Jan. 19, 1960 G. HEBERLEIN ET AL 2,921,864

PROCESS FOR METALIZING TEXTILES AND PRODUCTS THEREFROM

Filed July 25, 1955

Fig. 1.

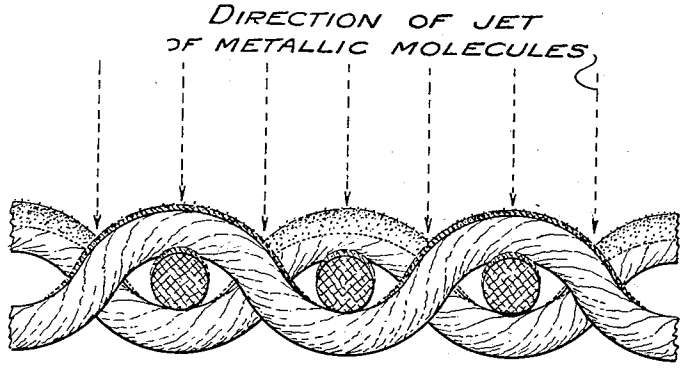
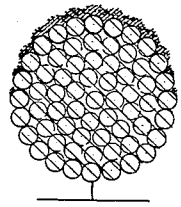


Fig. 2.



ENLARGED VIEW OF SINGLE THREAD SHOWING METALLIC DEPOSIT

INVENTORS.
GEORG HEBERLEIN.
BY KARL RISCH.

Ward Real Haselton Orme & McElhannon
ATTORNEYS.

United States Patent Office 2,921,864
Patented Jan. 19, 1960

2,921,864

PROCESS FOR METALIZING TEXTILES AND PRODUCTS THEREFROM

Georg Heberlein and Karl Risch, Wattwil, Switzerland, assignors to Heberlein Patent Corporation, New York, N.Y., a corporation of New York

Application July 25, 1955, Serial No. 524,299

Claims priority, application Germany July 27, 1954

5 Claims. (Cl. 117—56)

This invention relates to the production of metallized all-over and pattern effects on textiles, particularly natural and regenerated cellulose and cellulose derivatives.

Cellulosic fabric with a light metal coating is known. Such metal coating is apt to peel off, particularly when wet.

The principal object of the present invention is to provide a process for the production of cellulosic material, particularly fabrics, metallized with a vaporizable metal, and which shall produce products highly resistant to separation of the metal coating from the material when rubbed, especially when wet.

The invention accordingly comprises the novel products as well as the novel processes and steps of processes according to which such products are manufactured, the specific embodiments of which are described hereinafter by way of example and in accordance with which we now prefer to practice the invention.

In carrying out our process, in accordance with the invention, we vaporize and deposit a vaporizable metal on cellulosic material and heat the so-treated material to a temperature of at least 100° C. and below the scorching temperature of the material. Various metals may be vaporized and deposited on cellulosic material, including aluminum, copper, gold and similar metals.

The cellulosic material includes natural cellulose fibers and cellulose rayon fibers such as cotton, viscose rayon, acetate rayon and similar cellulose derivatives.

The vaporizing of the metals onto the cellulosic material is effected on the cellulosic material as such or after pretreatment including application of natural or synthetic resins thereto. Such pretreatment also includes subjecting the cellulose material to agents such as formaldehyde in order to reduce the swelling character of the cellulosic material. Thus textiles of natural cellulose fibers or cellulose rayon fibers are impregnated with a solution of formaldehyde, glyoxal or pyruvic aldehyde containing an acid catalyst and heated to elevated temperature. Furthermore, resins of amides and formaldehyde as well as acetone formaldehyde resins may be incorporated for this purpose.

Not only may cotton be treated, but transparentized cotton may be employed.

The metal may also be deposited on a fabric which has been provided with a permanent mechanical calendering effect produced in the customary manner by means of water-soluble resins.

The metal may be deposited as an all-over effect or may be applied on the material in a pattern. In applying a pattern to the fabric, the fabric may first be printed with a water-soluble resist in the form of a pattern before the treatment with the metal vapor. This resist is then washed off after the metallization. The resists which are employed include starch hydrolysis products such as British gum and the like. Patterned effects may also be produced by locally depositing a solution or emulsion of a water-insoluble natural resin or plastic. After the application of the resin or plastic, followed by the vaporization and deposit of the metal, the metal may be washed away from those portions which have not been treated with the resin or plastic, thus leaving a metallized pattern.

The resins or plastics employed for the all-over or pattern effects may be applied in the form of solutions in organic solvents or in the form of aqueous emulsions to the flat textiles. As natural resins we may use, for instance, shellac or colophony. As synthetic resins there are suitable, for instance, film-forming resins obtained by polymerization, particularly vinyl resins, for instance polymers of vinyl chloride, vinylidene chloride, vinyl acetate, vinyl acetal, vinylbutryral or copolymers thereof, as well as acrylic and methacrylic resins, and furthermore polystyrene resins. Furthermore, film-forming resins obtained by polycondensation may be used, particularly aminoplast ether resins, for instance urea or melamine formaldehyde ether resins, alkyd resins, for instance glyptal resin, alkyd-alkyl-aminoplast ether-mixed resins or ethoxylene resins.

The heating to at least 100° C. and below the scorching temperature of the material produces a substantial increase of the adhesion of the metal coating to the cellulosic material. We do not know the reason for this unexpected effect, but we do know it to be a fact that the metal deposited after such heating has such excellent adhesion and resists separation from the material in wet or dry condition. The effect exists whether the metal is applied directly to the cellulosic material or after treatment with natural or synthetic resins or other treatment herein described. Where natural or regenerated celluloses constitute the cellulosic material treated the heating is preferably conducted for 2–8 minutes at 120–240° C. Where cellulose derivative material is employed, such as cellulose acetate, the heating is preferably conducted for 1–8 minutes at a temperature of 120–190° C. The use of temperatures above 200° C. is advantageous in particular in the case of cotton fabrics where metal has been applied by vaporization without pretreatment with a resin layer.

The heating can be carried out in a customary curing machine, a singeing machine or by infrared radiation.

Further it has been found, in accordance with our invention, that the adherence of the metal layer which has been applied to textiles of cellulose containing fibrous material can be influenced by subjecting the textiles before the treatment with the metal vapour to the action of cathode rays emerging from a glow-cathode. By the combination of this measure with the heating to high temperatures of the textiles after the treatment with the metal vapour a further substantial increase of the adherence of the applied metal layer is obtained and thus a considerable increase in the resistance of metallized textiles for the requirements of practical use.

The action of the cathode rays emerging from the glow-cathode advantageously continues for about 1 to 2 minutes at a vacuum between 0.04 to 0.08 mm. mercury.

A still further development of the process according to the invention consists in the production of patterned metallized effects on flat textiles by pattern printing with a solution or emulsion of a water-insoluble natural resin or plastic, followed by the treatment with the metal vapour and washing off the metallization at the unprinted parts, whereby the flat textile is exposed before the application of the metal to the action of cathode rays emerging from a glow-cathode. After the application of the metal coating, the textile is subjected to heating to temperatures of more than 100° C.

It has surprisingly been found that in this manner the metallization can be removed more easily and completely at the areas not printed with the resin or plastic.

The following are examples of the process as we now

prefer to practice it. The Examples are illustrative and the invention is not to be considered as restricted thereto except as indicated in the appended claims.

Example 1

Black-dyed cotton muslin which has been transparentized in a well-known manner by a treatment with sulfuric acid of 54° Bé. for 8 seconds is impregnated with a polyvinyl acetate emulsion so that 4% polyvinyl resin is applied to the material. The impregnated fabric is coated with aluminum in a known manner by vaporizing the same at a temperature between 800 and 1000° C. in a high vacuum of about 5.10^{-5} mm. mercury and then heated in a curing machine at 160° C. for 3 minutes.

Two control-samples are made by directly coating with aluminum vapour, without previous resin impregnating and without after-heating similar specimens of the same fabric. One sample (I) of the fabric treated in accordance with Example 1 and one of the control-samples (II) are washed with a solution of 2½ grams soap per liter for 15 minutes at 30° C., then rinsed twice with distilled water of room temperature and dried in the air. The metal layer of sample I shows a satisfactory permanency against this washing treatment, whereas the metal layer of sample II is completely removed.

Another sample (III) of the fabric treated in accordance with Example 1 and the other control sample (IV) are washed with a solution of an aqueous solution containing 2 grams of a detergent namely the sodium salt of oleyl-methyl-taurin

$$(C_{17}H_{33}CON.C_2H_4SO_3Na)$$
$$|$$
$$CH_3$$

per liter for 15 minutes at 30° C., then rinsed twice with distilled water of room temperature and dried in the air. The metal layer of sample III shows an excellent permanency against this washing treatment, whereas the metal layer of sample IV is mainly removed.

Example 2

Green-dyed viscose toile is impregnated with an aqueous solution containing per liter 80 cc. of 40% formaldehyde, 16 grams zinc chloride and 8 grams potash alum, dried on a tenter frame, heated for 2½ minutes at 140° C., washed and dried. The fabric so treated has reduced swelling properties. It is then impregnated in a known manner with a polyvinyl butyral emulsion containing 4% resin, dried, treated in a high vacuum of about 5.10^{-5} mm. mercury, first of all with copper vapor at a temperature of about 1000 to 1100° C., with subsequent deposition and thereupon with gold vapor at a temperature of about 1100 to 1200° C., with subsequent deposition. Thereupon the fabric is heated for 4 minutes at 180° C.

A control sample is made by directly coating with copper vapor and with gold vapor without previous formaldehyde treatment and resin impregnating and without after-heating a similar specimen of the same fabric.

A sample (I) of the fabric treated in accordance with Example 2 and the control-sample (II) are washed with a solution of a detergent as in Example 1. The metal layer of sample I shows a good permanency, whereas the metal layer of sample II is mainly removed.

Example 3

Red-dyed rayon crepe satin, warp: acetate rayon, filling: viscose crepe is treated in a high vacuum on the satin side with aluminum vapor as in Example 1. The fabric metallized in this manner passes at a speed of 100 meters per minute through an open flame of a gas singeing machine of the type used for the singeing of gray goods.

A control sample is made by coating with aluminum vapors without after-heating a similar specimen of the same fabric. A sample (I) of the fabric treated in accordance with Example 3 and the control sample (II) are washed with a solution of a detergent as in Example 1, whereby the metal layer of sample I shows a good permanency, whereas the metal layer of sample II is mainly removed.

Example 4

Navy blue-dyed cotton muslin transparentized in a known manner with sulfuric acid is subjected in a high vacuum installation first of all at a pressure of about 0.05 mm. mercury for 1 minute to the action of cathode rays emerging from a glow-cathode and thereupon treated with aluminum vapor in a high vacuum as in Example 1 and thereupon heated in a curing machine for 4 minutes at 220° C.

A control-sample is made by directly coating with aluminum vapor, without previous treating with cathode-rays and without after-heating a similar specimen of the same fabric. A sample (I) of the fabric treated in accordance with Example 4 and the control-sample (II) are washed with a solution of a detergent as in Example 1, whereby the metal layer of sample I shows an excellent permanency, whereas the metal layer of sample II is mainly removed.

Example 5

A cotton percale is impregnated with an aqueous solution containing per liter 100 grams of tetramethylol melamine and 4 grams of triethanolamine lactate as catalyst, dried, friction-calendered with heated rollers, cured at 150° C. for 4 minutes, washed and dried. Thereupon the fabric is treated in a high vacuum with aluminum vapor as in Example 1 and then heated for 2 minutes at 200° C. in a curing machine.

A sample of the so treated fabric is washed with a soap solution as in Example 1 and another sample is washed with a solution of a detergent as in Example 1. The metal layers of both samples show a good permanency against these washing treatments.

Example 6

Dyed "Crepe lavable" of cuproammonium rayon is treated with formaldehyde as in Example 2 to make it resistant to swelling, thereupon treated in a high vacuum with aluminum vapor as in Example 1 and thereupon heated in a curing machine at 225° C. for 5 minutes.

Two control samples are made by directly coating with aluminum vapor, without previous formaldehyde treatment and resin impregnating and without after-heating similar specimens of the same fabric. A sample (I) of the fabric treated in accordance with Example 6 and one of the control samples (II) are washed with a soap solution as in Example 1, whereby the metal layer of sample I shows a satisfactory permanency, whereas the metal layer of sample II is mainly removed.

Another sample (III) of the fabric treated in accordance with Example 6 and the other control-sample (IV) are washed with a solution of a detergent as in Example 1, whereby the metal layer of sample III shows a good permanency, whereas the metal layer of sample IV is mainly removed.

Example 7

Black-dyed cotton muslin which has been transparentized in a known manner by a treatment with sulfuric acid of 54° Bé. for 8 seconds is printed in accordance with a pattern by means of a resist consisting of 450 grams of gum arabic, 450 cc. water and 100 grams Turkey red oil and dried, thereupon treated with aluminum vapor in a high vacuum as in Example 1, washed with cold water, dried and heated for 5 minutes at 220° C.

A control-sample is made by pattern printing the same resist on a similar specimen of the same transparentized fabric and coating with aluminum vapor but without after-heating. A sample (I) of the fabric treated in accordance with Example 7 and the control-sample are washed with a solution of a detergent as in Example 1, whereby the metal layer of sample I shows an excellent

permanency, whereas the metal layer of sample II is mainly removed.

Example 8

Blue-dyed crepe satin consisting entirely of viscose rayon is given a swelling-proof finish by formalizing as in Example 2 and thereupon printed in accordance with a pattern with a resist as given in Example 7 and dried, thereupon treated in a high vacuum with aluminum vapor as in Example 1, washed with cold water, dried and heated for 8 minutes at 200° C. There is obtained a metallic silver design on a colored background.

Two control-samples are made in the same way on a specimen of the same fabric but without previous formaldehyde treatment and without afterheating. A sample (I) of the fabric treated in accordance with Example 8 and one of the control-samples (II) are washed with a soap solution as in Example 1, whereby the metal layer of sample I shows a satisfactory permanency, whereas the metal layer of sample II is mainly removed.

Another sample (III) of the fabric treated in accordance with Example 8 and the other control sample are washed with a solution of a detergent as in Example 1, whereby the metal layer of sample III shows a good permanency, whereas the metal layer of sample IV is mainly removed.

Example 9

White acetate rayon taffeta is printed in accordance with a pattern with a resist as given in Example 7 and dried, then treated in a high vacuum with copper vapor and with gold vapor as in Example 2 and thereupon washed with cold water, dried and heated for 6 minutes at 180° C. There is obtained a metallic gold design on a white background.

Two control samples are made in the same way on specimens of the same fabric but without after-heating. A sample (I) of the fabric treated in accordance with Example 9 and one of the control samples (II) are washed with a soap solution as in Example 1 and another sample (III) of the fabric treated in accordance with Example 9 and the other control sample (IV) are washed with a solution of a detergent as in Example 1. The metal layers of samples I and III show a good permanency, whereas the metal layers of samples II and IV are mainly removed.

Example 10

Black-dyed viscose toile which has been made resistant to swelling by formaldehyde treatment as in Example 2 is subjected in a high vacuum installation first of all at a pressure of about 0.05 mm. mercury for 2 minutes to the action of cathode rays emerging from a glow-cathode and thereupon treated with aluminum vapor at a temperature between 800 and 1000° C. and at a pressure of about 0.00003 mm. mercury. The rayon fabric metallized in this manner is thereupon heated in an electrically heated furnace for 2 minutes at 225° C.

Two control-samples are made by directly coating with aluminum vapor, without previous formaldehyde treatment and treatment with cathode rays and without afterheating similar specimens of the same fabric. A sample (I) treated in accordance with Example 10 and one of the control samples (II) are washed with a soap solution as in Example 1 and another sample (III) treated in accordance with Example 10 and the other control sample (IV) are washed with a solution of a detergent as in Example 1. The metal layers of samples I and III show a good permanency, whereas the metal layers of samples II and IV are mainly removed.

Example 11

Black-dyed cotton muslin which has been transparentized in a known manner by a treatment with sulfuric

acid of 54° Bé. for 8 seconds is printed in a pattern with a printing paste consisting of

	Grams
Melamine formaldehyde butylether resin	450
Nitrocellulose	2
Butanol	6
Butylacetate	22
Tragacanth	20
Water	500
	1000

and dried. Thereupon the fabric is exposed in a high vacuum apparatus first of all at a pressure of 0.07 mm. mercury for 1 minute to the action of a cathode ray emerging from a glow-cathode and then treated with aluminum vapor at a temperature between 800 and 1000° C. and at a pressure of about 0.00007 mm. mercury. Thereafter the fabric is heated for 5 minutes at 140° C. and thereupon washed with hot water. During the washing, the metal which was applied by vaporization is removed from the unprinted parts while it remains adhering to the printed parts and a silvery pattern is thus obtained on a black background.

A sample of the so treated fabric is washed with a soap solution as in Example 1 and another sample is washed with a solution of a detergent as in Example 1. The metal layers of both samples show a good permanency against these washing treatments.

Example 12

Dyed viscose rayon satin which has been made resistant to swelling by a formaldehyde treatment as in Example 2 is printed in accordance with a pattern with a lacquer consisting of:

	Grams
Melamine formaldehyde butylether resin	400
Nitrocellulose	40
Butylacetate	560
	1000

The printed material is subjected in a high vacuum apparatus at a pressure of about 0.05 mm. mercury for 2 minutes to the action of cathode rays emerging from a glow-cathode and thereupon treated at a pressure of about 0.00003 mm. mercury first of all with copper vapor at a temperature of about 950 to 1050° C. and thereupon with gold vapor at a temperature of about 1050 to 1150° C. Thereafter the fabric is heated for 6 minutes at 130° C. and thereupon washed with hot water. Upon the washing, the metal layer which has been applied by vaporization is mainly removed from the unprinted parts and washed away, while the printed parts remain unchanged so that a gold pattern is produced.

A sample of the so treated fabric is washed with a soap solution as in Example 1 and another sample is washed with a solution of a detergent as in Example 1. The metal layers of both samples show a good permanency against these washing treatments.

Referring to the accompanying drawing which forms a part of this application:

Fig. 1 is an enlarged cross-sectional view of a fabric prepared in accordance with our invention, as for instance described in Example 3 herein. In this figure the direction of the metallic molecules in the vapor is shown as substantially perpendicular to the plane of the fabric; and

Fig. 2 is a still further enlarged view of a single thread showing a thin coating of vaporizable metal thereon, being a thread taken from the fabric of Fig. 1.

What we claim is:

1. A process which comprises vaporizing and depositing a vaporizable metal on fabric selected from the group consisting of natural and regenerated cellulose and thereafter heating the so-treated fabric for 2 to 8 minutes at 120° to 240° C.

2. A process which comprises vaporizing and deposit-

ing a vaporizable metal on a cellulose derivative fabric and thereafter heating said cellulose derivative fabric for 1 to 8 minutes at a temperature between 120° and 190° C.

3. A process which comprises subjecting fabric selected from the group consisting of natural and regenerated cellulose to the action of cathode rays from a glow-cathode, vaporizing and depositing a vaporizable metal on said fabric and thereafter heating the so-treated fabric for 2 to 8 minutes at 120° to 240° C. said glow-cathode being operated at an intensity to improve adherence of the metal to said fabric.

4. A process which comprises subjecting a cellulose derivative fabric to the action of cathode rays from a glow-cathode, vaporizing and depositing a vaporizable metal on said cellulose derivative fabric and thereafter heating said cellulose derivative fabric for 1 to 8 minutes at a temperature between 120° and 190° C. said glow-cathode being operated at an intensity to improve adherence of the metal to said fabric.

5. A cellulosic fabric prepared by the process of claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

1,661,517	Bosse	Mar. 6, 1928
1,758,531	Pfanhauser	May 13, 1930
1,982,774	Winkler	Dec. 4, 1934
2,039,372	Wickmann	May 5, 1936
2,101,518	Stewart	Dec. 7, 1937
2,139,640	Mall	Dec. 6, 1938
2,145,732	Nickle	Jan. 31, 1939
2,553,289	Alexander	May 15, 1951
2,559,389	Beeber	July 3, 1951
2,622,041	Godley	Dec. 16, 1952
2,630,620	Rand	Mar. 10, 1953
2,702,760	Barth	Feb. 22, 1955
2,709,663	McLean	May 31, 1955
2,748,031	Kafig	May 29, 1956
2,769,722	Converse	Nov. 6, 1956

FOREIGN PATENTS

1,058,934	France	Nov. 10, 1953