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METHOD OF METALLIZING AN ORGANIC SUBSTRATE

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ABSTRACT OF THE DISCLOSURE

Synthetic resinous substrates substantially free of volatile materials are activated by electric glow discharge treatment of the surface under reduced pressure in the presence of a gas. The surface is subsequently or simultaneously treated with an oxidizing agent and a ductile metal deposited from a gas to form a layer about 10 angstroms to about 10,000 angstroms in thickness. The metal layer deposited is coherent and has high barrier properties.

This application is a continuation-in-part of our copending application Ser. No. 682,582, filed Nov. 13, 1967, now abandoned.

This invention relates to the metallizing of synthetic resinous substrates, and more particularly relates to an improved method for the deposition of a coherent metallic layer on a resinous substrate.

Metallizing synthetic resinous substrates has been widely employed primarily for decorative effects. However, such deposits of metal are not known to exhibit barrier characteristics; that is, low gas transmission rates and moisture vapor transmission rates, which would be expected if a coherent layer were deposited, are not exhibited by such metallized substrates.

It would be advantageous if there were available an improved method of metallizing synthetic resinous substrates to provide a coherent high barrier layer thereon.

It would also be beneficial if there were available an improved method for the metallization of generally nonpolar synthetic resinous substrates.

It would also be advantageous if there were available an improved method for the preparation of synthetic resinous substrates to provide a coherent continuous metallic layer thereon having high resistance to the transmission of gases and vapors.

These benefits and other advantages in accordance with the present invention are achieved by a method for metallizing a surface of an organic synthetic resinous substrate wherein the deposited metal forms a generally continuous layer and provides a substantial barrier to the passage of gas and moisture vapor, the method comprising providing a synthetic resinous substrate having a surface to be metallized substantially free of volatile constituents, treating the surface of the substrate with an electric glow discharge treatment under a subatmospheric pressure of from about 0.01 to about 1.0 millimeter of mercury absolute in the presence of a member selected from the group consisting of oxygen, ozone, hydrogen peroxide, dimethyl peroxide, diethyl peroxide, methylethyl peroxide, hydroxymethyl hydroperoxide, 1-(hydroxyethyl)hydroperoxide, α-bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, peroxyacetic acid, formaldehyde, formic acid, acetonitrile, acrylonitrile, fluorine, chlorine, bromine, iodine, carbon dioxide, carbon monoxide, nitrogen, helium, neon, argon, krypton, and mixtures thereof, under an absolute pressure of from about 0.01 to 1.0 millimeter of mercury, exposing the electric glow discharge-treated surface to an oxidant selected from the group consisting of oxygen, ozone, hydrogen peroxide, dimethyl peroxide, diethyl peroxide, methylethyl peroxide, hydroxymethyl hydroperoxide, 1-(hydroxyethyl)hydroperoxide, α-bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, peroxyacetic acid, formaldehyde, formic acid, acetonitrile, carbon monoxide, acrylonitrile, fluorine, chlorine, bromine, iodine and mixtures thereof, until the surface exhibits a wetting angle of less than 50° when an oxygen bearing oxidant is employed; less than 75° when a halogen bearing oxidant is employed; less than 65° when a nitrile bearing oxidant is employed, subsequently depositing on the oxidant treated surface from a gaseous environment a layer of a ductile metal selected from the group consisting of aluminum, copper and magnesium, the layers being from about 10 angstroms to about 10,000 angstroms in thickness and the layer being deposited at a rate of at least one angstrom per second.

The term "electric glow discharge" is well known in the art and is occasionally referred to as corona low pressure discharge, low temperature gas plasma and the like. "Wetting angle" refers to the advancing contact angle with water as determined by the method set forth in Advances in Chemistry, No. 43, American Chemical Society, 1964, pp. 136–144, by Robert H. Dettre and Rulan E. Johnson.

The method of the present invention is particularly suited for the metallization of synthetic organic substrates having an average lateral growth nucleation factor less than about 0.25. The term "lateral growth nucleation factor" for a given polymeric or non-volatile component of the substrate is calculated by multiplying the dipole moment of each pendant polar group on such molecule along the backbone by the number of such groups and dividing by the sum of the bond lengths in angstroms from one end of the unit to the other along the backbone. The final value has the units of Debyes per angstrom. The average lateral growth nucleation factor is the sum of the weighted values of the lateral growth nucleation factor of all constituents of the polymer with each being weighed in direct proportion to the amount of the particular constituent present. In performing such calculations where benzene or other rings constitute part of the backbone or are pendant from the opposite side of the pendant polar group, the bond distances along only one side of the ring are included in the length of the backbone considered. When two polar groups are attached to the same or adjacent backbone atoms, a net dipole moment is taken. For example: the net dipole moment of four fluorine atoms attached to two adjacent backbone carbon atoms in a polytetrafluoroethylene, result in a net dipole moment of zero, but in the head to tail addition occurring

in polyvinylidene chloride, the two chlorines geometrically divide the resultant moment. For copolymers, a repeating unit is set up on the basis of the mole ratio of the two monomers and this repeating unit becomes the basis for calculating the average lateral growth nucleation factor of the copolymer. In the cases where chain branching occurs besides that at the site of the pendant polar group and extends more than one carbon away from the backbone, or where a group more than one carbon long is attached to the pendant polar group on the side opposite the main chain attachment (as in copolymers of butyl acrylate), those atoms more than one carbon atom removed from the backbone or more than one carbon atom removed from the pendant polar group shall be treated and weighted as comonomers according to the above copolymer rule even though it may be necessary to invoke hypothetical monomers (as in tertiarybutylvinyl ether).

Typical polymers exhibiting a low average lateral growth nucleation factor are polyolefins such as polyethylene and polypropylene; polyvinyl aromatics such as polystyrene, polystertiarybutylstyrene, poly-α-methylstyrene, polyvinyl toluene; polydiolefins such as polybutadiene and the like.

The term "volatile constituents" as employed herein refers to a material which exhibits a vapor pressure of greater than one micron of mercury absolute at 100° C. Such volatile materials are readily removed by vacuum treatment for short periods of time and the volatile constituents have a relatively high vapor pressure and the substrate is relatively thin, such as in the case of a one mil thick polyethylene film having hexane as a volatile contaminant. Oftentimes it is desirable to employ such techniques as solvent extraction and/or heating in combination with or followed by vacuum treatment at pressures of 1 to about 0.01 micron of mercury absolute for periods of time ranging from seconds to hours, depending on the particular contaminants. Oftentimes, stabilizers, lubricants, volatile plasticizers, additives and the like are employed in the preparation of synthetic resinous articles or substrates and in general they are not desirable in the practice of this invention and oftentimes require solvent extraction prior to the deposition of a metal layer. Some of the problems encountered in, and plasticizer tolerance for, decorative vacuum metallization are set forth in Vacuum Deposition of Thin Films, pp. 48–53, by Holland, published by Wiley, 1956. The presence of plasticizers on or adjacent to the surface of a thermoplastic substrate gives a value of the average lateral growth nucleation factor which differs from the calculated value in the presence of plasticizers is ignored.

The term "ductile metal" as employed herein refers to metallic elements, alloys or mixtures which have an elongation of at least 20 percent. Such elongation is determined in the following manner: an annealed foil of the metallic foil to be evaluated having a thickness of 2.5 to 50 microns is laminated between two layers of polyethylene terephthalate, each having a thickness of about 50 microns and an elongation of at least 50 percent at 27° C. A polyethylene terephthalate film eminently suitable for such applications is commercially available under the trade designation of Mylar A. Any one of a large number of extensible adhesives are suitable to prepare the test laminate, including one supplied under the trade designation of Du Pont 46975 polyester adhesive with Du Pont RL 805 curing agent. One particularly advantageous adhesive is a 30 micron thick film of a copolymer of 92 weight percent ethylene and 8 weight percent acrylic acid. The adhesive is disposed between the foil and cured at a temperature of about 110° C. for the polyester adhesive or heat laminated at a temperature of about 140° C. if the ethylene acrylic acid copolymer is employed. Three samples are cut from the resultant laminate each measuring 6 by 1 inch. In turn, each sample is grasped in the jaws of a tensile strength testing machine to provide a length of 3 inches between the jaws. Electrical connection is made to each end of the sample remote from the 3 inch section between the jaws by clips which perforate the film and contact the metal in about 3 locations at each end. Each of the clips is connected to an ohm meter and the test specimen stretched at a rate of one quarter inch per minute at a temperature of from 20° C. to 27° C. until the resistance of the sample doubles. The elongation of the sample is calculated and an average of three determinations is taken as the elongation. Some ductile metals suitable for the practice of the present invention are zinc, copper, nickel, tin, aluminum, magnesium, calcium, iron, sodium, lithium, potassium, lead and many alloys thereof.

A wide variety of synthetic thermoplastic resinous substrates are employed for the practice of the invention including polymers from Table I which follows.

TABLE I

Polymer:	Average lateral growth nucleation factor
Trans-polybutadiene	0.00
Polyethylene	0.00
Polypropylene	0.00
Polyvinyl-p-methylbenzene	0.00
Polyisobutylene	0.00
Polytetrafluoroethylene	0.00
Polyisoprene	0.033
Cis-polybutadiene	0.046
Poly-1,2-butadiene	0.112
Polyvinyl-p-tertiarybutylbenzene	0.139
Linear polymethyl polysiloxane	0.15
Polystyrene	0.191
Poly-o-methylstyrene	0.21
Polychlorotrifluoroethylene	0.17
Polyindene	0.17

The invention is further illustrated but not limited by the following examples. All oxygen transmission rates given are in cubic centimeters per 100 square inches per 24 hours per atmosphere at 72° F. All moisture vapor transmission rates given are in grams per 100 square inches per 24 hours at 100° F. and 100 percent relative humidity.

EXAMPLE 1

A polypropylene film is treated by electric glow discharge for 120 seconds at a pressure of 0.055 millimeter of mercury in an atmosphere of argon by moving the film past two linear electrodes spaced 5 centimeters from the film and 7 centimeters apart operating at a voltage of 1200 volts and a current of 200 milliamperes. The treated surface of the polypropylene film has an advancing contact angle for water of 75°. The treated film is subsequently subjected to an atmosphere of oxygen for a period of 120 seconds at a pressure of one millimeter of mercury, transferred to a vacuum metallizing system wherein a copper coating 410 angstroms in thickness is deposited in a period of 30 seconds to provide a metallization rate of about 13.7 angstroms per second. The oxygen transmission rate is 0.51. After being subjected to the oxygen treatment, the polypropylene film has an advancing contact angle for water of 45°. By way of comparison, when the oxygen after electric glow discharge treatment is omitted, the oxygen transmission rate is 1.18.

EXAMPLE 2

A plurality of samples of 25 micron thick polyethylene, 25 micron thick polypropylene and 50 micron thick polystyrene film is treated in a manner generally similar to Example 1 to provide an advancing contact angle for water of from 44 to 47°. The results are set forth in Table II wherein Samples 1–14 are polyethylene, Samples 15–20 are polypropylene and Samples 21–23 are polystyrene.

TABLE II

	Glow discharge conditions					Metallizing conditions			Permeability	
	Gases [1]		Time	Electrical			Deposition rate			
	O_2	HCOOH	minutes	Kv.	Ma.	Metal	Angstroms	Seconds	O_2-GTR	MVTR
Sample No.:										
1									338	0.5
2						Cu	670	45	43.2	0.06
3	200	0	2	1.5	200	Cu	670	45	0.725	
4	75	75	2	1.0	200	Cu	670	120	0.24	0.0025
5	18	6	2	2	130	Cu	670	45	0.15	0.005
6	9	3	2	2	75	Cu	670	30	0.13	0.028
7	0	45	0.25	2.5	80	Cu	670	96	0.006	0.008
8	0	200	2	1.5	200	Cu	670	45	0.11	0.002
9	12	38	2	1.4	200	Mg	1,150	20	0.074	
10						Al	740	20	1.82	
11	45	15	2	1.0	100	Al	740	25	0.278	
		CH_3-CN								
12	0	200	2	2	150	Cu	670	45	0.126	0.0018
13	100	100	2	1.2	200	Cu	670	45	0.430	0.013
		CH_2-CH-CN								
14	0	150	2	2	150	Cu	310	240	0.65	
		HCOOH								
15									180	0.7
16						Cu	110	360	78	
17	30	10	0.33	1.9	100	Cu	340	60	0.0125	
18						Al	3,700	210	13.2	0.035
19	0	100	2	1.5	200	Al	740	90	0.38	0.009
20	50	0	2	1.0	200	Mg	500	30	0.25	
21									138	4.0
22	0	50	1.5	0.8	30				88	
23						Al	370	30	6.2	
24	50	0	2	1	200	Al	370	90	0.98	
25	0	100	2	1.5	200	Al	740	60	0.45	0.01
26						Cu	670	60	25.10	
27	35	0	0.25	2	100	Cu	670	45	1.6	
28	0	85	1.5	0.75	30	Cu	560	30	0.5	
29						Mg	1,150	15	138	6.0
30	50	0	1.5	0.5	35	Mg	1,150	60	1.12	
31	0	65	1.5	0.8	30	Mg	1,150	15	0.4	

[1] Partial pressure of treating gases in microns of mercury absolute.

EXAMPLE 3

A quantity of polypropylene film having a thickness of 32 microns is treated with the electric glow discharge oxidation procedure as described in Example 1 and exposed to oxygen. The advancing contact angle for water of the treated film is 51°. The film is then supported on a water-cooled metal drum (18° C. water temperature) and exposed to a flowing stream of hydrogen at atmospheric pressure, saturated with the aluminum chelate of trifluoroacetylacetone which is heated to a temperature of 160° C. to provide chemical vapor deposition of an aluminum film about 215 angstroms in thickness on the polypropylene surface at a rate of about 5 angstroms per second. The oxygen transmission rate of the coated film is 0.1 and the water vapor transmission rate is 0.007. When the foregoing procedure is repeated with the excepton that the glow discharge and subsequent oxidation are omitted, the metallized film has an oxygen-gas transmission rate of 30 and a water vapor transmission rate of 0.006.

EXAMPLE 4

A biaxially oriented polypropylene film is treated with the glow discharge oxidation procedure set forth in Example 1 to provide an advancing contact angle for water of 48°. The film is supported on a water-cooled roll and exposed to a stream of gaseous nickel carbonyl heated to a temperature of 160° C. until a nickel layer 87 angstroms in thickness is deposited at a rate of 2 angstroms per second. The oxygen-gas transmission rate of the metallized film is 0.09 and the water vapor transmission rate is 0.06. By way of comparison, when the foregoing procedure is repeated omitting the pre-treatment of the surface by golw discharge and oxidation, the oxygen-gas vapor transmission rate is 60 and the water vapor transmission rate is 0.2.

When the foregoing examples are repeated with the exception that electric glow discharge treatment is carried out in the presence of ozone, dimethyl peroxide, hydrogen peroxide, methylethyl peroxide, hydroxymethyl hydroperoxide, 1-(hydroxyethyl)hydroperoxide, α-bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, peroxyacetic acid, formaldehyde, fluorine, chlorine, bromine, iodine, carbon dioxide, carbon monoxide, nitrogen, helium, neon, argon, krypton and mixtures thereof, to provide advancing contact angles for water as hereinbefore set forth, substantially similar results are obtained. When the procedure of the foregoing illustrations are repeated with the exception that the electric glow discharge treated-surface is exposed to oxygen, ozone, dimethyl peroxide, diethyl peroxide, hydrogen peroxide, methylethyl peroxide, hydroxymethyl hydroperoxide, 1-(hydroxyethyl)hydroperoxide, α-bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, carbon monoxide, peroxyacetic acid, formaldehyde, fluorine, chlorine, bromine, iodine and mixtures thereof, similar beneficial results are obtained. Similar beneficial results are also obtained. Similar beneficial results are also obtained when the foregoing illustrations are repeated employing the following synthetic organic substrates: trans-polybutadiene, polyvinyl-p-methylbenzene, polyisobutylene, polytetrafluoroethylene, polyisoprene, cis-polybutadiene, poly-1,2-butadiene, polyvinyl-p-tertiarybutylbenzene, linear polymethyl polysiloxane, polychlorotrifluoroethylene, polyindene and poly-o-methylstyrene.

As is apparent from the foregoing specification, the present invention is susceptible of being embodied with various alterations and modifications which may differ particularly from those that have been described in the preceding specification and description. For this reason, it is to be fully understood that all of the foregoing is intended to be merely illustrative and is not to be construed or interpreted as being restrictive or otherwise limiting of the present invention, excepting as it is set forth and defined in the hereto-appended claims.

What is claimed is:

1. A method for metallizing a surface of an organic synthetic resinous substrate wherein the deposited metal forms a generally continuous layer and provides a substantial barrier to the passage of gas and moisture vapor, the method comprising

providing an organic synthetic resinous substrate having a surface to be metallized substantially free of volatile constituents,

treating the surface of the substrate with an electric glow discharge treatment under a subatmospheric pressure of from about 0.01 to about 1.0 millimeter of mercury absolute in the presence of a member selected from the group consisting of oxygen, ozone, dimethyl peroxide, hydrogen peroxide, diethyl peroxide, methylethyl peroxide, hydroxymethyl hydroperoxide, 1 - (hydroxyethyl)hydroperoxide, α-bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, peroxyacetic acid, formaldehyde, formic acid, acetonitrile, acrylonitrile, fluorine, chlorine, bromine, iodine, carbon dioxide, carbon monoxide, nitrogen, helium, neon, argon, krypton and mixtures thereof, and

exposing the electric glow discharge-treated surface to an oxidant selected from the group consisting of oxygen, ozone, dimethyl peroxide, diethyl peroxide, hydrogen peroxide, methylethyl peroxide, hydroxymethyl hydroperoxide, 1-(hydroxyethyl)hydroperoxide, α-bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, carbon monoxide, peroxyacetic acid, formaldehyde, formic acid, acetonitrile, acrylonitrile, fluorine, chlorine, bromine, iodine and mixtures thereof under an absolute pressure of from about 0.01 to 1.0 millimeter of mercury, until the surface exhibits a wetting angle of less than 50° when an oxygen bearing oxidant is employed; less than 75° when a halogen bearing oxidant is employed; less than 65° when a nitrile bearing oxidant is employed, subsequently

depositing on the oxidant-treated surface from a gaseous environment a layer of a ductile metal, the layers being from about 10 angstroms to about 10,000 angstroms in thickness and the layer being deposited at a rate of at least one angstrom per second.

2. The method of claim 1 wherein the synthetic organic substrate has an average lateral growth nucleation factor of less than about 0.25.

3. The method of claim 1 wherein the substrate is treated prior to metallizing at a pressure of from about 0.01 micron to about 1 micron of mercury absolute to remove volatile materials therefrom.

4. The method of claim 1 wherein the ductile metal is aluminum.

5. The method of claim 1 wherein the ductile metal is copper.

6. The method of claim 1 wherein the synthetic resinous substrate is polypropylene.

7. The method of claim 1 wherein the synthetic resinous substrate is polyethylene.

8. The method of claim 1 wherein the electric glow discharge oxidation is carried out in an oxygen atmosphere having a pressure from about 0.01 millimeter to about 1 millimeter of mercury absolute.

9. The method of claim 1 wherein the metal layer is deposited by vacuum metallization.

10. The method of claim 1 wherein the metal layer is deposited by chemical vapor deposition.

11. A method for metallizing a surface of an organic synthetic resinous substrate wherein the deposited metal forms a generally continuous layer and provides a substantial barrier to the passage of gas and moisture vapor, the method comprising

providing an organic, synthetic resinous substrate having a surface to be metallized substantitlly free of volatile constituents and a lateral growth nucleation factor of less than about 0.25,

treating the surface of the substrate with an electric glow discharge treatment under a subatmospheric pressure of from about 0.01 to 1.0 millimeter of mercury absolute in the presence of a member selected from the group consisting of oxygen, ozone, dimethyl peroxide, hydrogen peroxide, diethyl peroxide, methylethyl peroxide, hydromethyl hydroperoxide, 1-hydroxyethyl)hydroperoxide, α - bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, peroxyacetic acid, formaldehyde, formic acid, acetonitrile, acrylonitrile, fluorine, chlorine, bromine iodine, carbon dioxide, carbon monoxide, nitrogen, helium, neon, argon, krypton and mixtures thereof, and

exposing the electric glow discharge-treated surface to an oxidant selected from the group consisting of oxygen, ozone, dimethyl peroxide, diethyl peroxide, hydrogen peroxide, methylethyl peroxide, hydroxymethyl hydroperoxide, 1-(hydroxyethyl)hydroperoxide, α-bis(hydroxymethyl) peroxide, α-bis(1-hydroxyethyl) peroxide, diformyl peroxide, diacetyl peroxide, formyl acetyl peroxide, peroxyformic acid, carbon monoxide, peroxyacetic acid, formaldehyde, formic acid, acetonitrile, acrylonitrile, fluorine, chlorine, bromine, iodine and mixtures thereof under an absolute pressure of from about 0.01 to 1.0 millimeter of mercury, until the surface exhibits a wetting angle of less than 50° when an oxygen bearing oxidant is employed; less than 75° when a halogen bearing oxidant is employed; less than 65° when a nitrile bearing oxidant is employed, subsequently

depositing on the oxidant-treated surface from a gaseous environment a layer of a ductile metal selected from the group consisting of aluminum and copper, the layers being from about 10 angstroms to about 10,000 angstroms in thickness and the layer being deposited at a rate of at least one angstrom per second.

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