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**EUROPEAN PATENT APPLICATION**

⑫<sup>1</sup> Application number: **88111345.0**

⑫<sup>2</sup> Date of filing: **14.07.88**

⑫<sup>1</sup> Int. Cl.4: **D06M 15/03 , D06M 10/00 ,  
D06Q 1/00 , D06M 15/17 ,  
D06M 15/333 , D06M 15/53 ,  
D06M 15/263**

⑬<sup>0</sup> Priority: **23.07.87 US 76968**

⑬<sup>3</sup> Date of publication of application:  
**25.01.89 Bulletin 89/04**

⑬<sup>4</sup> Designated Contracting States:  
**BE DE FR GB IT SE**

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⑮<sup>4</sup> **Coating compositions for textiles.**

⑮<sup>7</sup> A method for modifying the surface of a synthetic fibrous sheet material comprises applying to its surface a water-soluble polymer that is photoin-solubilizable, has a molecular weight from about 10,000 to about 5,000,000, and is selected from the group consisting of polysaccharides and aliphatic derivatives of polysaccharides, polyvinyl alcohol, polyacrylic acid, pectin and polyethylene oxide, and optionally, an abrasive material that is at least partially transparent to ultraviolet light and curing the composition by irradiation.

**EP 0 300 370 A2**

## COATING COMPOSITIONS FOR TEXTILES

This invention relates to a method for modifying the surface of a synthetic fibrous sheet material by applying to the surface of the sheet material a coating composition that accepts marking with pencil, ink pen, and printing equipment.

Sheet materials manufactured from fibers of synthetic polymers, such as polyethylene and polypropylene fiber, are frequently used to replace paper in reusable mailing envelopes and similar stationary articles that require a high degree of resistance to wear. However, such wear-resistant paper replacements has been limited by the fact that such synthetic papers are not receptive to being written on with lead pencils or ink pens or printed on with conventional printing media, apparently because their surfaces tend to be slippery and hydrophobic and lack any chemical functionality that would tend to interact with inks and dyes used in writing and printing.

One attempt to deal with that problem is disclosed in U.S. Patent No. 4,092,457, which describes a fibrous sheet material for improved off-set printing, which is composed at least partly of polyolefin fibers in which a hydrophilic component such as polyvinyl alcohol has been incorporated by polymer blending or graft polymerization before the fibers are spun. The sheet material is treated with a water-soluble polymer, such as polyvinyl alcohol and polyacrylamide, as well as with an aqueous emulsion of a high molecular weight polymer such as vinyl acetate. The coating composition is then dried by heating. Treatment of the sheet material either with a water-soluble polymer alone or an aqueous-polymer emulsion alone does not achieve the effect contemplated by the patent.

It would be desirable to provide a method for modifying the surface of a synthetic fibrous sheet material by applying to the sheet material a water-soluble coating composition that is curable by irradiation alone to form an water-insoluble surface coating that is more receptive to marking with pencil, ink pen, and printing equipment.

According to the invention, a method for modifying the surface of a synthetic fibrous sheet material by applying to its surface a coating composition comprising a water-soluble polymer, is characterized in that the water-soluble polymer is photoinsolubilizable, has a molecular weight from about 10,000 to about 5,000,000, and is selected from the group consisting of polysaccharides and aliphatic derivatives of polysaccharides, polyvinyl alcohol, polyacrylic acid, pectin and polyethylene oxide.

Preferably the water-soluble polymer has a molecular weight from about 500,000 to about

2,000,000, and is a hydroxyalkylcellulose, such as hydroxyethyl or hydroxypropylcellulose, an aminoethyl derivative of hydroxyethyl or hydroxypropylcellulose, a hydrophobically modified hydroxyethyl or hydroxypropylcellulose, or carboxymethylcellulose. Most preferred are hydroxypropylcellulose, hydroxypropylcellulose modified with about from 1 percent to about 10 percent by weight aminoethyl groups, and hydroxypropylcellulose modified with about from 0.1 percent to about 2 percent by weight of a 16-carbon alkyl chain.

Other suitable water-soluble polysaccharides include natural and synthetic polymers such as Guar Gum and their aliphatic derivatives such as carboxymethyl and hydroxypropyl modified Guar Gum, Agar, Gum Carrageenan, Gum Arabic, Gum Ghatti, Gum Karaya, Gum Tragacanth, Locust Bean Gum, Xanthan Gum and pectin, all of molecular weight from about 20,000 to about 500,000, and preferably from about 80,000 to about 400,000. Other useful water-soluble polymers are polyvinyl alcohol, polyacrylic acid and polyethylene oxide, all of molecular weight from about 10,000 to about 2,000,000 and preferably from about 100,000 to about 1,000,000.

Generally, the higher the molecular weight of a given water-soluble polymer, the shorter the duration of curing treatment needed to effect an aqueous insoluble coating. For example, a coating composition comprising hydroxypropylcellulose of average molecular weight 1,000,000 requires only about 15 percent of the photo exposure needed for such a composition employing hydroxypropylcellulose of average molecular weight 60,000. Likewise, a coating composition employing polyacrylic acid of average molecular weight 4,000,000 provides acceptable aqueous-insoluble coatings; when such a composition employing polyacrylic acid of average molecular weight 300,000 is irradiated for the same amount of time and in the same manner an unacceptable coating is provided that is not water-insoluble.

Curing of the photoinsolubilizable coating compositions of this invention can be conventionally performed by ultraviolet light, electron beam or corona discharge treatment. Exposure time can vary from about 0.5 seconds to about 5 minutes. The preferred exposure time can vary considerably, depending upon such parameters as the particular water-soluble compound employed in the photoinsolubilizable coating composition, and the molecular weight of said water-soluble compound. Other factors include method of curing and the amount and/or type of ultraviolet-transparent abra-

sive material used.

Preferably, in the method according to the invention the coating composition also comprises an ultraviolet-transparent abrasive material of particle size of less than about 0.05 mm (50 microns), which improves the ability to accept marking with pencil or ink pen, as opposed to printing with dyes. Any particulate abrasive material of the required particle size and having at least partial ultraviolet transparency is useful in the photoinsolubilizable coating compositions of this invention. Silica is the preferred abrasive material due in part to its hardness and excellent ultraviolet transparency properties. Other suitable abrasive materials are particles of glass, calcium carbonate, aluminum hydroxide, zinc oxide, titanium dioxide, calcium carbonate, and magnesium oxide.

The amount of water-soluble compound employed herein and the weight percent ratio of water-soluble compound to abrasive material can both vary depending on such parameters as the specific water-soluble compounds and abrasive substances employed, the particular synthetic fiber-containing textile surface to be coated and further described below, the degree of pencil, ink pen, printing or dye image receptivity desired of the textile surface, and the specific end uses contemplated of the thus coated synthetic fiber-containing textile material.

Preferably, coating compositions according to the invention comprise from about 0.1 percent to about 5 percent by weight of the water-soluble polymer, and up to about 1 percent by weight of the abrasive material. More preferably, the coating compositions contain about 0.3 percent to about 2 percent by weight of the water-soluble polymer, and about 0.05 percent to about 0.5 percent by weight of the abrasive material.

Water is the preferred vehicle in the photoinsolubilizable coating compositions of this invention, but surfactants or organic cosolvents, for example, acetone, may be employed as coating aids depending upon such end results contemplated as degree and thickness of coating.

Nonwoven and woven synthetic fiber-containing sheet materials are suitable substrates for the coating compositions of this invention. Preferred are spunbonded nonwoven fabrics comprising polyethylene or polypropylene fibers, such as are commercially available from E. I. du Pont de Nemours as Tyvek and Tyvar brands, respectively. Other examples of synthetic fiber-containing materials suitable as substrates for the coating compositions of this invention include woven or nonwoven materials made of polyolefins, and halogenated derivatives of polyolefins, polyester, polyacetyl, polyamide, polyacrylate or methacrylate, and silicone fibers.

The following examples more fully illustrate the preferred embodiments of this invention.

#### Example 1

This example demonstrates a preferred coating composition of this invention, and in particular, its unique photosensitive properties responsible for providing synthetic fiber-containing textile materials with improved pencil and ink pen image receptivity.

A photoinsolubilizable coating composition is prepared by dispersing 0.25 grams (0.14 weight percent) amorphous silica of a particle size of less than approximately 0.01 mm (10 microns). (Illinois Minerals IMSIL A-15), in a solution of 1.0 gram (0.56 weight percent) of hydroxypropylcellulose modified with 5 weight percent of aminoethyl groups (Hercules' Klucel® 6) in 139 milliliters of water and 55 milliliters of acetone.

A coupon of spunbonded polyethylene textile material (Du Pont's Tyvek) is then dipped in the above-described coating composition, dried for one hour at 60°C in a forced air oven and exposed for 2 seconds to the irradiation from a microwave-fired, high pressure mercury lamp. The coupon is then washed for one hour in a water/acetone mixture of weight percent ratio 76/24 to determine the resistance of the coating composition to dissolution, and then for pencil and ink pen image receptivity.

Writing on the photo exposed side of the coupon with a No. 2 graphite pencil and ordinary ink pen resulted in image quality comparable to that obtained on writing on a piece of ordinary writing paper. A similarly prepared coupon, not exposed to irradiation, gave after washing approximately the same pencil and ink pen image non-receptivity as observed on an untreated coupon.

#### Examples 2 to 4

Examples 2 to 4 further illustrate preferred embodiments of this invention.

In Example 2, 0.5 grams (0.1 weight percent) of IMSIL A-15 amorphous silica is dispersed in a solution of 2.0 grams (0.4 weight percent) hydroxypropylcellulose (Hercules' Klucel® H) in 500 milliliters of water.

A coupon of spunbonded polyethylene textile material is then coated in the above composition, photo exposed as in Example 1, with the exception that a 5-second exposure time is used, and further washed as set forth in Example 1. As in Example 1, pencil and ink pen image receptivity of the treated coupon are comparable to that obtained on writing

on ordinary writing paper.

In Example 3, 0.15 grams (0.09 weight percent) of IMSIL A-15 amorphous silica is dispersed in a solution of 0.6 grams (0.36 weight percent) of hydroxyethylcellulose having 0.55 weight percent modification with a 16-carbon chain (Hercules Incorporated WSP D-330) in 125 milliliters of water and 51 milliliters of acetone.

A spunbonded polyethylene coupon is coated and treated as in example 1. As before, pencil and ink pen image receptivity is comparable to that obtained on writing on ordinary writing paper.

In example 4, 0.5 grams (0.3 weight percent) of IMSIL A-15 amorphous silica is dispersed in a solution of 2.0 grams (1.2 weight percent) modified hydroxypropylcellulose (containing 0.3 weight percent of appended 16-carbon chains) in 125 milliliters of water and 51 milliliters of acetone.

A spunbonded polyethylene coupon is then treated as in Example 1, with the exception that a 30-second photo exposure is employed. Pencil and ink pen image receptivity of the thus treated coupon are comparable to that obtained on writing on ordinary writing paper.

#### Example 5

This example further illustrates an embodiment of the invention wherein a corona discharge source is employed, instead of an ultraviolet light, to produce a photoinsolubilizable coating composition in accordance with this invention.

0.4 pounds (0.1 weight percent) of IMSIL A-15 amorphous silica is dispersed in a solution of 1.6 pounds (0.4 weight percent) hydroxypropylcellulose in 400 pounds of water.

A coupon of spunbonded polyethylene textile material is then coated with the above composition and dried for one hour in a 70° C forced air oven, and then passed under a 200 watt corona treater at a rate of 70 feet/minute and at a distance of 1 1/16 inch from the source. The coupon is further washed for one hour in a mixture 176 milliliters of water and 76 milliliters of acetone then dried for one hour at 70° C as described in the above examples. Pencil and ink pen image receptivity of the thus treated coupon is comparable to that obtained on writing on ordinary writing paper.

#### Example 6

This example further illustrates an embodiment of this invention wherein electron beam treatment, instead of ultraviolet light or corona discharge, is

employed to produce a photoinsolubilizable coating composition in accordance with this invention.

A coupon of spunbonded polyethylene is coated with the composition used in Example 5 and dried in a forced air oven for one hour at 75° C, and then exposed to 0.5 megarads of 0.2 MEV electrons from a commercially available electron beam unit. The coupon is then washed in 200 milliliters of water for one hour followed by drying for one hour at 75° C in a forced air oven. Pencil and ink pen image receptivity of the thus treated coupon is found to be comparable to that obtained on writing on ordinary writing paper, such as described in the above examples.

#### Example 7

This example is further illustrative of an aspect of this invention wherein photoinsolubilizable coating compositions herein improved dye receptivity of synthetic fiber-containing textile materials.

A treated coupon of spunbonded polyethylene is prepared and photo exposed as illustrated in Example 2 above, and is then stirred for 70 minutes at 67° C in a dye bath consisting of 12 grams of RIT brand tint and dye dissolved in 214 milliliters of water. After removal from the bath and rinsing in water for 30 minutes, the coupon is found to have excellent dye retention. A control coupon that is dyed without any previous treatment shows essentially no dye retention after washing as above described.

#### **Claims**

1. A method for modifying the surface of a synthetic fibrous sheet material by applying to its surface a coating composition comprising a water-soluble polymer, characterized in that the water-soluble polymer is photoinsolubilizable, has a molecular weight from about 10,000 to about 5,000,000, and is selected from the group consisting of polysaccharides and aliphatic derivatives or polysaccharides, polyvinyl alcohol, polyacrylic acid, pectin and polyethylene oxide, and the composition is cured by irradiation to form a water-insoluble coating that accepts marking with pencil, ink pen, and printing equipment.

2. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 1 further characterized in that the polysaccharides and aliphatic derivatives of polysaccharides have a molecular weight from about 500,000 to about 2,000,000.

3. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 1 or 2, further characterized in that the water-soluble polymer is a hydroxyalkylcellulose or a modified hydroxyalkylcellulose.

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4. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 3 further characterized in that the water-soluble polymer is hydroxypropylcellulose, hydroxypropylcellulose modified with about from 1 percent to about 10 percent by weight of aminoethyl groups, or hydroxypropylcellulose modified with about from 0.1 percent to about 2 percent by weight of a 16-carbon alkyl chain.

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5. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 1 further characterized in that the water-soluble polymer is in an amount from about 0.1 percent to about 5 percent by weight.

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6. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 5 further characterized in that the water-soluble polymer is in an amount from about 0.3 percent to about 2 percent by weight.

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7. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 1 further characterized in that the coating composition also comprises an ultraviolet-transparent abrasive material of particle size of less than about 0.05 mm.

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8. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 7 further characterized in that the the abrasive compound is an amount up to about 1 percent by weight.

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9. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 8 further characterized in that the the abrasive compound is in an amount of about 0.05 percent to about 0.5 percent by weight.

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10. A method for modifying the surface of a synthetic fibrous sheet material as claimed in claim 7, 8, or 9, further characterized in that the abrasive compound is silica.

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