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(54) **Auxiliary support and process for the finishing of textile fabrics by heat transfer.**

(57) The new auxiliary support for the finishing of textile materials comprises a flexible basic substrate and on one of its surfaces a larger ccntaining at least one fluorocarbon resin which is transferable by heat and pressure to the textile material.

The layer on the basic substrate has a thickness of about 2 to 100 micrometers.

EP 0 436 463 A1

AUXILIARY SUPPORT AND PROCESS FOR THE FINISHING OF TEXTILE FABRICS BY HEAT TRANSFER

This invention relates to the finishing of textile fabrics by heat transfer. It is specifically related to a flexible, two-dimensional, normally web-like auxiliary support for the finishing of textile fabrics, and to a particular process for the preparation of such an auxiliary support, further to a process for the finishing of textile fabrics by the method of heat transfer based on the transfer of a finishing agent from the auxiliary support to the textile fabric using the auxiliary support of the invention.

When reference is made hereafter to "textile finishing", the term is to be construed as covering any treatment which improves the usefulness of the textile fabric or the finished product for the manufacturing process or the final application. For example, this term also covers dyeing and printing.

The heat transfer printing of polyester textile fabrics is known from French patents no. FR-A-1,233,330 and 1,585,119. The method is used today by routine and has a great success.

One of the advantages of heat transfer printing is the absence of the environment pollution: The by-products of conventional finishing processes are large amounts of water charged with various forms and quantities of polluting agents which demand special treatments.

The principal by-product of the heat transfer method is only paper which can easily be eliminated by incineration.

In spite of various efforts and until now, heat transfer printing has been limited to polyester fabrics, it has only recently been possible to extend this elegant printing method to other fibers, in particular cotton, silk and wool.

The conventional heat transfer printing of polyester fabrics is based on the transfer of dyestuff from the auxiliary support to the textile fabric by sublimation. Intensive studies have shown that it is impossible to select from the family of dyestuffs which sublimate at atmospheric pressure, a group for the heat transfer printing of cotton, the most important natural fiber, which gives prints of satisfactory washfastness.

EP-A-0,146,509 teaches a heat transfer printing process for fibers of cellulose or mixtures of cellulose and polyester. This patent describes a process based on the transfer of a printed image from an auxiliary support to the textile fabric by fusion, where simultaneous sublimation is not excluded.

This process depends on flexible auxiliary supports or carriers which are coated with special non-polymeric impregnating agents. The coated face of the carrier substrate can be printed by any known printing technique, e.g. heliogravure, rotary screen, flatbed screen or offset.

During the heat transfer process, the impregnating agent melts and transfers the print to the textile fabric. Examples of such impregnating agents are amides of organic acids, e.g. ε-caprolactam, nicotinic acid amide, isonicotinic acid amide, urea, propylene urea, ethylene urea, glyoxal monoureine, 5-5-dimethyl hydantoin, imidazole, 2-methyl imidazole, N-methyl pyrrolidone, N-hydroxysuccinimide, biuret, dicyandiamide, benzamide, toluene sulfonamide and long chain organic acids, e.g. hippuric acid, suberic acid, azelaic acid, sebacic acid.

These products melt between about 100° and 250°C. Detailed descriptions can be found in published patent application EP-A-0,146,504.

For this process, commercially available heat transfer calenders can be used, and after printing, no other dyestuff fixation processes, e.g. steaming, need to be applied. It is however necessary to remove after transfer the impregnating agents by washing with water at 40°C.

A significant difference between the conventional heat transfer printing process which is based on sublimation, i.e. vapor phase transfer, and the new process based on fusion, i.e. transfer by the liquid phase, concerns the binding agents: For sublimation processes, all binding agents remain on the auxiliary paper while for the fusion process at least a partial transfer of binding agents to the textile fabric occurs.

The experts consider the transfer of binding agents during heat transfer as disadvantageous, which is pointed out quite clearly in most patent publications covering heat transfer printing. The authors discuss steps to reduce the effect of binder on the textile fabric when a transfer of binder cannot be avoided.

It is an objective of the present invention to show how the transfer of a resin from the auxiliary support to the textile fabric can be used to obtain a resin finished with properties that fulfill a commercial need.

A further objective of this invention is a particular finishing problem, namely the treatment of natural and synthetic fibers with fluorocarbon resins.

These types of finishings have been known for many years. Most fluorocarbon resins are in general olefines which are completely or partially fluorine substituted. Until now, aqueous emulsions of fluorocarbon resins have usually been used alone or in combination with other resins.

These emulsions typically contain about 30 % of solids. They are diluted and are applied to the textile material e.g. by means of a pad mangle with a pick-up of 0.3 % solid fluorcarbon, referred to the

weight of the fabric. The application is followed by drying at about 80° to 120°C and condensation at 150° to 180°C. Fluorocarbon resins can be applied to practically all natural and synthetic fibers.

Finishing with fluorocarbon resins serves to tne improvement of the following textile properties:

1. water repellency
2. oil repellency
3. dry soil resistance.

The quality of the water repellency is normally analyzed under at least two different aspects:

1. The resistance of a textile surface against the absorption of water (e.g. rain test according to Bundesmann DIN 53'888). This test is important for e.g. the clothing industry.
2. The resistance of a treated textile fabric against the penetration of water through the textile on the application of a certain water pressure. The quality of the finish is measured by the highest water pressure that can be applied without penetration of water through the fabric (DIN 53'886).

This property is important for e.g. awnings and tents.

The oil repellency of a textile surface is evaluated by studying the resistance against wetting by liquid hydrocarbons of various surface tensions.

The combination of oil and water repellency results in a resistance of the finished fabrics against stains. Also, fluorcarbon finished fabrics show increased resistance against dry soil.

It is a further objective of this invention to improve the possibilities of conventional finishing processes and to obtain effects which are impossible or difficult to obtain by conventional means.

In order to achieve this, the present invention was based on the technical background defined by EP-A-0'146'504.

The above discussed objectives are attained by means of the auxiliary support of the invention, which carries on a flexible base, in particular paper, a layer of a heat transferable finishing agent, that layer having a thickness of about 2 to 100 micrometers and having hydrophobic properties, the main ingredient of that layer being a fluorocarbon resin.

Special embodiments of this support which can be combined with each other, are characterized by the following properties:

1. The base paper and the layer containing the finishing agent may be separated by a release film.
2. The layer containing one or several fluorocarbon resins can further contain another polymer which is at least partially transferred to the textile fabric during heat transfer.
3. The layer can contain one or more impregnating agents which serve to improve speed and efficiency of the transfer process.
4. The auxiliary support can carry other agents, in particular dyestuffs and pigments which improve the results of the heat transfer process.

The transfer process of the invention is defined in further independent claims which are associated with dependent claims for special application forms.

Furthermore, the invention is related to a process for the preparation of the new and useful auxiliary support; this process is the subject of another independent claim together with dependent ones.

The various application forms of the invention shall now be discussed in detail.

The textile fabrics which can be treated according to the invention comprise knitted, woven or nonwoven fabrics of natural or synthetic fibers or their mixtures, e.g. cotton, linen, silk, wool, rayon, polyester, polyamide, polyolefines, acrylics, polyurethane etc.

In one embodiment of this invention, the auxiliary supports contain in the layer of the finishing agent at least one impregnating agent for the textile material. Suitable impregnating agents are mentioned in EP-A-O, 146,504, in particular benzamide, nicotinic acid amide, urea and its derivatives, p-toluene sulfonamide, 5,5-dimethyl hydantoin, dicyandiamide, hippuric acid, suberic acid, azelaic acid and sebacic acid and their mixtures. In this embodiment of the auxiliary support, the impregnating agents will have at least a double function: They form at the transfer temperature a melt having a low viscosity and effect the transfer of the finishing agent from the surface of the auxiliary support into the fiber structure. It is important to know that the process of the invention is not a "reverse coating", used for polyurethane coatings, but after transfer there remains virtually no film on the treated surface of the textile material, its fiber structure being treated by the molten product in a way similar to a conventional finishing process with aqueous emulsions.

The impregnating agents also facilitates the process of paper coating because the coated surfaces show no blocking after drying.

The commercially available fluorocarbon resins comprise in general a mixture of several different fluorocarbon resins. Among these, it is possible to find resins having a low temperature softening range. One of these is e.g. Dipolit 451 of "Chemische Fabrik Theodor Rotta GmbH & Co. KG", Mannheim, Germany, having a melting range of 70° to 140°C.

Resins of this type can be used as a kind of "internal" impregnating agent for another embodiment of the present invention:

They can be used alone or in mixture with other higher melting fluorocarbon resins or other

polymers to give a coating which melts and can be transferred from a release paper into the fabric without the addition of the normal impregnating agents. The evident advantage of this embodiment of the invention is that no impregnating agent has to be eliminated after transfer. It is further recommended that the fabric is padded with water and dried at 160°C after transfer.

For this system, a higher contact pressure, e.g. 0.5 to 1 MPa, is recommended.

For many types of textile fabrics, in particular flat constructions, conventional textile calenders can be used for the process of the invention instead of special heat transfer calenders. In these cases, a linear contact pressure of 50 to 400 N/mm is recommended at 130° to 210°C and a working speed of the fabric of about 10 to 100 m/min.

The process of the invention is of interest for all fibers because it presents a fast and low risk process.

If fabric samples of unknown origin are to be treated by conventional finishing methods, there is always the risk that the entire finishing bath may be rendered unusable by coloured or uncoloured impurities which may be released by the fabric.

A further objective of the invention is the finishing of polyester fabrics with fluorocarbon resins in order to give them flame retardant properties ("Trevira CS", Hoechst AG).

"Flame retardant" are called textile fibers which, after a 15 seconds' exposure to a propane gas flame forming an angle of 45° with the fabric samples, burn no longer than 6 seconds after the extinction of the flame.

In German patents 2,236,037, 2,442,002, 2,328,343, 2,346,787, flame retardant fibers of polyester are disclosed wherein about 5 to 15 mole % of the acid component of the polyester are phosphorus containing groups. The total phosphorus content of the polyester molecule is less than 1 %.

It has been known at least since 1978 (see e.g. Dr. H. Zimmermann, "Chemiefasern/Textilindustrie", 28/80 (1978), 1054-1060) that the flame retardant properties of these fibers are degraded by a finish with fluorocarbon resins if this finish is applied by any of the techniques known before the process of the present invention.

Fabrics of Trevira CS are not changed in their flame retardant properties if they are finished with fluorocarbon resins according to the processes of the present invention. It is now possible to impart fabrics of Trevira CS a finish which makes them water repellent, oil repellent, dry soil resistant and watertight while conserving their flame retardant properties.

In addition to the fluorocarbon resin, the layer of the auxiliary support may contain other auxiliary agents such as polymer softeners, dyestuffs, pigment etc. to obtain special finishing characteristics of the textile fabrics treated by the process of the invention.

The following Examples are given for illustration purposes exclusively and will not limit the scope of this invention.

EXAMPLE 1

Finishing of polyester to obtain flame retardant properties (Trevira CS, Hoechst AG) with a fluorocarbon resin using impregnating agents

A coating composition is prepared by grinding in a ball mill 72 parts of an aqueous emulsion of a fluorocarbon resin (Scotchgard (TM) FC-247 (3M Corp.)) with 28 parts of sebacic acid until the average particle size of the sebacic acid is less than 10 µm. A silicone coated release paper of 40 g/m2 is coated by a roll bar with 8 g/m2 of this composition and dried. This layer is transferred by means of a heat transfer printing calender under an increased contact pressure of 0.2 MPa at 160°C in 25 seconds into an upholstery fabric of Trevira CS having a basic weight of 350 g/m2.

The low viscosity melt of the coating penetrates into the fabric without changing its appearance or hand. Afterwards, the fabric is washed with water of 40°C and dried at 160°C. "3M" has developed Scotchgard (TM) specifications and control methods for various application of fluorocarbon finishes (Scotchgard (TM) Fabric Protector Quality Specifications for Home Furnishings, Technical Information of 3M, 1.10.1988).

For the present example the fluorocarbon content of the finished product was found to be 0.35 % (3M specification 0.3 %).

For oil repellency the note 6 was found (minimum value 4), for water repellency the note 7 (minimum value 3), for the abrasion resistance the note 6 (minimum value 3) and for dry soil resistance the note 5 (minimum value 3).

The flame retardant properties of this fabric were measured according to DIN 4102, B1 and no difference was found between finished and unfinished fabric.

In both cases, i.e. with the untreated and with the finished fabric, the samples burned less than 0.5 sec after extinction of the test flame, and the length of the destroyed fabric was the same in both samples.

EXAMPLE 2

Watertight awnings with fluorocarbon finished Trevira CS fabrics

A fabric for awnings having a basic weight of 300 g/m2 was constructed from Trevira CS fibers.

The coated paper of example 1 was used for treating this fabric with a heat transfer printing calender under a contact pressure of 0.5 MPa at 160°C and during a contact time of 25 sec. After heat transfer, the fabric was washed with water of 40°C and dried at 180°C.

The fabric was subsequently treated on a textile calender (surface of the first cylinder: steel, surface of the second cylinder: compressed cotton).

The test of water tightness according to DIN 53886 showed that the fabric treated in this manner resisted to a pressure of 250 mm of water column without leakage.

The treated fabric passed the flammability test of DIN 4102 B1.

EXAMPLE 3

Heat transfer finishing of textile fabrics with fluorocarbon polymers without impregnating agents

A coating composition is prepared by mixing 2 parts of the aqueous fluorocarbon emulsion "Scotchgard TM FC-247" (3M) with one part of an aqueous emulsion of a low melting range fluorocarbon polymer "Dipolit 451" of "Chemische Fabrik Theodor Rotta GmbH & Co. KG", Mannheim, Germany. This composition is used to coat the base paper of example 1 by means of a heliogravure machine. After drying, the basic weight of the coating was about 3 g/m2.

The coating was transferred into the upholstery fabric of example 1 by means of a heat transfer printing calender of 180°C, a contact pressure of 1 MPa and a contact time of 25 sec.

After transfer, the fabric was first padded with water which was partially removed on a pad mangle, and then it was dried at 160°C.

The finishing values were virtually identical with those of example 1. The treated fabric passed the flammability test according to DIN 4102, B1.

EXAMPLE 4

Finishing of polyester fabric with fluorocarbon resin and impregnating agent using a textile calender

The fabric and the paper of example 1 were used for treatment on a conventional textile calender at 160 ° C. One drum of the calender had a steel surface and the other a surface of compressed cotton.

Paper and fabric passed the calender at a linear contact pressure of 300 N/mn and with a speed of 20 m/min. The high pressure resulted in the transfer of 80% of the removable coating from the paper into the fabric.

After washing with water of 40°C and drying at 160°C, excellent finishing parameters were obtained without negative influence on the flame retardant properties of the fabric.

EXAMPLE 5

Finishing of a polyester fabric with special fluorocarbon resins without impregnating agent using a textile calender

The procedure of example 4 was repeated using the paper of example 3. It was found that about 65% of the removable coating had been transferred from the paper to the fabric. After transfer, the fabric was treated with water as described in example 3.

Finishing and flammability tests gave excellent results.

Claims

1. A twodimensional auxiliary support for the finishing of textile materials, made from natural or synthetic fibers or their mixtures, by the heat transfer method, said support comprising a flexible substrate and on one of its surfaces a layer having a thickness of about 2 to 100 µm, containing at least one fluorocarbon resin which is transferable by heat and pressure from the flexible substrate to the textile material to be finished.

2. The auxiliary support according to claim 1 wherein said transferable layer is separated from said flexible substrate by a release layer.

3. The auxiliary support according to claim 1 or 2 wherein the transferable layer further contains an impregnating agent for the textile material to be finished consisting of one or more substances selected from the group comprising ϵ-caprolactam, nicotinic acid amide, isonicotinic acid amide, hippuric acid, suberic acid, azelaic acid, sebacic acid, urea, propylene urea, ethylene urea, glyoxal monoureine, 5,5-dimethyl hydantoin, imidazole, 2-methyl imidazole, N-methyl pyrrolidone, N-hydroxysuccinimide, biuret, dicyandiamide, benzamide, toluene sulfonamide.

4. The auxiliary support according to any one of claims 1 to 3, wherein the transferable layer further contains a polymeric binder which is at least partially transferable to the textile material during the heat transfer process.

5. The auxiliary support of any one of claim 1 to 3 wherein said layer contains a fluorocarbon resin having a softening range comprised between 70° and 140°C.

6. A process for the manufacture of the auxiliary

support according to claim 1, comprising the following steps:

(a) providing a twodimensional flexible substrate,

(b) providing a liquid coating composition containing an aqueous emulsion of at least one fluorocarbon resin,

(c) coating the flexible substrate of step (a) with the coating composition of step (b) in such a manner that the layer of said coating composition, after drying on said flexible substrate, results in a coating layer having a thickness comprised between 2 and 100 micrometers, and

(d) drying the coated flexible substrate.

7. The process of claim 6 wherein further an impregnating agent selected from the substances defined in claim 3 is incorporated in step (b) into said liquid composition.

8. The process of claim 6, further comprising the step of coating said flexible substrate of step (a) with a release layer.

9. A process for the application of a fluorocarbon finish to textile materials comprising natural or synthetic fibers mixtures thereof, wherein the textile material is brought into contact with an auxiliary support according to any one of claims 1 to 5 in a heat transfer printing calender at normal atmospheric pressure, at a contact pressure between textile material and auxiliary support of about 0.01 to about 1 MPa, during a contact time of about 5 to about 100 seconds, and at a temperature comprised between about 130°C and about 250°C.

10. A process for the application of a fluorocarbon finish to textile materials comprising natural or synthetic fibers or mixtures thereof, wherein the textile material is brought into contact with an auxiliary support of any one of claims 1 to 5 in a textile calender at normal atmospheric pressure, at a linear contact pressure beween textile material and auxiliary support of about 50 to about 500 N/mm, and at a temperature of about 130° to about 220°C.

11. The process of claim 9 or 10 wherein the textile fabric is made from polyester fibers.

12. The process of claim 9 or 10 wherein an auxiliary support of claim 5 is used whose said layer is free from impregnating agents, further comprising padding the obtained, finished textile material with water and drying the padded textile material at about 160°C.

13. A textile fabric which has been finished according the process of any one of claims 9 to 12.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 81 0880

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-2 105 019 (KANEGAFUCHI BOSEKI) * Whole document *	1,3,5-13	D 06 M 15/256 D 06 M 23/02
X	FR-A-2 391 069 (DOLLFUS & NOACK) * Whole document *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 06 M
D 06 G

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	21 March 91	HELLEMANS W.J.R.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

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