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3,445,264

METHOD AND COMPOSITION FOR TREATING THE SURFACE OF POLYMERIC ARTICLES TO IMPROVE ADHESION

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9 Claims

ABSTRACT OF THE DISCLOSURE

Surface treatment of polymeric articles to activate them and render them more adherent toward coating compositions is accomplished by exposing the surface of the polymeric article to an activating solution consisting of alkaline metals, alkaline earth metals, hydrides, or amides of alkaline metals or alkaline earth metals, in a dialkyl sulfoxide solvent vehicle.

The present invention relates to the surface treatment of polymeric materials. More specifically, it relates to the surface activating of polymeric materials with solutions of alkali metals, alkaline earth metals or certain salts of these metals in a dialkyl sulfoxide solvent vehicle.

It has been found that polymeric materials require pretreatment before they can be wetted or otherwise effectively coated. Failure to activate a polymeric surface will normally cause subsequent coatings to be poorly adhered and easily cracked, blistered or otherwise removed. These shortcomings have been especially troublesome in the plating of polymers with metals. Many methods have been used in attempting to render polymeric materials susceptible to metal plating. However, the presently known methods have been insufficient, at least to the extent that they have not been universally adopted.

Therefore, it is an object of this invention to provide a novel and improved process for treating the surface of a polymeric material so that coatings may be adherently applied thereto.

Another object is to provide a novel and improved process for rendering a polymeric surface susceptible and adherent to a plated metal coating.

Another object is to provide a treating composition suitable for use in rendering polymeric material adherent to coatings.

Other objects include: providing an improved method of activating adhesion properties on the surface of polymeric products without unduly reducing the desirable physical properties of the material; providing an improved polymeric product with a hydrophilic surface; and providing an economical and efficient process for activating a polymeric material in the manner indicated below.

The foregoing and other objects, and the features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention.

As used herein, the term plating is intended to include electroplating, electroless plating (chemical reduction), vapor deposition and vacuum deposition.

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Briefly, in accordance with the present invention, the surface of a polymeric material is activated by the process of exposing the surface to a unique activating solution. The activating solution consists of one or more reactive substances, such as alkali metals, alkaline earth metals, or hydride or amide salts of these metals in a dialkyl sulfoxide solvent vehicle.

The solution preferably contains sodium metal or lithium metal or a mixture of these metals in a dialkyl sulfoxide vehicle. Metals other than sodium and lithium may also be used in the activating solution. These metals include other alkali metals and alkaline earth metals. The hydrides and amides of the above enumerated metals have also been found suitable for use as reactive substances.

Most dialkyl sulfoxides have been found suitable as vehicles for the reaction mixture, however, it is preferred to use the alkyl-methyl sulfoxide or lower dialkyl sulfoxides. A particularly preferred representative of these vehicles is dimethyl sulfoxide.

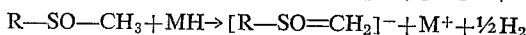
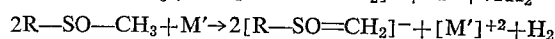
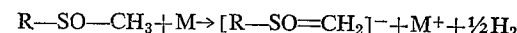
To produce additional desirable effects, wetting agents or surfactants may be added to the activating solution.

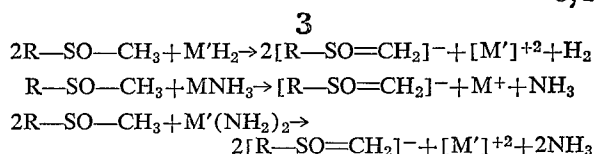
The duration of treatment, the concentration of the solution, and the temperature of the solution may vary considerably and still remain within the scope of the present invention. The concentrations of the metal or metal salts have been varied successfully over a substantial range from about 0.5% to about 20% by weight. Similarly, the duration of treatment has been varied over a substantial range and has been found to be directly related to the concentration of the solution and the temperature of the solution. The reaction has been found to be successful at room temperature, at temperatures lower than room temperature and also to proceed successfully at higher temperatures. In view of these parameters, the optimum conditions for a particularly desired result may be determined readily by one skilled in the art wishing to apply the teachings of the present invention. The fact that the reaction may be carried on at room temperature removes the necessity for the use of special heating equipment during the course of the reaction and reduces the dangers which are inherent in working with highly reactive substances at elevated temperatures.

The process of the present invention comprises immersing a polymeric material in the activating solution, removing the polymeric material, and then rinsing the polymeric material with water or other suitable solvents to stop the activating reaction and remove any adhering reaction products. In another form of the present invention a strip of polymeric material may be continuously passed through the activating solution, passed out of the solution and rinsed, and then further treated by printing upon it or by passing it through a plating environment.

While applicant does not wish to be limited by any theory as to the nature of the invention, it is believed that in the reaction mechanism of the present invention, the metal or metal salt reacts with the dialkyl sulfoxide solvent vehicle with the subsequent formation of hydrogen or ammonia.

Possible typical reaction mechanisms are:





In which R is an alkyl radical, M is an alkali metal, and M' is an alkaline earth metal. The resulting interaction between the various ions and the polymeric material leads to a reaction at the surface of the polymeric material causing it to become activated.

When properly carried out, this treatment does not physically degrade the surface of the polymeric material or cause shrinkage of the material as prior art treatments have been known to do.

In each of the following examples a quantitative test of the adhesion between the activated polymeric surface and the coating subsequently plated thereon was made. The method used for the study of the adhesion is a form of tape peel test. This technique has proved to be a reliable tool in the study of adhesion. In performing this test a one-half inch strip of the to-be-tested activated and coated polymeric material is thoroughly cleaned and dried, and immersed in gently stirred ethyl alcohol for a short period of time. The sample is then removed from the alcohol, dried and, on its coated side, treated with a thin uniform layer of Goodyear Tire and Rubber Co. Pliobond Adhesive CIX 1059, a butadiene-acrylonitrile phenolic resin. The thus prepared strip is then placed upon the surface of a clean stainless steel plate which has also been coated with Pliobond. A small strip of material is allowed to extend beyond the steel plate. The thus joined plate and tape are then placed in an oven with a weighted plate upon them and dried for 5 minutes at 120° C. At this point the material is ready to be tested. The overlapping portion of the polymeric strip is firmly gripped and peeled back upon itself at a 180° angle, thus urging it to peel from the material coated on its activated surface. The force required to pull the tape from the material coated on its surface is an indication of the adhesion of the coating to the activated substrate. The force is nominally measured in grams, and as the samples are one-half inch in width, the figures are given in terms of grams/½". Experience has shown that a value of 600 grams/½" or greater is indicative of superior adhesion between a substrate and the material coated thereon.

The following descriptions and specific examples will detail and describe the methods and compositions utilized in activating various polymeric materials. They are set forth as preferred embodiments and are not intended to limit the scope of the invention.

EXAMPLE 1

A sample of a 1 mil thick sheet of polyethylene terephthalate was immersed in a 1% solution of sodium in dimethyl sulfoxide at room temperature for a period of 15 seconds. The thus treated film was washed with distilled water and dried and further activated and sensitized for

plating by the well known SnCl₂ and PdCl₂ method described in Bergstrom U.S. Patent 2,702,753. The polymeric material was then plated with nickel by electroless deposition. The resulting plated surface appeared to be smooth and continuous. In testing the adhesion a force of 750 grams/½" was required to peel the polyester substrate from the plated nickel metal.

When the same process was repeated with a sample of polyethylene terephthalate which had been activated by the heretofore widely used acid-base dip method a force of only 400 grams/½" was necessary to peel the substrate from the plated metal.

EXAMPLE 2

The procedure of Example 1 was followed substituting lithium for sodium as the reactive substance in the activating solution. In attempting to peel the substrate from the plated nickel the polyethylene terephthalate split and broke before the plated metal could be peeled off. Such a result is indicative of the fact that the plated metal was more tenaciously adhered to the polyethylene terephthalate than the polyethylene terephthalate was adhered to itself. This of course indicates extremely strong adhesion between the substrate and the plated metal.

EXAMPLE 3

The procedure of Example 1 was repeated once more using 1% lithium hydride as the reactive substance in the activating solution. In the subsequent adhesion test 730 grams/½" of force was required to separate the substrate from the plated metal.

EXAMPLE 4

A 1 mil thick tape of polyethylene terephthalate was immersed in a 5% solution of sodium hydride in methyl ethyl sulfoxide for a period of 30 seconds. The thus treated tape was then further activated and plated as in Example 1. A force of 710 grams/½" was required to separate the substrate from the plated metal.

EXAMPLE 5

A tape of polyethylene terephthalate was continuously passed through a 0.5% solution of sodium in dimethyl sulfoxide solvent vehicle. The tape was further continuously passed through a rinse bath, a stannous chloride sensitizing bath, another rinse, a palladium chloride activating bath, another rinse and then through an electroless cobalt plating bath. In testing the adhesion a force of 765 grams/½" was required to peel the polyester substrate from the plated cobalt. The cobalt plated tape was found to be usable as a magnetic recording media.

In order to more fully describe the present invention, additional specific examples are set forth in the following tables. In Table A, solution constituents, bath parameters and the types of polymeric materials treated are set forth. In Table B the coatings and the results of adhesion tests are set forth.

TABLE A.—SUBSTRATE, CONSTITUENTS AND PARAMETERS

Example	Polymeric material	Solvent vehicle	Metal or salt, weight percent	Solution temp. ° C.
6	Polytetrafluoroethylene	Dimethyl sulfoxide	15% Na	25
7	do	Methyl propyl sulfoxide	20% NaNH ₂	40
8	do	N-dibutyl sulfoxide	10% Na, 10% Li	25
9	Polyethylene	N-dipropyl sulfoxide	12% K	22
10	do	Di-isopropyl sulfoxide	10% Ba	50
11	do	Dimethyl sulfoxide	2% Ca	60
12	Polyamide	Methyl ethyl sulfoxide	5% Mg	75
13	do	Methyl propyl sulfoxide	1% Rb	23
14	do	N-dipropyl sulfoxide	12% LiNH ₂	25
15	Polyimide	Di-isopropyl sulfoxide	3% K	25
16	do	N-dibutyl sulfoxide	1% CaH ₂	55
17	do	Dimethyl sulfoxide	1% NaNH ₂	25
18	Polycarbonate	do	1% KH	25
19	do	Methyl ethyl sulfoxide	0.5% Ca	20
20	Cellulose Acetate	N-dibutyl sulfoxide	1% Ca(NH ₂) ₂	10

TABLE B.—COATINGS AND ADHESION

Example	Coating	Adhesion test results, g./1/2"
6.....	Electroless copper.....	640
7.....	Butadiene-acrylonitrile resin topped with copper foil.....	(1)
8.....	Electroless nickel.....	710
9.....	Electroless cobalt-nickel.....	670
10.....	Alkyd varnish black ink.....	
11.....	Epoxy varnish black ink.....	
12.....	Electroless silver followed by electroplated copper.....	650
13.....	Electroless nickel.....	720
14.....	do.....	690
15.....	do.....	730
16.....	Vacuum deposited cobalt.....	(2)
17.....	Electroless cobalt.....	750
18.....	Electroless nickel.....	710
19.....	Nickel by carbonyl decomposition.....	690
20.....	Electroless nickel.....	650

¹ "Sandwich" opened at 680.

² Substrate broke.

In Examples 8, 16 and 17 ultrasound agitation techniques were utilized in the activating baths to enhance the dispersion of the solutions upon the polymeric surfaces.

In Examples 10 and 11 the adhesion of the ink to the polyethylene was tested by sticking a piece of cellophane tape upon the printed surface. Upon removing the tape the printing was found to remain adhered to the polyethylene with only small bits of ink adhered to the tape.

The above series of specific examples set forth non-limiting illustrations of polymeric materials, dialkyl sulfoxide solvent vehicles, and metals and salts, which can be utilized in practicing the present invention. To one skilled in the art, it will be abundantly clear that other related materials may be substituted and similar results achieved. For example, cesium, beryllium and strontium and their salts will give similar results. Also other dialkyl sulfoxides can be utilized as solvent vehicles in the system.

In accordance with the invention, polymeric surfaces are provided which are readily plated or otherwise coated by conventional techniques. The invention is not necessarily limited to the applications herein described, however, since it can be utilized in any application in which adhesion between polymeric material and a surface coating is desired.

While the invention has been particularly described and shown with reference to preferred examples thereof, it will be understood by those skilled in the art that various changes in constituents and environment may be made without departing from the spirit and the scope of the invention.

I claim:

1. A composition for treating the surface of a synthetic organic polymeric article to render it hydrophilic consisting essentially of:

a liquid dialkyl sulfoxide vehicle; and
about 0.5% to about 20% by weight of one or more

reactive substance selected from the group consisting of alkali metals, alkaline earth metals, and the hydrides and amides of alkali metals and alkaline earth metals.

2. The composition of claim 1 wherein the dialkyl sulfoxide is an alkyl-methyl sulfoxide.

3. The composition of claim 2 wherein the alkyl-methyl sulfoxide comprises dimethyl sulfoxide.

4. The composition of claim 3 wherein the reactive substance includes sodium.

5. A process for rendering the surface of a synthetic organic polymeric article hydrophilic including the step of: contacting the surface of the polymeric material with an activating solution consisting essentially of a dialkyl sulfoxide vehicle and one or more reactive substances selected from the group consisting of alkali metals, alkaline earth metals, and the hydrides and amides of alkali metals and alkaline earth metals.

6. The process of claim 5 wherein the vehicle comprises dimethyl sulfoxide.

7. The process of claim 5 wherein the reactive substance includes sodium.

8. The process of claim 5 wherein the polymeric article is polyethylene terephthalate.

9. A method of making a magnetic recording member including the steps of:

rendering the surface of a synthetic organic polymeric substrate hydrophilic with a solution consisting essentially of a dialkyl sulfoxide vehicle and one or more reactive substances selected from the group consisting of alkali metals, alkaline earth metals, and the hydrides and amides of alkali metals and alkaline earth metals; followed by the steps for coating the surface of the hydrophilic polymeric substrate with ferromagnetic material.

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252—182; 117—118, 121, 138.8

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,445,264 Dated May 20, 1969

Inventor(s) ROBERT S. HAINES

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the specification, Column 1, line 26, "mtaerials" should read --materials--. Column 3, line 2, that portion of the formula reading "MNH₃" should read --MNH₂--.

SIGNED AND
SEALED

NOV 25 1969

(SEAL)

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