1% of a levelling/fold inhibitor agent on the basis of a sulphonated fatty acid and the suitable percentage of the reactive dye are added, circulating again for 10 minutes at 40°C. An alkali is added, it is circulated for a further 10 minutes and heated to 60°C at 2°C/minute. The system is once again circulated for a further 45 minutes after which it is emptied, washed and kept for 10 minutes at 50°C.

[0035] It is filled again, and 1 gm/litre of a dispersant/sequestering agent on the basis of poly(hydroxycarboxylate), hydroxypolycarboxilate, polycarboxilate and phosphonate with water is added, heated to 80°C and circulated for 10 minutes after which it is washed, kept at 70°C a further 10 minutes, washed again and the system kept at 40°C a further 10 minutes, after which it is discharged.

EXAMPLE 7

Process for polyamide or polyamide/elastomer mixtures in a nozzle or jet process or in an autoclave.

[0036] The system is filled and 1.5 gm/litre of the surfactant is added. The textile material is loaded, the temperature is raised to 30°C, circulating is performed for 5 minutes after which a suitable percentage of the levelling agent, acetic acid, 1.5 gm/litre of sodium acetate, 0.3 to 1% of a fold/sliding inhibitor on the basis of alkylenepolyglycolether oleate and a suitable percentage of acid dye are added. It is heated to 110°C at 1°C/minute and this temperature is maintained between 45 and 60 minutes and then cooled down to 60°C, and the system is emptied, washed and finally discharged.

Claims

1. A process for simultaneously desizing and dyeing synthetic fibres and their blends characterized because a high dispersant power surfactant is used together with other auxiliary products. This surfactant is composed of an alcohol of 8 to 14 carbon atoms with between 2 and 10 moles of ethylene oxide plus 1 to 7 moles of propylene oxide mixed with an alcohol of between 7 and 15 atoms of carbon, oxyethylenated with 1 to 8 moles of ethylene oxide and then phosphated and/or phosphorylated. This agent will be used in a concentration of 1.5 gm/litre.

- A process according to the foregoing claim characterized because the treated fibres are pure polyesters and polyamides or polyester/viscose or polyamide/elastomer mixtures and the treatment will be performed by an autoclave process or nozzle or jet system.
- Process according to the foregoing claims, characterized because, for the pure polyester treatment, the system is filled and the surfactant is added at a concentration of 1.5 gm./litre, and the system heated to a temperature of 50°C at a rate of 2°C/minute and after circulating the system for 5 minutes, a levelling/dispersant agent on the basis of a mixture of an ethoxylated fatty acid with non-ionic surfactants, a levelling/dispersant agent on the basis of a linear polycondensate in an aqueous solution and a fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate are added, adjusting the pH to a value of 5 by means of acetic acid whilst, after 5 minutes, a suitable percentage of a dispersed dye is added and the temperature is raised to 130°C by heating at 2°C/minute. After maintaining this temperature for 30 to 45 minutes, it is cooled down to 80°C, and the system is emptied, washed and then discharged.
- Process according to the previous claims, characterized because in pure polyesters treated with acrylic sizers, the surfactant and a fold/sliding inhibitor agent on the basis of an alkylenepolyglycolether oleate, a levelling/dispersant agent on the basis of a linear polycondensate or on the basis of a mixture of ethoxylated fatty acid with non-ionic surfactants are initially added. At the end of the dyeing operation, sodium carbonate is added in a concentration preferably of 4 gm/litre.
- A process according to the foregoing claims, characterized because for dyeing polyester/viscose mixtures, a levelling/dispersant agent on the basis of an ethoxylated fatty acid with non-ionic surfactants at 1%, a fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate or a levelling/fold inhibitor agent on the basis of a 0.3-1.0% sulphonated fatty acid are added, after the first load cycle with the surfactant has finished. Dispersed and direct dyes are used and sodium sulphate or

sodium chloride are added after fixing the dyes.

- 6. Process according to claim 5, characterized because a disperse dye is used for polyester/viscose mixture dyeing and sodium chloride or sulphate is added. One percent (1%) of a levelling/fold inhibitor agent on the basis of a sulphonated fatty acid and reactive dye is added, and are circulated for 10 minutes at 40°C, after which the necessary amount of sodium carbonate or sodium hydroxide is added as an alkali for fixing the reactive dye. It is then all circulated for 45 minutes at 60°C and 1 gm/litre of a dispersant/sequestering agent on the basis of polyhydroxycarboxylate, hydroxypolycarboxilate, polycarboxilate and phosphonate with water is then added and circulated for 10 minutes at 80°C, washed and then discharged.
- 7. Procedure according to previous claims, characterized because, for polyamide or polyamide/elastomer mixture dyeing, the system is filled with 1.5 gm/litre of the surfactant, the textile material is loaded and the temperature is raised to 30° by heating. A suitable percentage of a dye levelling agent, the acetic acid necessary to control the medium's pH, together with 1.5 gm/litre of sodium acetate of 0.3 to 1% of a fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate and a certain percentage of an acid dye are added, the temperature is raised to 110°C by heating at a rate of 1°C/min. and this temperature is maintained for 45 to 60 minutes and then the system is cooled to 60°C, emptied, washed and discharged.
- 8. A process according to claim 7, in which 1.5 gm/litre 35 of the surfactant is initially added together with 0.3 to 1% of a fold/sliding inhibitor agent on the basis of alkylenepolyglycolether oleate.

40

45

50

55

EP 0 945 542 A1

Inte onal Application No INTERNATIONAL SEARCH REPORT PCT/ES 96/00211 A. CLASSIFICATION OF SUBJECT MATTER IPC 6 D06L1/14 D06P3/54 D06P1/00 D06P1/667 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) IPC 6 DO6L D06P 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) C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category Citation of document, with indication, where appropriate, of the relevant passages 1 EP 0 210 318 A (MEISEI CHEMICAL WORKS LTD) A 4 February 1987 see the whole document CHEMICAL ABSTRACTS, vol. 81, no. 14, 1 A 7 October 1974 Columbus, Ohio, US; abstract no. 79299h, page 80: XP002036076 see abstract & JP 48 042 274 B (TEIJIN LTD.) 11 December 1973 1 A GB 1 589 020 A (OEFFENTILICHE PRUEFSTELLE UND) 7 May 1981 see claims -/--Patent family members are listed in annex. X Further documents are listed in the continuation of box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled "O" document referring to an oral disclosure, use, exhibition or in the art. document published prior to the international filing date but later than the priority date claimed "A" document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search

Form PCT/ISA/218 (second sheet) (July 1992)

25 July 1997

European Patent Office, P.B. 5818 Patendaan 2 NL - 2280 HV Rijewijk Tal. (+31-70) 340-2040, Tx. 31 651 epo nl, Faze (+31-70) 340-3016

Name and mailing address of the ISA

0 5. 08. 97

Authorized officer

Blas, V

EP 0 945 542 A1

INTERNATIONAL SEARCH REPORT

Intr onal Application No PCT/ES 96/00211

		PCT/ES 96/00211				
C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT						
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.				
A	FR 2 641 476 A (SANDOZ SA) 13 July 1990 see the whole document	1				
A	GB 1 594 596 A (PROD SANDOZ SA) 30 July 1981 see page 4, line 56 - line 60; claims	1				
A	GB 2 121 835 A (SANDOZ LTD) 4 January 1984 see the whole document	1				
A	GB 2 079 328 A (SANDOZ LTD) 20 January 1982					

Form PCT/ISA/2i0 (continuation of record sheet) (Jely 1992)

EP 0 945 542 A1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intu !onal Application No PCT/ES 96/00211

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0210318 A	04-02-87	NONE	
GB 1589020 A	07-05-81	DE 2727112 A BE 863626 A CH 641306 A,B FR 2394637 A NL 7800085 A	11-01-79 29-05-78 29-02-84 12-01-79 19-12-78
FR 2641476 A	13-07-90	CH 679155 A DE 4000061 A GB 2228274 A,B IT 1241396 B JP 2229537 A US 5259963 A	31-12-91 19-07-90 22-08-90 10-01-94 12-09-90 09-11-93
GB 1594596 A	30-07-81	AR 221695 A BE 863589 A BR 7800720 A DE 2803309 A FR 2393877 A JP 53126394 A US 4168142 A	13-03-81 02-08-78 31-10-78 10-08-78 05-01-79 04-11-78 18-09-79
GB 2121835 A	04-01-84	DE 3319851 A FR 2528459 A JP 59026580 A US 4501589 A	15-12-83 16-12-83 10-02-84 26-02-85
GB 2079328 A	20-01-82	DE 3124961 A FR 2486116 A JP 57042988 A	09-09-82 08-01-82 10-03-82

Form PCT/ISA/210 (patent family annex) (July 1992)