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J. L. AMOS

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MOLDED PLASTIC ARTICLE

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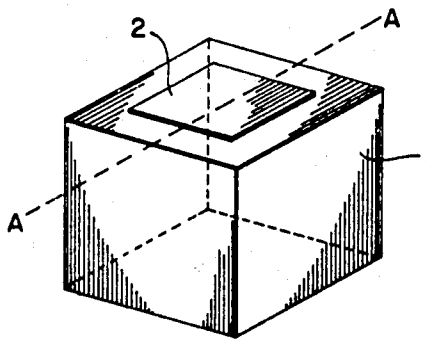


Fig. 1

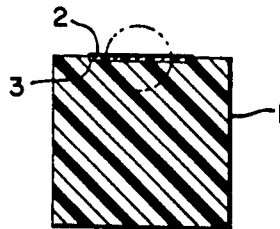


Fig. 2

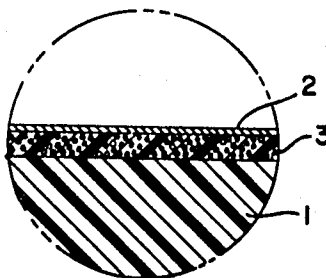


Fig. 3

INVENTOR

JAMES L. AMOS

BY *Walter J. Monacelli*
ATTORNEY

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MOLDED PLASTIC ARTICLE

James L. Amos, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

The molded plastic article disclosed herein comprises a main body of plastic having a metal plating on at least a portion of the outer surface and having expanded graphite embedded at least in the outer region of the molded article adjacent to the metal plating. The expanded graphite has a bulk density per se of less than 2 pounds per cubic foot and is incorporated in the outer region of the molded article in the range of 0.05–40% by weight of expanded graphite based on the combined weight of plastic and graphite. The molded article can be prepared by incorporating the expanded graphite in at least the outer region of the composition to be molded and adjacent to the area in which the metal plating is to be positioned. Then after the article is molded, it is placed in a plating bath with appropriate electrical connections and the metal plating deposited thereon.

This invention relates to a method of plating metal on conductive plastics. More specifically it relates to a method of plating metal on a non-conductive plastic which has been made conductive by incorporation of expanded graphite, and to the plated products prepared thereby.

The various methods of plating on plastics have disadvantages of one type or another. In most cases, a thin metal layer is deposited on the surface of the plastic to serve as an electrode for the electroplating of a thicker layer of metal.

In the chemical reduction method, a very thin layer of metal is formed on the surface of the plastic by chemically reducing an aqueous solution of a metal salt with a reducing agent. For example, a silver film is formed on the plastic surface, after appropriate cleaning and pretreatment, by the reduction of an ammoniacal silver salt, such as silver nitrate, with formaldehyde. This method requires a number of steps including roughening or deglazing of the plastic surface, cleaning the surface, "sensitizing" the surface, such as with a stannous chloride solution, and then forming the metallic film thereon by chemical reduction. This latter step is performed by using two separate solutions such as a silver nitrate-ammonia hydroxide solution and a reducer solution which is generally formaldehyde aqueous solution.

The resultant thin layer of silver or other appropriate metal serves as a base for electrodeposition of an intermediate layer of metal, such as copper to give a thickness of about 0.001 to 0.003 inch to serve as a base for the ultimate metal layer which is applied by electroplating after the copper layer is hand polished. This process has the disadvantage of excessive cost, because of the considerable number of steps and the manual operations required.

In the mirror-spraying method, similar steps are performed in the preparation and application of the initial silver layer. However, the silver layer is applied by means of a specially designed spray-gun adapted to mix the two solutions at or just prior to entering the spray nozzle. While this method has reduced the number of manual operations required by the chemical reduction method, it has the disadvantage that extreme care must be exercised. For example, the water must be closely controlled in purity and the temperature and humidity conditions also

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carefully controlled. Here again, this is followed by the subsequent electrodeposition previously described.

In a third method, a thin layer of metal is deposited by vacuum vaporization of metal or vacuum metallizing.

In this method, the metal is vaporized under a high vacuum and the plastic article is placed in a position exposed to the vaporizing metal and thereby a coating of the metal is deposited thereon. This method has a number of disadvantages in the initial high cost of equipment, the requirement for high vacuum, the danger of contamination of pump and oil, excessive time consumed in the pump-down cycle, etc. The initial layers of metal can also be deposited on plastic for subsequent electroplating by the thermal decomposition of various metal carbonyls, such as copper, iron, lead, nickel, chromium, tungsten and molybdenum. While this method has certain advantages, the high cost of the plating materials is a disadvantage.

In accordance with the present invention, a process of plating plastic articles with metal has been devised which comprises incorporating into the plastic prior to the molding thereof an appropriate amount of an expanded graphite of a bulk density less than two pounds per cubic foot in an amount of about 0.05 to about 40 percent by weight of vermicular expanded graphite based on the total weight of the plastic-expanded graphite composition. This weight percentage involves only the immediate surface to be plated, and while the expanded graphite can be dispersed throughout the entire plastic molding, it is only necessary for plating purposes to have the expanded graphite of the type and amount described as a surface layer at the surface to be plated. However, for various reasons, it may be desirable to have the expanded graphite distributed throughout the entire molding, and in such cases the molded product is equally effective for use in the practice of this invention.

In the drawings, FIG. 1 is a perspective view of a molded plastic cube having a plated metal area on the outer surface.

FIG. 2 is a vertical cross-sectional view of the molded cube of FIG. 1 taken at line A—A.

FIG. 3 is a blow-up of the cross sectional view of FIG. 2 enlarged in the encircled portion of FIG. 2.

Expanded graphite used in the practice of this invention is prepared from particulate naturally occurring crystalline flake graphite and crystalline lump graphite, flake graphite being preferred. The crystalline graphite is given a particular acid treatment and the so treated flake is heated at certain operable temperatures thereby expanding into the low density vermicular feed stock suitable for use in the present invention. The particle size of graphite starting material to be used is not critical although ordinarily particles of from about 10 to about 325 mesh U.S. Standard Sieve, preferably 10 to 60 mesh, are used. Normally, unexpanded natural graphite flake has a bulk density of from about 47 to 60 lbs./ft.³ in the above stated 10 to 60 mesh particle sizes.

Plastic materials or polymeric substances suitable for use herein include all natural or synthetic organic solid polymers or copolymeric systems and include, for example, polyethylene, polypropylene, polyvinyl chloride, polymethylmethacrylate, phenolformaldehyde, polyacetals, polystyrene, epoxides, polytetrafluoroethylene, silicone rubbers, and copolymers of the same, such as styrene-acrylonitrile, methyl methacrylate- α -Me-styrene, acrylonitrile-methyl methacrylate-styrene, ethylene-acrylic acid, etc.

Thermosetting resins suitable for use in these applications include, for example, epoxy resins, phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, silicones, and polyesters and urethanes.

Various methods of preparing the mixture of expanded

graphite and resin or plastic or polymeric material can be used. For example, the resin in powder form can be mixed with the expanded graphite and the mixture used to mold an object in which the graphite is distributed throughout the molded object. Alternatively, such a mixture can be cast in film form and the resultant film used as an outer layer in molding an object which in its interior is predominantly of the plastic material and the outer surface is comprised of the film containing the expanded graphite. The plastic material in the interior can be the same or different from that in the exterior film. Other methods of producing molded objects containing the expanded graphite throughout can also be used. For example, the graphite can be suspended in a solution of resin or polymer and polymerization continued to solidification, or a suspension of the expanded graphite can be made in a monomer and then polymerization effected to produce a solid polymer therefrom.

It is also possible to make a preform of the expanded graphite by pressing the vermicular expanded graphite to the desired shape or form and thereafter soaking the preform in a liquid prepolymer system and thereafter converting the prepolymer to a solid polymer. In impregnating such a preform with a liquid prepolymer system, it is desirable to use a low viscosity liquid so as to more easily penetrate the compressed vermicular graphite shape. In preparing a preformed vermicular expanded graphite for subsequent impregnation in a prepolymer system, the vermicular expanded graphite is compressed and shaped in a suitable mold or form to yield rectangular solids, spheres, toroids, cylinders and the like or solids having complex surface indentations. The vermicular expanded graphite should be volumetrically compressed by at least a factor of two, and preferably should undergo a volumetric compressive change of from about 4 to about 20 times that of the loose expanded vermicular graphite, having an apparent bulk density of about 0.2 lb./ft.³ which is compressed to a predetermined shape having a bulk density in the range of from about 0.8 to about 10 lb./ft.³. The amount of compression that the loose expanded vermicular graphite is subjected to is dependent on the final bulk density of the plastic-graphite matrix desired, the rigidity required for the graphite preform, the degree of impermeability in the graphite required for the appropriate prepolymer system and the degree of electrical conductivity desired in the plastic-graphite matrix. As the degree of compression on the loose vermicular graphite increases, the bulk density, rigidity, impermeability and electrical conductance of the resulting form increases.

The prepolymer soaked graphite matrix can be cured by any of a number of conventional curing techniques including for example amines or organic acid crosslinkers when the prepolymer is an epoxy, heat when the prepolymer is condensable such as phenol-formaldehyde or urea-formaldehyde, or heat crosslinkable polymers.

Polymeric substances suitable for use in the instant novel method include any organic polymer in liquid or solution form that can be cured to yield a solid resin and include epoxy resins, polyvinyl chloride, silicone rubber, dissolved methyl methacrylate, polyurethane, phenol formaldehyde and the like.

Thus, the expanded graphite can be physically mixed with polymer or copolymer powders, liquid polymers and copolymers, and even with liquid monomers that will be subsequently polymerized. The expanded graphite-polymer mixture can then be molded and set following normal polymer handling and processing procedures with or without compressing, depending upon the desired use. The resulting solid organic polymer shaped article, containing mixed in vermicular expanded graphite, is much more suitable for metal plating than a corresponding solid polymer shaped article containing other known types of carbon or graphite at the same carbon concentrations.

In preparing expanded graphite for use in the present

invention, a particulate natural flake or lump crystalline graphite is contacted at about room temperature with (1) a mixture of from about 8 to about 98 weight percent concentrated sulfuric acid (at least about 90 weight percent H_2SO_4) and from about 92 to about 2 weight percent concentrated nitric acid (at least about 60 weight percent HNO_3), or (2) fuming nitric acid, or (3) fuming sulfuric acid, or (4) concentrated sulfuric acid (at least about 90 weight percent H_2SO_4), or concentrated nitric acid (at least about 60 weight percent HNO_3) plus at least about 2 weight percent of a solid inorganic oxidizer such as, for example, manganese dioxide, potassium permanganate, chromium trioxide, potassium chlorate and the like. The resulting mix components usually are employed on a weight proportion basis of from about 0.2-2/1 (acid member/graphite). These are maintained in contact for at least about one minute, although a lengthy contact time of hours or days is not detrimental. The acid-treated graphite now expandable, is separated from any excess acid, washed and dried if desired. The acidified graphite is then rapidly heated until exfoliation or expansion to an apparent bulk density of less than about 2 lbs./ft.³ occurs. The preferred method of heating is to contact the acidified graphite with a hydrocarbon flame (for example, a propane flame).

Alternatively, another method of preparing the expandable graphite which is subsequently expanded for use in the method of the instant invention is to treat with an aqueous peroxy-halo acid, preferably perchloric or periodic acid, using an acid concentration of from about 2 to about 70 weight percent or more and an acid/graphite weight proportion of from about 0.05-2/1. The acid treated graphite, now expandable, is separated from excess acid, and dried if desired and heated to give the expanded feed stock.

The natural crystalline graphite also can be anodically electrolyzed in an aqueous acidic or aqueous salt electrolyte at an electrolyte temperature of from about 0 to about 80° C. at a minimum cell potential of about 2 volts. The total quantity of electricity passed is equivalent to from about 10 to about 500 ampere-hours per pound of graphite. The electrically treated graphite, now expandable is separated from the electrolyte solution and heated. The so-formed expanded graphite feed stock has a bulk density as low as 0.1 lb./ft.³ and preferably less than about 2 lb./ft.³.

The actual apparent bulk density of the final expanded product is determined in part by the temperature employed in the expansion operation. Satisfactory expansion of the aqueous peroxy-halo acid treated or anodically electrolyzed crystalline natural graphite results at temperatures above about 150-200° C. However, ordinarily a gaseous environment having a temperature of from about 750 to about 2000° C. or higher is used with instantaneous heating-up of the graphite to about 1000° C. or higher being preferred. Generally, as the temperature increases, the bulk density of the expanded product decreases. Ordinarily graphite from all the acid treatments set forth hereinbefore are subjected to hydrocarbon fuel flames, e.g. propane torch (flame causing graphite to attain a temperature of about 1500° C. or higher) etc. for expansion. Generally, the acid-treated or anodically electrolyzed graphite flake particulate material is placed in contact with the flame thereby to effect expansions of from 200 to 600 fold substantially instantaneously, e.g. within a second.

The time required for expansion also is dependent to a large extent on the heating temperature. Generally as the temperature rises, the time required for heating decreases. However, within the operable expansion temperature range set forth herein ordinarily the expansion is completed in less than a minute and a maximum heating period of five minutes has been found to be more than sufficient.

The expanded graphite resulting from this process is

a vermicular, particulate product having a low apparent bulk density as set forth hereinbefore in comparison to the high density of crystalline graphite starting material. (To illustrate, a commercially available Madagascar flake graphite used as a starting material having a carbon content of greater than 80% and a nominal mesh size of from about 30 to about 50 U.S. Standard Sieve had an apparent bulk density of about 51.2 pounds per cubic foot.) The term "apparent bulk density" as used herein is the density determined from the volume occupied by a given mass of the product subjected to free fall (by gravity) into an open top container, e.g. a graduated cylinder.

The plating of the molded object can be effected with any metal capable of being plated from a solution of an appropriate compound of the metal. For example, the process of this invention can be effectively applied in plating with copper, gold, silver, nickel, chromium, cadmium, zinc, tin, indium, iron, lead, palladium, platinum, rhodium, etc. The types of plating solutions and conditions for plating are those generally used for plating with the particular metal. As shown herein, the expanded graphite portion of the molding can be restricted to the surface regions. Moreover, even limited areas of the surface can be made plateable by this invention so that limited or even small areas of the total surface are plateable, for example, for electrical connections, printing, application of decals, etc. This can be effected by placing appropriate sizes of film containing the expanded graphite against the appropriate inside areas of the mold.

A molded plastic article is illustrated in FIG. 1 in which 1 is the main body of the molded plastic article in the shape of a cube. The metal plating 2 is on the top of the cube. In the cross sectional view of FIG. 2 taken vertically at line A—A in FIG. 1, the metal plating 2 is shown positioned adjacent to the embedded expanded graphite layer 3. In the blow-up of FIG. 3 shown for the encircled section of FIG. 2, the relationship of the metal plating 2, the expanded graphite layer 3 and the main body of the plastic 1 is more clearly shown.

The invention is best illustrated by the following examples. These examples are intended merely for purpose of illustration and are not intended in any way to restrict the scope of the invention or the manner in which it may be practiced. Parts and percentages are given by weight.

EXAMPLE I

Approximately 20 grams of Standard No. 1 natural graphite flake (that is graphitic carbon having flake sizes ranging from about 20 mesh to about 60 mesh and a bulk density of about 47 lb./ft.³) is mixed with about 15 grams of concentrated sulfuric acid and about 10 grams of concentrated nitric acid. After the acid-treated graphite flake is maintained at room temperature for about 5 minutes, the flake is washed free of acid with water, spread out in a thin layer and subjected to direct contact with a propane-air flame and thereby rapidly heated to a temperature above 800° C. The graphite flakes, under flame, expand to yield long worm-like structures of exceedingly low bulk densities (about 0.1 to 0.2 lb./ft.³).

In a second preparation, about 20 grams of a natural graphite flake having particle size of about 14 to 40 mesh are wetted with about 10 grams of concentrated sulfuric acid and about 5 grams of nitric acid for about 2 minutes at room temperature. The graphite flakes are washed free of acid with water and expanded by direct contact with a propane-air flame. The resulting expanded graphite is a particulate vermicular product having an apparent bulk density of about 0.2 lb./ft.³.

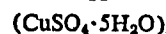
Microfine polyethylene powder is mixed in and homogeneously blended with each of the above types of graphite flakes in proportions of 2%, 5%, 10% and 20% by weight of expanded graphite respectively. These resulting mixtures are compressed in a 2 inch diameter die to

about 2000 p.s.i. and then baked in an oven at about 125° C. to about 135° C. for about 30 minutes.

Corresponding moldings are also made using similar amounts of polystyrene, polypropylene, polyvinylchloride, polymethyl-methacrylate, phenol-formaldehyde, polyacetal, epoxy resin from diglycidyl ether of bisphenol, polytetrafluoroethylene, same epoxy resin as above with 10% glass fibers, urea-formaldehyde, melamine-formaldehyde, 75-25 styrene-acrylonitrile, 90-10 ethylene-acrylic acid, 10-30-60 acrylonitrile-methyl methacrylate-styrene, and 10% fiber glass impregnated polystyrene, polyethylene, and ethylene glycol maleic anhydride styrene respectively in place of the polyethylene, with the molding conditions modified appropriately for the particular resin. The resulting cured resin bonded-vermicular graphite slugs are plated according to the procedure described hereinafter in Example II.

EXAMPLE II

A copper plating solution is prepared containing about 30 ounces per gallon of copper sulphate



and 9 ounces of sulphuric acid per gallon. The temperature of the bath is maintained in the range of 70-120° F. and the solution circulated during plating in order to provide agitation. The various carbon or graphite-containing molded plastic articles are suspended in the plating solution with a lead wire clamped to the surface of the molded article. An electrolytic copper anode is also immersed in the solution with a lead wire leading to a source of D.C. current. A current density of 20-70 amps per sq. ft. is maintained between the anode and the plastic article serving as the cathode. Plating conducted for approximately 10 minutes gives a satisfactory plating but can be continued to give any thickness of coating desired. Each of the various resin-bonded expanded graphite slugs prepared in Example I is plated satisfactorily by the above procedure and much more effectively than when corresponding slugs prepared with powdered carbon are plated.

EXAMPLE III

A chromium plating bath is prepared containing 53 ounces per gallon of chromic oxide (CrO₃) and 0.53 ounce per gallon of sulphate (SO₄) in the form of sodium sulphate or sulphuric acid. A lead anode containing 7 percent of tin is used with a bath temperature of 105° F. and a current density of 115 amperes per sq. ft. The cathodes are the various molded plastic articles produced according to Example I. The plating results are equally satisfactory to those obtained in Example II.

EXAMPLE IV

A cadmium plating bath is prepared containing approximately 3 ounces per gallon of cadmium oxide, 16 ounces per gallon of sodium cyanide and 1.5 ounces per gallon of caustic soda. The bath temperature is maintained in the range of 70-100° F. and cadmium bars are used as the anodes with a voltage of 7-12 volts and a current density of 5-25 amps per sq. ft. The molded plastic articles of Example I are plated and are equally satisfactory with the results obtained in Example II.

EXAMPLE V

A gold plating solution is prepared as follows:

Gold, as KAUCN,	-----dwt.* per gallon--	4
Sodium cyanide NaCN	-----ounces per gallon--	2
Sodium phosphate	-----do-----	2
Sodium carbonate	-----do-----	2

The bath is maintained at a temperature of 140-160° F., stainless steel bars are used as the anodes, and the molded plastic articles of Example I are used as cathodes with a current density of 20-30 amps per sq. ft. to give

satisfactory plating. *Pennyweights (a pennyweight is equivalent to 24 grains).

EXAMPLE VI

An indium plating solution is prepared containing approximately 25 grams per liter of indium (as chloride), 150 grams per liter of potassium cyanide, 35 grams per liter of potassium hydroxide, and 35 grams per liter of dextrose. The bath is maintained at room temperature using steel anodes and molded plastic articles of Example I as the cathodes with a current density of 15-30 amps per sq. ft. In preparing the solution, the hydroxide and cyanide are dissolved in separate portions of water. The hydroxide solution is cooled and is then added to the cyanide solution. The indium chloride solution is diluted and the dextrose dissolved in it. Then this is added slowly with stirring to the cyanide hydroxide solution. When the solution has cleared, water is added to the desired volume. The molded products of Example I are effectively plated with this solution.

EXAMPLE VII

A nickel plating solution is prepared containing 32 ounces per gallon nickel sulphate, 6 ounces per gallon of nickel chloride and 4 ounces per gallon of boric acid. The pH is maintained in the range of 4.5-6.0 and the bath temperature at 115-160° F. With the current density maintained in the range of 20-100 amps per sq. ft. plating is effected on the various molded plastic articles of Example I.

EXAMPLE VIII

A tin plating solution is prepared having a composition of tin sulphate (SnSO_4) of 100 grams per liter, 30 grams per liter of concentrated sulphuric acid, 30 grams per liter of tartaric acid, 5 grams per liter of animal glue, 6 grams per liter of cresol. Satisfactory plating is conducted at room temperature with a current density of 10-40 amps per sq. ft. and a voltage of 0.6-4 with the molded plastic articles of Example I.

EXAMPLE IX

A lead plating bath is prepared having a composition of 320 grams per liter of fluoboric acid (42%), 130 grams per liter of basic carbonated lead, $\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, 2 grams per liter of animal glue and 5 grams per liter of goulac. This bath has a composition of about 105 grams per liter of lead as fluoborate, 40 grams per liter of free fluoboric acid, and the animal glue and goulac as given above. Plating is effectively conducted at room temperature at a current density of 5-20 amps per sq. ft., using as cathodes the various molded plastic articles of Example I.

EXAMPLE X

Respective mixtures of 5% by weight of each of the two types of expanded graphite prepared according to Example I are made with 95% each of polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polyvinylchloride, polyvinylacetal, and polyvinyl acetate respectively and the resultant mixture converted to film form. In each case a film is applied to the inner surface of a mold, and the mold then filled with a molding composition, respectively polystyrene, polyethylene, polypropylene, polyvinylacetal, polyvinyl chloride, phenol-formaldehyde, melamine-formaldehyde, the epoxy resin derived from diglycidyl bisphenol and corresponding compositions containing 10% of chopped glass fibers. The molded products have their exterior corresponding to the film

applied to the inner surface of the mold and the interior of the product is the molding composition added to the interior of the mold. A slug of molded product of each type is plated respectively by the plating procedures of Examples II through IX with effective results.

EXAMPLE XI

The procedure of Example I is modified by reducing the time of contact with the acid mixture so as to produce expanded graphite of greater bulk density. With expanded graphite of bulk densities of approximately .5, 1, 1.5 and 1.8 lbs./cu. ft. molded plastic slugs containing 5% of expanded graphite are prepared according to the procedure of Example I. These are effectively plated using the procedure of Example II.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications can be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

The invention claimed is:

1. A molded plastic article comprising a main body of plastic, having a metal plating on at least a portion of the outer surface thereof and having expanded graphite embedded at least in the outer region thereof adjacent to said metal plating, said expanded graphite being of a size and density as to have a bulk density, when measured independent of the plastic, of less than 2 pounds per cubic foot and said expanded graphite being incorporated in said plastic in a proportion in said outer region of 0.05-40 percent by weight of expanded graphite based on the combined weight of plastic and expanded graphite composition in said outer region.

2. The plated article of claim 1 in which said proportion of expanded graphite is in the range of 2-20 percent by weight.

3. The plated article of claim 2 in which said plastic is polyethylene.

4. The plated article of claim 2 in which said plastic is an epoxy resin.

5. The plated article of claim 2 in which said plastic is a glass fiber-impregnated epoxy resin.

6. The plated article of claim 2 in which said plastic is a phenol-formaldehyde resin.

7. The plated article of claim 2 in which said plastic is a maleic anhydride-ethylene glycol-styrene polyester resin.

8. The plated article of claim 2 in which said plastic is polystyrene.

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HAROLD ANSHER, *Primary Examiner*.

U.S. Cl. X.R.

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