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(54) **A PROCESS FOR NON-UNIFORM DYEING OF TEXTILE PRODUCTS**

VERFAHREN ZUR NICHT EINHEITLICHEN FÄRBUNG VON TEXTILEN ERZEUGNISSEN

PROCEDE DE COLORATION NON UNIFORME DE PRODUITS TEXTILES

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(56) References cited:
EP-A2- 0 298 412 WO-A-98/45527
GB-A- 1 337 702 GB-A- 1 505 497
US-A1- 2003 171 249

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DescriptionTechnical Field

[0001] The invention relates to a process for non-uniform dyeing of textile products.

Background Art

[0002] It is well-known that for some types of textiles or articles of clothing, such as for example trousers, jerkins, pullovers, an artificial ageing treatment is required, which is obtained by localized discolouring or de-colouring of the original and already-dyed material.

[0003] A process for obtaining this effect is the one known as "stone-washing". This process consists in immersing the textile products in water or in a bath containing a chemical agent which decolours and/or bleaches, such as for example, a hypochlorite solution, and agitating the articles together with granules or stones made of an abrasive material and having sizes of between 1 and 10 cm. This process produces textile products that are discoloured or lightened in colour, with dark-light tones at the stitching areas and with uniformity of colour contrast in the remaining part of the textile product, typical of the natural wear to which the textiles are subjected during use.

[0004] The prior art also describes a dry decolouring process for textiles, i.e. without immersion in a water-based bath as happens in the stone-washing process.

[0005] This process is described in EP-A-0238779. The process consists in bringing the already-dyed textile products into random contact with a granular material which is permeable, porous and highly-absorbent, such as for example pumice granules, which has been first impregnated with a de-colouring chemical agent. The textile products can be in the dry or damp state when they come into contact with the porous granular material and the contact is prolonged for a time sufficient for obtaining the desired effect.

[0006] With this process a particular type of discolouring of the textile product is obtained, consisting in an irregular de-colouring characterised by a non-uniform staining effect that is irregularly distributed over all the textile product.

[0007] Only the zones that come into contact with the porous granular material containing the bleaching agent are decoloured by combined chemical effect of the bleach and mechanical effect of the porous material, while the remaining zones are left unchanged.

[0008] The processes of the known art exhibit some drawbacks which limit the use thereof.

[0009] They are, in fact, difficult to apply to delicate textiles, such as wool, which cannot survive the bleaching treatment with aggressive chemical agents and/or the mechanical abrading action exerted by the granules.

Disclosure of invention

[0010] There is, therefore, a strong need to have available a process which enables the ageing effect to be obtained with delicate textiles such as wool, without any need to use bleaching treatments and/or to employ mechanical actions based on abrasion.

[0011] The aim of the present invention is to provide a process having structural and functional characteristics such as to satisfy the above-mentioned requirements and also such as to obviate the drawbacks mentioned with reference to the prior art.

[0012] The aim is attained by the process for non-uniform dyeing of textile products as set out in claim 1.

[0013] The dependent claims delineate preferred embodiments which are particularly advantageous of the process for non-uniform dyeing of textile products of the invention.

Best Mode for Carrying Out the invention

[0014] Further characteristics and advantages of the invention will emerge from a reading of the following description, which is provided by way of non-limiting example.

[0015] For the purposes of the following description the term "textile products", refers to textiles in the form of cloth as well as already-made articles of clothing, such as trousers, jeans, jackets, jerkins, shirts, skirts, overcoats, pullovers and so on.

[0016] In its broadest aspect, the process of the present invention enables non-uniform dyeing of textile products as set out in claim 1.

[0017] By the term "inert" in relation to dyeing, a resistance to dyeing by the usual dyes commonly used for colouring textiles is meant.

[0018] Substantially, a part of dye-inert textile will not absorb the dye colour and therefore will not be coloured.

[0019] It is specified that in the present invention the parts of textile wet with the inertizer can be made totally inert to the dye, and will not colour, or can be made partially inert to the dye, and will colour more blandly than the parts of the same textile which have not come into contact with the inertizer.

[0020] This enables a "modulating" of the process of the present invention according to a desired final effect, enabling zones of different intensities to be obtained in the dyed textile.

[0021] In order to eliminate any traces of dirt, especially water-repellent dirt, such as, for example, oily residues, the textile products are subjected to a preliminary wash using water and detergent or a dry-cleaning process.

[0022] Thereafter the washed products are dried before being placed in the drum with the granules. However, it is possible to subject still-damp products to the treatment.

[0023] The permeable granules usable in the process of the present invention can be selected according to the

absorption capacity and the resistance to strong acidity, and a subsequent release of the inertizing substance they are drenched with.

[0024] In substance, the permeable granules can be made using any material able to be drenched with a liquid which will have to be released when the granules are made to rotate together with the textile products in the drum.

[0025] Among the materials that can be used for making the granules are porous polymer gels, in particular polyoxometallates (POMs). The size of the granules can be selected according to the desired final result; generally they are between 1 and 30 mm in size.

[0026] According to the present invention, the inertizing substance used for drenching the porous granules is a sulphamic acid in water solution. The quantity of sulphamic acid used is comprised between 1% and 30% of the overall weight of the water solution with which the granules are drenched.

[0027] The quantity of solution used to drench the granules to be placed in the drum for treating the textile products depends on the desired final effect and on the contact time between the drenched granules and the products present in the drum, as well as the rotation velocity of the drum. An example will be reported herein below.

[0028] Usually a sufficient time for obtaining different dyeing intensities is considered to be between 10 minutes and one hour with a drum rotation velocity comprised between 5 and 50 rpm, the drum having a mean diameter of between 50 and 200 cm.

[0029] Once the contact between the granules wet with the sulphamic acid and the textile products has been concluded, the textile products exhibit zones, arranged randomly, which are wet with the sulphamic acid released by the granules. These zones are at least partially inert to dyeing, i.e. it is not possible to die them, or they can be dyed only less intensely.

[0030] In substance, the sulphamic acid behaves as an inhibitor, i.e. it prevents the zones of textile wet by the acid from absorbing the colouring material. Naturally, as the textile is wet by random zone and amount with the sulphamic acid, the final effect after dyeing will be a varied localized intensity of colour which is more or less random.

[0031] This is obtained without occasioning abrasive wear to the textile and without using bleaching and/or decolouring products.

[0032] To make the zones of sulphamic acid-dampened textile impervious to the dye, the already-treated textile products in the drum are dried at a temperature comprised between 100°C and 150°C for a sufficient time to enable the sulphamic acid to bond with the fibres of the textile, preventing the subsequent dyeing thereof.

[0033] By way of example, it is sufficient to dry the textile at a temperature of 135°C for about 25 minutes.

[0034] At the end of the drying period the textile products can be dyed using the typical dyeing techniques and dyes of the sector, and thus not described in detail herein, obtaining textile products that are not uniformly dyed, as

the dye will not take (or will take only partially) in the zones of the textile previously dampened with sulphamic acid.

[0035] In order to optimise the reaction between the sulphamic acid and the fibres of the textile, urea can be used as a catalyst to the reaction.

[0036] Further, to prevent the strong acidity of the sulphamic acid from attacking textile fibres of vegetable origin (cellulosic), the acidity is reduced by adding a base, for example isobutanolamine (2-amine-2methyl -1-propanol).

[0037] In addition, to control the release velocity of the sulphamic acid from the granules to the textile, a compound for increasing the viscosity thereof, such as for example glycerol, is added to the sulphamic acid.

[0038] Further, the water-repellent quality of the textile can be increased, with respect to the sulphamic acid-based solution with which the granules are drenched, by adding chemical compounds which improve the water-repellent properties, such as, for example, caprolactam.

[0039] Herein below two examples are reported, for purposes of non-limiting illustration, of watery solutions used for wetting the granules for the treatment of, respectively, cotton and wool textiles.

1. *Solution used for textile products made of cotton:*

sulphamic acid	6
urea	9
glycerol	3
caprolactam	3
isobutanolamine	9
softened water	70

2. *Solution used for textile products made of wool:*

sulphamic acid	15
urea	10
glycerol	1.5
softened water	73.5

[0040] All the values in the two above-reported examples are expressed in percentages of weight with respect to the solution for drenching the granules. Each of the two above solutions is used for a quantity comprised between 50 and 200 grams per dm³ of polyoxometallate (POM-GEL).

[0041] The process of the present invention can be used for any type of textile material either made of natural fibres (wool, silk, cotton etc) or of synthetic fibres (nylon, polyester etc).

[0042] As can be appreciated from the above description, the process for non-uniformly dyeing textile products of the present invention satisfies the requirements and obviates the drawbacks mentioned in the introduction to the present description with reference to the prior art.

[0043] Indeed, the process of the invention allows an

ageing effect to be obtained in textile products without the use of any bleaches and/or de-colouring agents, such as sodium hypochlorite or potassium permanganate, which inevitably attack the most delicate textile fibres, apart from having a high environmental impact as waste.

[0044] Further, the process of the invention requires no further mechanical abrading action on the textile, such as the effect produced using pumice, and therefore ensures longer life in comparison with textiles treated using traditional processes.

[0045] Obviously an expert in the sector, with the aim of satisfying contingent and specific requirements, might make numerous modifications and changes to the process for non-uniform dyeing of textile products, all relating to the ambit of protection sought for the invention as defined in the following claims.

Claims

1. A process for non-uniform dyeing of textile products, comprising at least the following stages:

- arranging the textile products to be dyed in a chamber together with a plurality of permeable and absorbent granules impregnated with a sulphamic acid solution in water at a quantity comprised between 1% and 30% in weight for rendering the textile to be dyed at least partially inert to dyeing;
- bringing the textile products to be dyed into contact with the granules, the granules and the textile products being moved together in a relatively random way, for a sufficient amount of time to wet parts of the textile of the textile products with the sulphamic acid solution; then
- separating the textile products from the granules;
- drying the textile products at a temperature comprised between 100 °C and 150 °C and for a sufficient amount of a time to cause the sulphamic acid to react with the parts of the textile which were dampened with the sulphamic acid to enable the sulphamic acid to bond with the fibres of the textile to make the zones of sulphamic acid-dampened textile impervious to the dye; and finally
- dyeing the textile products.

2. The process of claim 1, wherein the textile products to be dyed are subjected to washing before being placed in the chamber.
3. The process of claim 1, wherein the textile products are placed in a dry state in the chamber.
4. The process of claim 1, wherein the chamber is a rotating drum.

5. The process of claim 1, wherein the granules are a porous polymer in gel form.

6. The process of claim 5, wherein the granules are based on polyoxometallates (POMs).

7. The process of claim 1, wherein the solution is used in a quantity comprised between 50 and 200 g per dm³ of granules.

8. The process of claim 1, wherein the solution comprises urea as a catalyst for the sulphamic acid-fibre reaction.

9. The process of claim 1, wherein the solution comprises a first base compound for modifying the acidity of the solution containing the acid.

10. The process of claim 10, wherein the first compound comprises isobutanolamine.

11. The process of claim 1, wherein the solution comprises a second compound for increasing a viscosity of the solution.

12. The process of claim 12, wherein the second compound comprises glycerol.

13. The process of claim 1, wherein the solution comprises a third compound for improving water-repellent qualities of the textile with respect to the solution.

14. The process of claim 14, wherein the third compound comprises caprolactam.

15. The process of claim 1, wherein the granules impregnated with the substance are placed in contact with the textile products for a time comprised between 10 minutes and one hour.

Patentansprüche

1. Verfahren zum ungleichmäßigen Färben von Textilprodukten, mindestens die folgenden Schritte umfassend:

- Anordnen der zu färbenden Textilprodukte in einer Kammer zusammen mit mehreren durchlässigen und absorbierenden Körnchen, die mit einer Sulfaminsäurelösung in Wasser in einer Menge zwischen 1 Gew.-% und 30 Gew.-% imprägniert sind, um die zu färbende Textilie zumindest teilweise inert gegenüber dem Färben zu machen,
- In-Kontakt-Bringen der zu färbenden Textilprodukte mit den Körnchen, wobei die Körnchen und die Textilprodukte auf relativ willkürliche

- Weise miteinander bewegt werden, über eine Zeitdauer, die ausreicht, um Teile der Textilie der Textilprodukte mit der Sulfaminsäurelösung zu benetzen, dann
- Trennen der Textilprodukte von den Körnchen,
 - Trocknen der Textilprodukte bei einer Temperatur zwischen 100 °C und 150 °C und über eine Zeitdauer, die ausreicht, um zu bewirken, dass die Sulfaminsäure mit den Teilen der Textilie reagiert, die mit der Sulfaminsäure befeuchtet wurden, um es der Sulfaminsäure zu ermöglichen, an die Fasern der Textilie zu binden, um die Bereiche der mit Sulfaminsäure befeuchteten Textilie für den Farbstoff undurchlässig zu machen, und schließlich
 - Färben der Textilprodukte.
2. Verfahren nach Anspruch 1, wobei die zu färbenden Textilprodukte einem Waschen unterzogen werden, bevor sie in der Kammer platziert werden.
 3. Verfahren nach Anspruch 1, wobei die Textilprodukte in trockenem Zustand in der Kammer platziert werden.
 4. Verfahren nach Anspruch 1, wobei die Kammer eine sich drehende Trommel ist.
 5. Verfahren nach Anspruch 1, wobei es sich bei den Körnchen um ein poröses Polymer in Gelform handelt.
 6. Verfahren nach Anspruch 5, wobei die Körnchen auf Polyoxometallaten (POM) basieren.
 7. Verfahren nach Anspruch 1, wobei die Lösung in einer Menge zwischen 50 und 200 g pro dm³ der Körnchen verwendet wird.
 8. Verfahren nach Anspruch 1, wobei die Lösung Harnstoff als Katalysator für die Sulfaminsäure-Faser-Reaktion umfasst.
 9. Verfahren nach Anspruch 1, wobei die Lösung eine erste basische Verbindung zum Modifizieren des Säuregrades der die Säure enthaltenden Lösung umfasst.
 10. Verfahren nach Anspruch 10, wobei die erste Verbindung Isobutanolamin umfasst.
 11. Verfahren nach Anspruch 1, wobei die Lösung eine zweite Verbindung zum Erhöhen der Viskosität der Lösung umfasst.
 12. Verfahren nach Anspruch 12, wobei die zweite Verbindung Glycerol umfasst.

13. Verfahren nach Anspruch 1, wobei die Lösung eine dritte Verbindung zum Verbessern der wasserabweisenden Eigenschaften der Textilie in Bezug auf die Lösung umfasst.

14. Verfahren nach Anspruch 14, wobei die dritte Verbindung Caprolactam umfasst.

15. Verfahren nach Anspruch 1, wobei die mit der Substanz imprägnierten Körnchen über eine Zeit mit den Textilprodukten in Kontakt gebracht werden, die zwischen 10 Minuten und einer Stunde liegt.

15 Revendications

1. Processus de teinture non uniforme de produits textiles, comprenant au moins les étapes suivantes :

- agencement des produits textiles à teindre dans une chambre conjointement à une pluralité de granulés perméables et absorbants imprégnés d'une solution aqueuse d'acide sulfamique à raison d'une quantité comprise entre 1 % et 30 % en masse pour rendre le textile à teindre au moins partiellement inerte à la teinture ;
- mise en contact des produits textiles à teindre avec les granulés, les granulés et les produits textiles étant mis en mouvement ensemble de manière relativement aléatoire, pendant une durée suffisante pour mouiller les parties de textile des produits textiles avec la solution d'acide sulfamique ; puis
- séparation des produits textiles et des granulés ;
- séchage des produits textiles à une température comprise entre 100 °C et 150 °C pendant une durée suffisante pour provoquer une réaction de l'acide sulfamique avec les parties de textile qui ont été mouillées par l'acide sulfamique, de manière à permettre à l'acide sulfamique de se lier aux fibres du textile pour rendre les zones de textile mouillées à l'acide sulfamique insensibles à la teinture ; et finalement
- teinture des produits textiles.

2. Processus selon la revendication 1, dans lequel les produits textiles à teindre sont soumis à un lavage avant d'être placés dans la chambre.

3. Processus selon la revendication 1, dans lequel les produits textiles sont placés dans la chambre à l'état sec.

4. Processus selon la revendication 1, dans lequel la chambre est un tambour rotatif.

5. Processus selon la revendication 1, dans lequel les

granulés sont constitués d'un polymère poreux sous forme de gel.

6. Processus selon la revendication 5, dans lequel les granulés sont basés sur des polyoxométallates (POM). 5
7. Processus selon la revendication 1, dans lequel la solution est utilisée à raison d'une quantité comprise entre 50 g et 200 g par dm³ de granulés. 10
8. Processus selon la revendication 1, dans lequel la solution comprend de l'urée comme catalyseur pour la réaction entre l'acide sulfamique et la fibre. 15
9. Processus selon la revendication 1, dans lequel la solution comprend un premier composé de base pour modifier l'acidité de la solution contenant l'acide. 20
10. Processus selon la revendication 10, dans lequel le premier composé comprend de l'isobutanolamine.
11. Processus selon la revendication 1, dans lequel la solution comprend un deuxième composé pour augmenter la viscosité de la solution. 25
12. Processus selon la revendication 12, dans lequel le deuxième composé comprend du glycérol. 30
13. Processus selon la revendication 1, dans lequel la solution comprend un troisième composé pour améliorer les qualités hydrofuges du textile par rapport à la solution. 35
14. Processus selon la revendication 14, dans lequel le troisième composé comprend du caprolactame.
15. Processus selon la revendication 1, dans lequel les granulés imprégnés avec la substance sont placés en contact avec les produits textiles pendant une durée comprise entre 10 minutes et une heure. 40

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- EP 0238779 A [0005]