

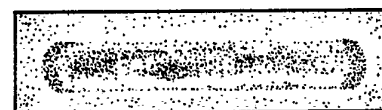
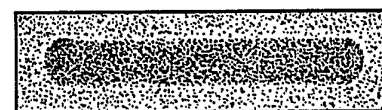
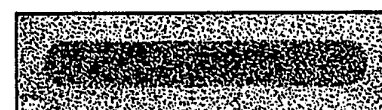


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(54) Title: CATALYTIC EMULSIONS FOR ELECTROLESS DEPOSITION**(57) Abstract**

Aqueous, catalyst emulsions adapted for forming cross-linked, polymeric coatings which can catalyze the electroless deposition of metal comprise (a) water, (b) surfactant-stabilized particles of a cross-linkable, water-insoluble polymer dispersed as an emulsion in said water, (c) a water soluble compound of a Group 8 metal, and (d) a cross-linking agent. Such emulsions are adapted to forming catalytically inert, dry films which can be simultaneously thermally cross-linked and activated to catalyze electroless deposition of strongly adhering metals such as copper, nickel and silver. Cross-linkable polymers include polybutadiene and copolymers of butadiene, poly(vinylchloride), poly(methacrylate), poly(alkylmethacrylate) and poly(vinylacetate).

**5 RATING****4 RATING****3 RATING****2 RATING****1 RATING**

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CATALYTIC EMULSIONS FOR ELECTROLESS DEPOSITION

Disclosed herein are catalytic emulsions, catalytic polymeric films prepared from such emulsions, and metal coated articles, including metal-coated textile materials, where the metal is electrolessly deposited onto catalytic polymeric films prepared by such emulsions. Also disclosed are methods of preparing and using such catalytic emulsions, films and articles.

BACKGROUND OF THE INVENTION

Metal-coated textile articles are useful for a variety of electromagnetic radiation shielding applications, e.g. wall coverings, gaskets, composite housings, protective clothing, and the like. The shielding performance of such metal-coated textile materials is influenced by adhesion and electrical conductivity of the metal coating, especially the long term durability of such properties in common environments, e.g. metal-oxidizing environments of high humidity, rain, fog or salt spray or laundering. Such metal-coated articles are advantageously produced by electroless deposition onto a catalytic coating on such articles.

Morgan et al. in U.S. Patent 4,910,072, O'Connor et al. in U.S. Patent 4,900,618 and Vaughn in U.S. Patent (application Serial No. 07/609,718), all of which are incorporated herein by reference, disclose catalytically inert polymeric films comprising complexes of a polymer and catalytic metal which can be activated to catalyze electroless deposition by the application of energy, e.g. heat or light, to the surface of the inert polymeric film. In particular Vaughn discloses the preparation of such films from aqueous solutions of water soluble polymers or emulsions of water-insoluble polymers. Such aqueous catalytic solutions are environmentally

advantageous for preparing polymeric films that catalyze the electroless deposition of metals because the organic solvents typically used in prior art formulations is replaced by water.

5 Maintaining adhesion of catalytic material on the substrate is of considerable importance since loosely adhered catalytic material, e.g. palladium, can be washed from the surface in the agitation of the plating bath causing depletion of the metal value of
10 the plating bath as uncontrolled metal deposition occurs, resulting in what is commonly referred to as a "crashed" bath. Vaughn teaches the use of crosslinking agents, e.g. dialdehydes, with water-soluble polymers to provide more stable, catalytic,
15 polymer coatings. See also U.S. Patents 3,615,471; 3,719,490 and 3,779,758 for other disclosures of crosslinked catalytic coatings of water-soluble polymers.

A disadvantage of coatings of water-soluble
20 polymers, including crosslinked water soluble polymers, is that high pH plating baths and/or incomplete crosslinking and/or failure to wash away deliberately uncrosslinked polymer coating can cause undesired transfer of catalytic metal into a plating
25 bath causing the plating bath to crash, i.e. undergo an uncontrolled metal reduction and deposition throughout the plating bath.

An object of this invention is to provide catalytic coatings of essentially water-insoluble
30 polymers to minimize the opportunity for complexes of catalytic metal and polymer to solubilize into a plating bath with attendant crashing of a plating solution.

A further object is to provide essentially
35 water insoluble polymeric coatings that catalyze the electroless deposition of metal that is highly adherent, even after severe environmental exposure

such as laundering in the case of metal-coated textiles.

These and other objects of this invention will be apparent from the following description of the invention and illustrative examples.

SUMMARY OF THE INVENTION

We have discovered that metal coatings having enhanced adhesion can be electrolessly deposited onto articles coated with a catalytic, crosslinked polymeric film prepared from aqueous, catalyst emulsions. Thus one aspect of this invention is exceptionally adhesive, electrolessly-deposited metal coatings, e.g. on textile materials. Another aspect of this invention is crosslinked, polymeric coatings which can catalyze the electroless deposition of such adherent metal. And, another aspect of this invention is aqueous catalytic emulsions which comprise (a) water, (b) surfactant-stabilized particles of a crosslinkable, water-insoluble polymer dispersed as an emulsion in said water, (c) a water soluble compound of a Group 8 metal, and (d) a crosslinking agent. Still other aspects of this invention are methods of preparing catalytic, crosslinked polymeric coatings and abrasion-resistant metal coatings.

BRIEF DESCRIPTION OF THE DRAWINGS

The figure is a reference scale for metal adhesion ratings based on the amount of metal removed by a layer of adhesive tape after standardized rubbing under a fixed load.

DETAILED DESCRIPTION OF THE INVENTION

Throughout this specification, percentages of compositions are by weight and temperatures are in degrees Celsius, unless indicated otherwise.

The term "emulsion" as used herein means a suspension in a liquid of small particles or globules of a polymer where coagulation of the suspended polymer particles is prevented by the presence of

surfactant, e.g. a synthetic latex of polystyrene, poly(vinylchloride) or polybutadiene in water. Coherent polymeric films of the polymer are provided by removing the liquid medium, e.g. by evaporation of water.

The term "aqueous solution" as used herein refers to solutions consisting essentially of water and low levels of organic solvents, e.g. as solubilizing agents for catalytic metal compounds.

The term "Copper Bath-A" as used herein refers to an agitated electroless plating solution comprising about 8 g/l formaldehyde, about 4 g/l copper, and about 0.12 M ethylenediaminetetraacetic acid (EDTA) which is maintained at pH 11.5-12.5 and about 35 °C.

The term "Copper Bath-B" as used herein refers to an agitated electroless plating solution comprising about 5 g/l formaldehyde, about 1.5 g/l copper, 5.5 g/l of sodium hydroxide and about 0.05 M EDTA (sodium salt) which is maintained at about 20-25 °C.

The term "catalytically inert" as used herein refers to films of polymer and catalytic metal compounds having surfaces onto which metal is not effectively deposited from standard electroless plating solutions such as a Copper Bath.

The term "catalytically activatable" as used herein refers to catalytically inert films comprising polymer and a compound of a catalytic metal which can be made catalytic, e.g. receptive to effective deposition of metal such as copper or nickel from a standard electroless plating bath, by exposing selected areas of the catalytically inert film to heat or heat generating radiant energy. For instance, heat can be provided to the polymer film by exposing selected areas to heat transfer fluid, e.g. hot air, or coherent electromagnetic radiation such as from a laser, electron beam radiation, etc., which can be

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adsorbed generating sufficient heat to allow activation.

Abrasion resistance of textile fabrics is commonly determined using an A.A.T.C.C. Crockmeter Model CM1 (obtained from Atlas Electric Devices Company, Chicago, Illinois) which comprises a sandpaper-surfaced support for holding in position a piece of textile fabric located within a open-topped bracket. Abrasion resistance is characterized by measuring the weight loss of the fabric caused by abrasion from the reciprocating rubbing of an acrylic finger back and forth over the fabric surface; the acrylic finger is mounted under the end of a reciprocating arm.

The "durability test method" used to characterize the durability of metal-coated textile fabrics of this invention is performed using a modified Crockmeter where the acrylic finger is provided with a 9.5 mm (3/8 inch) diameter, flat bottomed tip under a 2 kilogram load. The loaded finger effects 50 reciprocating rubbings (i.e. 25 cycles) on the surface of 2 layers of adhesive tape (Highland™ 6200 permanent mending tape from 3-M Company) applied to a metal-coated textile fabric. After the double layer of adhesive tape is rubbed on the metal coating, the tapes are pulled from the fabric and compared against standards set forth in the Figure of Metal Adhesion Ratings to determine the amount of metal removed from the textile by the tape. As illustrated in the Figure, a "5 RATING" applies to a sample of very durable metal-coated textile where metal adhesion to the textile is so good that only a very slight amount of metal is removed by the adhesive tape after rubbing according to this durability test method; a "4 RATING" applies where more metal is removed so that the outline of the path of the acrylic finger is barely visible; a "3 RATING" applies where

sufficient metal is removed so that a distinct outline of the finger's path is clearly visible; a "2 RATING" applies where the rubbed pathway is completely filled in with metal; and a "1 RATING" applies where the path
5 filled and metal is adhered to areas of the tape outside of the path of the finger. Samples rating substantially better than 5 are designated as "5+"; and samples rating substantially worse than 1 are rated as "1-".

10 This invention provides emulsions which are useful for providing catalytically activated film comprising a crosslinked polymer and catalytic metal of Group 8, which can catalyze the electroless
15 deposition of metal that is of superior adhesion and durability even after laundering. Thus, this invention also provides strongly adherent metal-coated articles comprising metal electrolessly deposited on
20 areas of an article coated with a catalytic, crosslinked polymer and Group 8 metal. Such strongly adherent metal coatings exhibit a Metal Adhesion Rating of at least 4, preferably 5. Preferred
25 adherent metal coated articles of this invention are textile articles, e.g. fiber, yarn, tow, sliver, woven fabric or non-woven fabric, coated with metal such as copper, nickel or silver. Preferred metal coated
30 textile articles are sufficiently durable so as to maintain a Metal Adhesion Rating of at least 3, preferably 4, and more preferably 5 even after the article is washed for 5 minutes in 20-30 °C water containing 1.8 g/l laundry detergent.

The aqueous, catalyst emulsions of this invention are adapted for forming crosslinked, polymeric coatings which can catalyze the electroless
35 deposition of metal. Such emulsions comprising (a) water, (b) surfactant-stabilized particles of a crosslinkable, water-insoluble polymer dispersed as an emulsion in said water, (c) a water soluble compound

of a Group 8 metal, and (d) a crosslinking agent. The surfactant-stabilized particles can comprise a variety of crosslinkable, water-insoluble polymers, preferably having a glass transition temperature less than about 200 °C, more preferably less than 100 °C. Such water-insoluble polymers can include thermoplastics or rubbers. Useful thermoplastic polymers include vinyl polymers such as poly(vinylchloride), poly(acrylates), poly(vinylacetate), poly(methacrylates), polystyrene and copolymers such as poly(vinylacetate/ethylene), poly(vinylchloride/vinylacetate), poly(vinylacetate/acrylate) and mixtures of such polymers and/or copolymers. Useful synthetic rubbers include polybutadiene and polybutylacrylate and copolymers of butadiene and vinyl monomers such as poly(butadiene/styrene), poly(butadiene/acrylonitrile) and mixtures of such polymers and/or copolymers, including mixtures with thermoplastic polymers and/or copolymers. At least a portion of the polymers used in the emulsions of this invention will have one or more reactive groups to facilitate crosslinking. For instance in the case of polybutadiene such reactive groups can comprise unsaturation, e.g. in the backbone or on branches. In the case of unsaturated polymers reactive groups can be inherent in the polymer or grafted onto the polymer; such reactive groups can be hydroxyl groups, carboxylic acid groups, vinyl groups, ester groups and amine groups.

Suspended particles of water-insoluble polymer are maintained in the emulsion, e.g. inhibited against coagulation by the use of a surfactant, e.g. a cationic, anionic or neutral charged molecule, oligomer or polymer. Preferred surfactants which are compatible with many water insoluble polymers are neutral polymeric surfactants such as polyoxy-ethylenes. When catalytic metals are added to

latexes, it is often necessary to provide additional surfactant to maintain the stability of the latex.

The emulsions of this invention also comprise a crosslinking agent which can initiate or participate in a crosslinking reaction. Initiating crosslinking agents can include free radical initiators, e.g. for crosslinking vinyl groups of polybutadiene. Participating crosslinking agents can be monomers, oligomers or polymers having two or more reactive groups which can reactively combine with the reactive groups of the polymer. The cross linking agent can be inherent in the polymer or dispersed or dissolved in the polymer particles or dissolved or dispersed in the water medium of the emulsion. Depending on the nature of the reactive group of the polymer, an appropriate crosslinking agent can readily be selected by those skilled in the polymer coatings arts. A useful inherently crosslinkable polymer is carboxy-modified polyvinyl chloride. Useful crosslinking agents for use with other polymers include acrylamide, methacrylamide, dialdehydes, polyols, polyalkoxides, etc.

The emulsions of this invention also comprise a water-soluble compound of a catalytic metal, for instance a metal of Group 8 of the Periodic Table of Elements, i.e. iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium, osmium and platinum. Preferred Group 8 metals are the noble catalytic metals, i.e. ruthenium, rhodium, palladium, iridium and platinum. The most preferred metal used in emulsions according to this invention is palladium. Such catalytic metals are desirably employed as water soluble compounds, e.g. salts or complexes with ligands such as acetonitrile, acetone, acetate, chloride or nitrate. In addition it is often useful to employ a metal solubilizing agent selected from the group consisting of ammonia, primary amines, secondary

amines, tertiary amines and inorganic hydroxides. The metal can be provide in solution as a complex of an water miscible organic ligand where there is molecular interaction, e.g. coordinate bonding, between
5 nucleophilic groups on the organic ligand the metal atom. The term "complex" as used herein also refers to the intermolecular bonding between the catalytic metal and nucleophilic groups of the polymeric species in the films of the invention.

10 In the emulsions of this invention the polymer can be present at high levels, e.g. about 50 percent solids, or at low levels, e.g. less than about 10 percent by weight of the emulsion, preferably not more than 2 percent by weight. In more preferred emulsions
15 the polymer will advantageously comprise not more than 1 percent by weight of the emulsion or less. The emulsions of this invention can comprise polymer and Group 8 metal in the weight ratio of polymer to metal between 100:1 and 1:1, preferably about 10:1 to 2:1.
20 Preferably the Group 8 metal is present in a low level, e.g. less than 5 percent by weight of the emulsion or lower, e.g. less than about 1 percent.

The emulsions according to this invention are adapted to forming dry films which can be crosslinked,
25 e.g. preferably thermally, to provide stable catalytic polymeric films that can catalyze electroless deposition, e.g. of copper from a Copper Bath. In certain preferred aspects of this invention the emulsions are adapted to forming catalytically inert
30 polymeric films which can be activated, preferably thermally, to catalyze electroless deposition. Preferably such catalytically inert films can be simultaneously thermally crosslinked and activated at moderate temperatures, e.g. by exposure to heat at
35 less than 200 °C.

Catalytic, crosslinked polymeric coatings can be prepared by depositing on a substrate a film of

aqueous emulsion according to this invention, i.e. an aqueous emulsion comprising surfactant-stabilized particles of a crosslinkable, water-insoluble polymer dispersed as an emulsion, a water soluble compound of a Group 8 metal, and a crosslinking agent. The choice of method for applying the aqueous emulsions to provide catalytic films depends on the nature of the substrate and the metallized layer desired. For instance in the case of textile materials such fibers, yarns, woven and nonwoven fabrics, catalytically inert films can be provided by dipping the textile substrate into an aqueous solution and letting the solution drip off or passing the textile through squeeze rolls to remove excess solution. The water can be evaporated by letting the wet coated substrate stand in air or be facilitated by placing the textile material in a warm air stream. In the case of flexible or rigid films, the aqueous solution can be applied by roller, doctor blade, spray and such to provide large area coverage of a wet film which can be dried to a catalytically inert film by allowing the water to evaporate. Fine patterns can be applied to film substrates by printing techniques, e.g. intaglio, rotogravure or ink jet printing onto a moving web of the substrate. Methods for coating other types of substrates, e.g. foams, elastomers, housings, containers, etc., will be readily apparent to those skilled in the art of coatings. Depending on the composition of the substrate those skilled in the art can readily prepare aqueous emulsions with an appropriate polymer that will be sufficiently compatible with the substrate to allow superior adhesion of the catalytically film to the substrate. The following description of preparing catalytic films on common substrates, e.g. films and fibers, is not intended as a limitation but an illustration of the ease in which the aqueous emulsions of this invention can be applied to unique

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substrates. The application of this invention to other substrates should be readily apparent.

It is believed that drying is an important step in the practice of this invention regardless of the nature of the substrate. Evaporation can be advantageously facilitated by exposing the wet film to evaporation conditions, e.g. vacuum or warm air flow, either of which provides an environment having a partial pressure of water low enough to expedite evaporation. Although not necessary it is often desirable to employ moderate evaporation conditions to avoid boiling of water from the wet emulsion film surface. In most cases this can be assured by maintaining the forming film at a temperature less than 95 °C. In many cases it is desirable that drying is effected at a temperature less than 80 °C, say less than about 60 °C. In many preferred cases it may be desirable to evaporate water by drying the emulsion film at a temperature less than 45 °C or lower, for instance at a temperature less than 30 °C, e.g. at room temperature. It has observed that in removing water from an emulsion applied to a tow of thousands of fibers, the capillary effects, at least in the case on non-crimped fiber, causes the polymer to wick as it is dried leaving portions of the tow devoid of a catalytic metal-containing, polymeric coating. Thus spreading the diameter of a tow bundle facilitates uniform film formation.

Depending on the crosslinking agent, drying the wet emulsion film at low or moderate temperature will form an uncrosslinked precursor film unless the crosslinking agent is thermally activated at such drying temperatures. When the precursor film is not crosslinked, the film can be treated to effect crosslinking, e.g. exposure to actinic radiation or heat such as at a temperature above 100 °C for sufficient time to crosslink said polymer. In many

embodiments of this invention drying will be effected to produce precursor films which will be catalytically inert and uncrosslinked. In certain cases the catalytically inert and uncrosslinked films can be simultaneously activated and crosslinked by the same treatment, e.g. exposure at a temperature above 100 °C for sufficient time to crosslink the polymer and cause catalytic clusters of said metal to form on the surface of the film. In certain cases it is desirable to effect such crosslinking and catalytic activation by exposing the surface of the polymeric film to a fluid at a temperature in the range of about 150 °C to about 500 °C for sufficient time to catalytically activate portions of said film exposed to said fluid so that metal can be uniformly electrolessly deposited on the activated surfaces, e.g. from a Copper Bath. For instance, exposure to forced air streams heated to about 250 °C for short periods of time, e.g. 5-10 seconds, has been sufficient to activate films to catalyze electroless deposition without adverse effect on a film of water soluble polymer. Longer exposure, e.g. on the order of 1-30 minutes is typically required to effect thorough crosslinking of thermally curing polymers. The section of appropriate thermal exposure times and temperatures is believed to be well within the skill of those skilled in the art in view of the description of this invention.

The metal coated articles of this invention comprise a layer of electrolessly deposited metal on a catalytic layer of crosslinked polymer and Group 8 metal. Such articles can comprise molded articles where the metal layer provides shielding against electromagnetic radiation, e.g. for electronic equipment housings, or environmental resistance, e.g. for automotive trim or fixtures. Other articles can comprise printed circuits on rigid polymeric substrates or on flexible polymeric films. An

especially preferred aspect of this invention provides metal coated textile materials, e.g. woven, non-woven, knitted or needle-punched fabrics, threads, yarns, chopped fiber sliver or monofilament tow and the like.

5 The substrate of the metal coated articles can comprise any of a variety of materials including inorganic materials such as metals, metal oxides, stone, ceramics, glass, quartz, alumina, carbon and graphite; organic polymers including organic thermoset
10 polymers such as epoxy and phenolic resins and thermoplastic polymers such as polyamides, polyaramides, polyesters, polyolefins, polycarbonates, polysulfones, styrenics, and cellulosics; and natural materials such as wood. In the case of textile
15 materials the substrate can comprise natural fibers such as cellulosics, synthetic fibers of acrylic, nylon, polyester, polyaramide, inorganic fibers such as glass, quartz, graphite and the like. The metal-coated textile materials of this invention are
20 especially useful in electromagnetic radiation shielding applications. For instance, copper-coated nylon non-woven fabric according to this invention exhibited greater than 60 dB attenuation in near field shielding of radiation between 100 and 800 megahertz.
25 Metal-coated nylon non-woven fabric according to this invention comprising a first layer of copper and a second layer of tin exhibited far field shielding effectiveness of greater than 60 dB for radiation up to 10 gigahertz. Metal coatings of this invention
30 exhibiting enhanced adhesion will also experience substantially less degradation of shielding performance after severe environmental exposure, e.g. as simulated by laundering, as compared to metal coatings applied by prior art catalytic polymeric
35 surfaces.

Metal coatings on the articles of this invention can comprise any of a variety of the metals

which can be deposited electrolessly from aqueous solutions onto palladium catalyzed surfaces, e.g. copper, nickel, cobalt, silver, palladium, platinum, etc. In many cases it is desirable to provide the metal-coated textiles of this invention with a multilayered metal coating, e.g. a first electrolessly deposited layer of copper or nickel and one or more subsequent layers applied electrolessly, electrolytically or by replacement, e.g. in the case of silver. Depending on the application the subsequent layer can comprise copper, nickel, zinc, cobalt, gold, silver, zinc, platinum, palladium, iridium, etc.

The following examples serve to illustrate certain embodiments and aspects of this invention but are not intended to imply any limitation of the scope of the invention.

EXAMPLE 1

This example illustrates the preparation and use of a catalytic emulsion of this invention and its use in providing durable metal coatings. A palladium solution was prepared by mixing 2.1 g of palladium acetate suspended in 50 ml of water with 2.4 g of a 70% aqueous solution of ethylamine. The suspension was stirred for about 30 minutes to dissolve the palladium salt followed by the addition of 2 ml of a 25 % aqueous solution of Triton X-100 polyoxyethylene surfactant and 150 ml of water to provide 205 ml of palladium solution. The surfactant serves to prevent the palladium salt for coagulating the latex. The palladium solution was added to 8.6 g of a heat curing nitrile rubber latex (Hycar® 1572X64 polybutadiene/acrylonitrile latex, 47.3% solids from B.F. Goodrich Company, Cleveland, Ohio) diluted to 700 ml water, followed by 95 ml of rinse water from the palladium solution container, providing 1000 ml of catalyst emulsion, containing 0.1 weight percent palladium and

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0.4 weight percent polymer. A plainweave polyester fabric was dipped in the catalytic emulsion, squeezed dry to remove excess emulsion and dried in room temperature air to provide a catalytically inert, uncrosslinked polymer coated fabric which was heated for 15 minutes in 180 °C air to effect crosslinking and catalyst activation. The crosslinked, catalytically activated polymer-coated fabric was immersed in Copper Bath-B to provide a strongly adherent copper coating. The copper-coated fabric exhibited a metal adhesion rating of 5 when tested according to the modified Crockmeter abrasion test. The fabric was laundered in a commercial household washing machine for 5 minutes using 1.8 g/l of ERA brand laundry detergent (from Procter & Gamble) in 20-25 °C water, rinsed and dried, and retested for adhesion; the fabric had a metal adhesion rating of 4.

EXAMPLE 2

The procedure of example 1 was essentially repeated except that the polymer latex was replaced with one of the following crosslinkable polymer latexes:

- (a) a heat curing copolymer of polyvinyl chloride/vinyl acetate (Geon® 590X20 phosphate ester plasticized vinyl chloride copolymer from the B.F. Goodrich Company), providing a metal-coated textile exhibiting a metal adhesion rating 5+ (2-3 after laundering);
- (b) a heat curing, carboxy-modified copolymer of butadiene and acrylonitrile (Hycar® 1570X55 nitrile latex from the B.F. Goodrich Company), providing a metal-coated textile exhibiting a metal adhesion rating of 5 (3 after laundering); and
- (c) a crosslinkable, copolymer of butadiene and acrylonitrile (Hycar® 1562X103 nitrile latex from the B.F. Goodrich Company), providing a metal-coated

textile exhibiting a metal adhesion rating of 5+ (5 after laundering).

COMPARATIVE EXAMPLE

The procedure of example 1 was essentially repeated except that the polymer latex was replaced by the following non-crosslinking polymer and/or latex:

(d) an aqueous solution of polyvinyl alcohol (Airvol® 540-S poly(vinylalcohol), 125k MW, 88% hydrolized from Air Products & Chemicals, Inc) providing metal-coated textile with a metal adhesion rating of 1-;

(e) a non-crosslinkable vinyl chloride latex (Geon 151 from the B.F. Goodrich Company) providing metal-coated textile with a metal adhesion rating of 2-3; and

(f) a copolymer of vinyl acetate and ethylene (Airflex 405 latex from Air Products & Chemicals, Inc.), providing a metal-coated textile with a metal adhesion rating of 5+; (1 after laundering).

EXAMPLE 4

This example illustrates the application of emulsions of this invention for providing electrolessly deposited metal on flat film substrates. A high solids catalytic emulsion was prepared by adding an aqueous solution of ammonia and palladium acetate to an aqueous latex (50.5% solids) of a heat curing copolymer of polyvinyl chloride/vinyl acetate (Geon® 590X20 phosphate ester plasticized vinyl chloride copolymer from the B.F. Goodrich Company) to provide an high solids (49%) catalytic emulsion containing 20 weight percent polymer and about 1 weight percent palladium. The high solids catalytic emulsion was diluted with 231 ml of waer and 0.8 ml of 25% Triton X-100 surfactant to provide a catalytic emulsion of about 5% solids. Each of the catalytic emulsions, i.e. 49% solids and 5% solids, was coated on a polyethylene terephthalate (PET) film substrate using a NO. 5 draw bar; the wet emulsions were dried and cured in a air oven at 160 °C, then immersed in a

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Copper Bath-A providing a strongly adhering copper coatings.

While specific embodiments have been described, it should be apparent to those skilled in the art that various modifications thereof can be made without departing from the true spirit and scope of the invention. Accordingly, it is intended that the following claims cover all such modifications within the full inventive concept.

WHAT IS CLAIMED IS:

1. An aqueous, catalyst emulsion adapted for forming crosslinked, polymeric coatings which can catalyze the electroless deposition of metal, said emulsion comprising (a) water, (b) surfactant-stabilized particles of a crosslinkable, water-insoluble polymer dispersed as an emulsion in said water, (c) a water soluble compound of a Group 8 metal, and (d) a crosslinking agent.
2. An emulsion according to claim 1 wherein said polymer and Group 8 metal are in the weight ratio of polymer to metal between 100:1 and 1:1.
3. An emulsion according to claim 1 which is adapted to forming catalytically inert, dry films which can be thermally crosslinked and activated to catalyze electroless deposition of copper from an agitated solution comprising about 8 grams/liter formaldehyde, about 4 grams/liter copper, and about 0.12 M ethylenediaminetetraacetic acid and which is maintained at pH 11.5-12.5 and about 35 °C.
4. An emulsion according to claim 1 comprising not more than 2 percent by weight of polymer selected from the group consisting of polybutadiene, copolymers of butadiene and one or more vinyl monomers, poly(vinylchloride), poly(acrylate), polystyrene, poly(methacrylate), poly(alkylacrylate), poly(alkylmethacrylate) and mixtures of such polymers.
5. An emulsion according to claim 4 wherein said Group 8 metal is palladium.
6. An emulsion according to claim 5 further comprising a metal solubilizing agent selected from the group consisting of ammonia, primary amines, secondary amines, tertiary amines and inorganic hydroxides.

7. An emulsion according to claim 4 wherein said crosslinking agent comprises a monomer, oligomer or polymer having two or more reactive groups selected from the group consisting of hydroxyl groups, carboxylic acid groups, vinyl groups and amine groups.

8. An emulsion according to claim 7 wherein said crosslinking agent is inherent, dispersed or dissolved in said polymer.

9. An emulsion according to claim 7 wherein said crosslinking agent is dissolved or dispersed in said water.

10. An emulsion according to claim 7 wherein said polymer is capable of forming a coherent film from a dried coating of said emulsion at a temperature of less than about 200 °C.

11. A catalytically activated film comprising a crosslinked polymer and catalytic metal of Group 8.

12. A metal-coated article comprising metal electrolessly deposited on areas of said article comprising a catalytic, crosslinked polymer and Group 8 metal; wherein essentially none of said metal is removed by stripping an adhesive tape from said article after 50 reciprocating rubbings on said tape by the flat end of a 2 kilogram-loaded vertical rod having a 9.5 mm diameter.

13. An article according to claim 12 comprising a metal coating of at least one of copper, nickel or silver on a textile article coated with said catalytic, crosslinked polymer.

14. An article according to claim 13 wherein said textile article is fiber, yarn, tow, sliver, woven fabric or non-woven fabric.

15. An article according to claim 14 having a Metal Adhesion Rating of 5.

16. An article according to claim 15 which has a Metal Adhesion Rating of at least 3 after said article is washed for 5 minutes in 20-25 °C water containing 1.8 g/l laundry detergent.

5 17. A method of preparing a catalytic, crosslinked polymeric coating comprising:

(i) depositing on a substrate a film of aqueous emulsion comprising (a) water, (b) surfactant-stabilized particles of a crosslinkable, water-
10 insoluble polymer dispersed as an emulsion in said water, (c) a water soluble compound of a Group 8 metal, and (d) a crosslinking agent;

(ii) drying said film of aqueous emulsion to form an uncrosslinked precursor film;

15 (iii) heating said precursor film to a temperature above 100 °C for sufficient time to crosslink said polymer and cause the surface of said film to become catalytic active to electroless deposition from a Copper Bath.

20 18. A method according to claim 17 wherein said drying is effected at a temperature less than the boiling point of water in said emulsion.

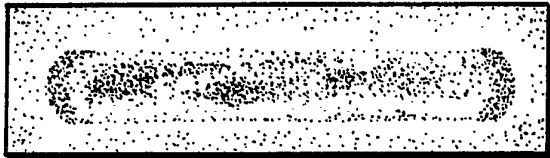
19. A method according to claim 18 wherein said drying is effected at less than about 50 °C.

25 20. A method according to claim 17 wherein said heating comprises exposing the surface of said film to a fluid at a temperature in the range of about 150 °C to about 500 °C for sufficient time to catalytically activate portions of said film exposed
30 to said fluid so that copper will be uniformly electrolessly deposited on said exposed surfaces from an agitated solution comprising about 8 grams/liter formaldehyde, about 4 grams/liter copper, and about 0.12 M ethylenediaminetetraacetic acid and which is
35 maintained at pH 11.5-12.5 and 35 °C.

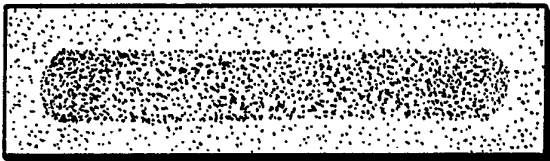
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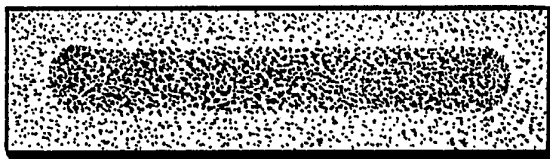
5 RATING



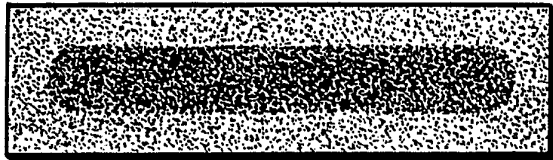
4 RATING



3 RATING



2 RATING



1 RATING

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/06395

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 23 C 18/20, 18/26, D 06 M 11/83											
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="height: 40px; vertical-align: top; border-right: 1px solid black;">IPC5</td> <td>C 23 C; D 06 M</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 23 C; D 06 M					
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 15%; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black;">X</td> <td style="border-right: 1px solid black;">EP, A1, 0327057 (HIMONT ITALIA S.R.L.) 9 August 1989, see column 3, line 5 - column 4, line 40 examples 1,3,5,7 and 8 --</td> <td style="vertical-align: top;">1-19</td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black;">A</td> <td style="border-right: 1px solid black;">US, A, 4910072 (ALBERT W. MORGAN) 20 March 1990, see the whole document -- -----</td> <td style="vertical-align: top;">1-19</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	EP, A1, 0327057 (HIMONT ITALIA S.R.L.) 9 August 1989, see column 3, line 5 - column 4, line 40 examples 1,3,5,7 and 8 --	1-19	A	US, A, 4910072 (ALBERT W. MORGAN) 20 March 1990, see the whole document -- -----	1-19
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<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>											
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border-bottom: 1px solid black;">27th October 1992</td> <td style="border-bottom: 1px solid black; text-align: right;">11 NOV 1992</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center;">Britt-Marie Lundell</td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	27th October 1992	11 NOV 1992	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	Britt-Marie Lundell	
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 92/06395

SA 63316

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 30/09/92
The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0327057	09/08/89	JP-A- 2006660	10/01/90
		US-A- 5035924	30/07/91
US-A- 4910072	20/03/90	US-A- 5075037	24/12/91
		AU-B- 598055	14/06/90
		AU-D- 8087387	12/05/88
		EP-A- 0271466	15/06/88
		JP-A- 63159410	02/07/88
		US-A- 4900618	13/02/90

For more details about this annex : see Official Journal of the European patent Office, No. 12/82