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METALLIZING PLASTICS BY GAS PLATING

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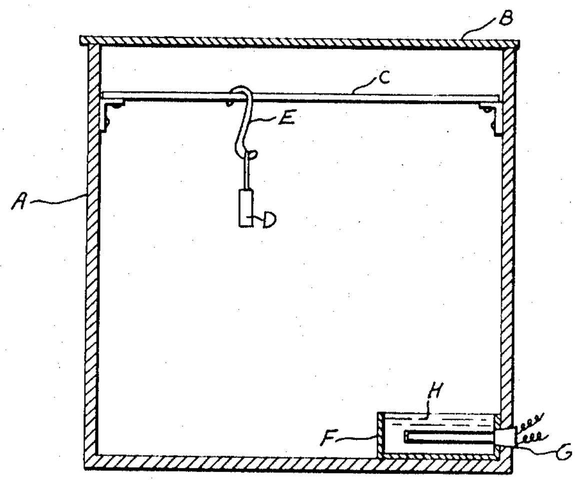

FIG-I

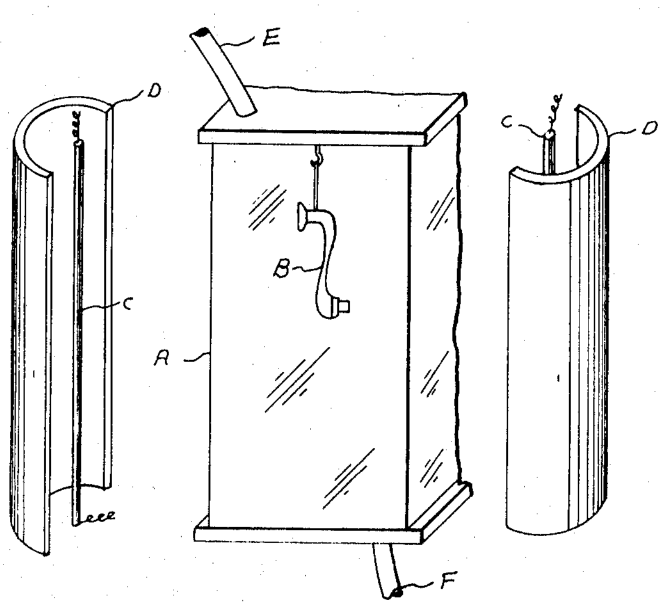

FIG-II

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METALLIZING PLASTICS BY GAS PLATING

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ABSTRACT OF THE DISCLOSURE

The present invention relates to an improvement in the method of applying highly adherent, durable coatings of metals by gas plating to the surfaces of synthetic resins which have been subjected to molding or extrusion, by subjecting said resins, prior to metal plating, to a treatment cycle including sand blasting with a very fine abrasive, followed by complete removal of any adhering abrasive, preferably by immersion in a hot agitated solution of detergent, washing with water, subjecting the treated surface to the action of vapors of a high boiling organic acid having a vapor pressure of less than 0.1 mm. Hg at ambient temperatures, followed by conventional gas plating of the surface thus treated.

The present invention relates to metallizing plastics. More particularly it relates to a process for applying highly adherent, durable coatings of metals to the surfaces of synthetic resin plastics by gas plating. More particularly still, it relates to the preparation of synthetic resin surfaces for electroplating.

For many years extensive efforts have been made to apply metal coatings to many different types of surfaces. Sometimes this has been for protecting a material from the effects of chemicals or other agencies; sometimes it has been for the purpose of making a particular material useful for a new or different purpose. Some of these processes have been successful for a particular purpose; others have been only reasonably successful or even complete failures. A process which may be successful for one purpose may be a complete failure for other purposes. For example, a process which permits the application of a satisfactory coating of nickel to iron surfaces may be wholly unsuited for the application of nickel to a glass or synthetic resin surface. Also, a coating of metal may be applied to a particular surface which appears to be entirely satisfactory but subsequently is found not to have suitable adherence to the surface, or satisfactory strength. It is accordingly not feasible to attempt to predict in advance of actual trial the suitability of a particular process for a given use, no matter how satisfactory it may be for some other use.

Examples of methods of applying metals to other surfaces include the vaporization followed by condensation of metals under high vacuum on the surface to be coated. Such methods generally give only thin films, having only relatively satisfactory adhesive properties. "Silvering," or the application of a conductive coating by reduction of silver salts on a surface, followed by electroplating, likewise gives coatings with relatively low adhesion. "Electroless" plating with nickel or copper has become a common method of applying a conductive layer for electroplating and gives coatings of somewhat better adhesion than those previously described. Recently a new pretreatment was discovered that makes electroless coatings substantially adherent to one specially compounded grade of ABS plastic.

Prior to the present invention, there has been no generally satisfactory method for applying metal coatings of satisfactory properties to non-metallic surfaces as are

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characteristic of synthetic resins, such as the injection-moldable resins having high strength and impact resistance, with the one exception referred to in the paragraph above. Such resins include acetal resin, copolymers of acrylonitrile, butadiene and styrene, polycarbonate resins, and phenoxy resins, but not phenolic or urea- or melamine-formaldehyde resins. The formation of metal coatings by thermal decomposition of volatilized metal compounds has during recent years become one of the generally most satisfactory methods of applying metal coatings to various types of surfaces. Even with this type of process referred to as "gas plating" it has not been possible previous to the present invention, to obtain satisfactory coatings of films of metals on synthetic resin surfaces. Without special treatment of such surfaces it has been generally impossible to obtain coatings or films of good physical structure and appearance which adhere satisfactorily to the synthetic resin surface. However, when used in accordance with the process of the present invention, which comprises special treatment of the synthetic resin surfaces, prior to gas plating, metal films or coatings of excellent appearance and physical structure are obtained which have the added advantage of forming a strong bond with the synthetic resin surface on which the metal is deposited, resulting in coated objects which can be subjected to the strong abuse of functional applications without the film separating from the synthetic resin surface. Synthetic resin objects thus coated with metals by gas plating lend themselves to many industrial uses not previously possible. They are particularly suitable for the production of adherent conductive layers subjected to rough usage.

The synthetic resin surface to be treated in accordance with the process of the present invention must first be thoroughly cleaned. During the molding or extrusion of synthetic resin plastic objects the latter becomes coated with small amounts of products used to prevent the synthetic resin from sticking to the molds. Also, during such operations some decomposition of the synthetic resin itself may take place and traces of the decomposition products adhere to the synthetic resin surface. Such products generally adhere strongly to the synthetic resin surface and usually are difficult to remove. Unless such products are completely removed from the synthetic resin surface to be metal coated, unsatisfactory films of deposited metal will be obtained and adhesion in particular will be poor.

While any satisfactory method may be employed for complete removal of the surface contaminants from the synthetic resin surfaces to be metal coated, a satisfactory and preferred method consists of subjecting the said surfaces to sand blasting using a very fine abrasive (e.g., 80–40 micron particle size) which may either be dry or suspended in a liquid such as water or other cheap, inert liquid suspending agent. The use of very fine abrasive is particularly important where the appearance of the final metal film or coating is of importance. Where this is not an important factor, coarser abrasive may be satisfactorily used.

After the synthetic resin surface to be metal coated has been completely freed from contaminating materials by abrasives blasting, any abrasive which adheres to the surface at the end of the blasting operation must be completely removed. While any suitable effective means can be employed a most effective means has been found to be treatment of the blasted surface with an agitated solution of detergent. The character of the detergent is of minor importance so long as it is an effective detergent which is completely inert to the synthetic resin surface to be metal coated and which after washing does not leave on the surface traces of any material which interferes with the subsequent gas plating operation, e.g., the sodium salts of organic sulfonates or sulfates, sodium lauryl sulfate, sodium dodecylbenzene sulfonate, alkyl benzene sulfonates, etc. A particularly effective method of treating the abrasive blasted surface is to immerse the latter in a hot, ultrasonically agitated solution of the detergent, preferably dissolved in water. After treatment in the detergent bath for a few minutes, the surface to be metal plated is removed and washed with water, also preferably ultrasonically agitated, in order to remove traces of detergent or other contaminant.

The cleaned synthetic resin surface to be metal coated is then suitably transferred to a closed chamber in a manner so as to prevent soiling the cleaned surface, and therein treated with the vapors of a high boiling (above 200° C.) organic acid having a vapor pressure of less than 0.1 mm. at ambient temperatures (e.g., ethyl hexanoic acid, benzene sulfonic acid, toluene sulfonic acid, etc.). Alkyl or aryl sulfonic acids, or an organic compound containing one or more polar groups in the molecule are particularly suitable for use. Removal of the air from the chamber before this treatment is unnecessary. The vapors of the treating agent can be produced in any suitable manner, as, for example, by boiling the selected agent and introducing the vapors into the treating chamber, or by boiling a mixture of the selected agent and an inert solvent, such as for example, perchlorethylene, and passing the resulting mixture of vapors of inert solvent and treating agent into the treating chamber, or by vaporizing the selected agent under vacuum and introducing them into the treating chamber. Other suitable methods will readily suggest themselves to one skilled in the art.

After treating the cleaned synthetic resin surface, as above described, it is then ready for gas plating with the desired metal, which may be effected either in the treating chamber above described if suitably constructed, or in a second chamber, as desired. The time of treatment may vary from a few seconds to several minutes, e.g., 5 minutes, depending upon various factors such as material being treated, treating agent, temperature of treatment, etc. The gas plating can be carried out by any of the conventional methods, such as for example that disclosed in U.S. Patent No. 2,638,423, using conventional forms of gas plating equipment, such as for example that shown in U.S. Patent No. 2,785,651.

The gas plating operation can be effected with any metal compound which is decomposable to metal at a temperature at which the synthetic resin surface to be coated is not materially affected during the time required for the plating operation. Carbonyls, hydrides, alkyls, carbonyl halides, arenes, nitroxyls, nitroxyl carbonyls, etc. of metals the compounds of which decompose at temperatures below which the particular resin being coated would be damaged are suitable for use. Compounds of metal such as chromium, cobalt, copper, iron molybdenum, nickel, osmium, ruthenium, etc. can generally be used. The plating can advantageously be carried out in the presence of inert gases such as helium, hydrogen, neon, nitrogen, argon, carbon dioxide, etc.

The temperatures used usually range from 180° F. to 425° F. but temperatures outside of this range can be satisfactorily used, depending upon the decomposable metal compound used, the particular resinous surface to be coated, and other similar factors.

The plating operation can be carried out either by introducing the heat-decomposable metal compounds into the coating chamber in gaseous form and heating the vapors therein to decomposition temperature, or the object to be coated can be heated to slightly above the temperature of decomposition of the metal compound vapors and the latter then brought into contact with the object to be coated.

One convenient method of carrying out the coating operation comprises placing the obpect to be metal coated in a gas plating chamber of the type shown in the attached FIGURE II, where the object is heated to a pre-

determined temperature, conveniently by infrared radiation, the chamber having transparent walls in the appropriate areas of the transmission of infrared rays. Other suitable methods of heating may, of course, be used. The heat-decomposable metal compound vapors are then passed into or through the chamber containing the preheated object to be coated and as they come in contact with the heated object the metal compound vapors are decomposed leaving a thin film of metal adhereing to the object.

Or, if more convenient, the object to be coated can be preheated and then moved into a coating chamber containing the vapors of the decomposable metal compounds where the heated object decomposes the metal compounds and a metal film forms on the object. When desired or necessary, the residual heat in the object can be augmented by some such means as infrared radiation.

The plating operation requires only a relatively brief interval of time, the exact amount depending primarily upon the thickness of the coating desired. Usually, from one to two minutes treatment in the coating chamber gives an electrically conductive film of the order of 10 microinches thickness which adheres strongly to the object being coated. For decorative purposes, the coating may be continued until a film of 0.001 to 0.002 inch of a bright metal such as nickel is obtained. Usually, however, the thin film is coated with other metals such as nickel, copper or chromium by electroplating.

The advantages of the method of metal coating of synthetic resin objects of the present invention are readily evident from a comparison of the amount of force required to strip films of metal from synthetic resin objects coated by the process of the present invention and by other previously available methods. To illustrate this fact, a synthetic resin object was consecutively abrasive blasted, detergent cleaned, rinsed with water, gas plated, and then electroplated with 0.001 inch of low stress nickel. A force of approximately one pound was required to peel off a one inch strip of this metal coating in a tensile testing machine, as compared to a force of three pounds required to peel off a one inch strip prepared in accordance with the present invention where the abrasive blasted synthetic resin object was subjected to vapor treatment with ethylhexanoic acid prior to gas plating. In a similar experiment in which the abrasive blasted object was subjected to vapor treatment with an aromatic sulfonic acid a force of approximately 7 pounds was required to strip the metal film from the synthetic resin object.

The degree of adhesiveness of the coated metal film applied to synthetic resin objects in accordance with the present invention will vary to some degree, depending upon the chemical composition of the resinous object being coated, the physical structure of the surface being coated, the degree and character of abrasive blasting to which the object was subjected, as well as the particular treating compound of the type hereinabove described as suitable for use. One skilled in the art, however, will have no difficulty in selecting the particular treating agent best suited for a particular type synthetic resin object to be gas plated so as to obtain metal coated films of a higher degree of adhesiveness than obtainable without the use of the treating agent.

FIGURE I illustrates a form of apparatus suitable for use in treating the abrasive blasted synthetic resin object with the treating agent prior to gas plating. In this figure A represents a metal tank with a removable cover B, a support C from which the synthetic resin object to be treated is suspended by a hook E. At the bottom of the tank A is placed a liquid container F provided with an electrical heating unit G, or other suitable means of heating the liquid polar group material H placed in the vessel F. By boiling the liquid in the vessel F vapors of the treating agent are produced and fill the treating chamber A and thus come into intimate contact with synthetic resin object D for the required period of time. While the described operation illustrates the treatment of a single object, it can be applied to the batch treatment of a large number of objects suspended in the chamber. Or, the apparatus can be modified so that the objects to be treated continuously and automatically pass through the treating chamber, and then through a washer and finally to the gas plating apparatus.

FIGURE II illustrates a gas plating apparatus suitable for batch gas plating of a synthetic resin object which has been abrasive blasted, treated with the treating agent, and washed. In the figure, A represents a plating apparatus with transparent walls, B a synthetic resin object pretreated, as above described, the object B being heated to the desired temperature by the infrared lamps C, provided with reflectors D. The heat decomposable metal compounds are introduced into the chamber A through inlet E and the undecomposed gases leave the chamber through exit F. If desired, an inert gas can be mixed with the heat-decomposable gases either prior to or after admission to the chamber. If desired, the heat-decomposable metal compounds can be preheated to slightly below this decomposition temperature before introduction into the plating chamber. The gas plating operation, likewise can be operated either batchwise or continuously.

The following examples are given for the purpose of illustrating the operation of the present invention. It is understood however, that these examples are for the purpose of illustration only and that various modifications therefrom may be made by one skilled in the art without departing from the concept of the invention and that any such variations which come within the scope of the appended claims are included in the present invention.

Example I

A synthetic resin plastic of the polymerized formaldehyde type generally referred to as acetal, was cleaned by abrasive blasting, immersed into a ultrasonically agitated solution of commercial detergent maintained at a temperature of 100° C., rinsed with water, dried and then exposed for five minutes to an atmosphere containing vapors of boiling trichlorethylene containing 1% by weight of paratoluene sulfonic acid, and finally placed in a gas plating chamber provided with transparent walls. The chamber was then purged free of air by admitting argon, the synthetic resin object heated to 200° F. by infrared radiation, and plating gases consisting of argon containing 20% by vol. of nickel carbonyl vapors and 0.1% hydrogen sulfide catalyst were admitted. After two minutes exposure to the plating gases, heating was discontinued, and the plating gases removed by purging the chamber with argon. The coated object was then removed and electroplated with nickel and the final film tested for appearance, strength, and adhesiveness to the resinous object. A force of 50–60 oz. was required to peel of a one inch strip of metal thus prepared, as compared to approximately 16 oz. for a one inch strip similarly prepared without treatment with the high-boiling organic acid treating agent.

Example II

This experiment was carried out exactly as described in Example I with the exception that the synthetic resin object was an acrilonitrile-butadiene-styrene copolymer, commercially known as "ABS," and the plating temperature used was 180° F. In this case a force of 62–78 oz./in. was required to peel off the coated film.

Example III

This experiment was carried out exactly as described in Example I with the exception that the synthetic resin object was composed of acetal and the latter was treated with perchloroethylene vapor containing 1% ethylhexanoic acid. In this experiment a force of 40 oz./in. was required to peel off the coated film.

Example IV

A synthetic resin object molded from a copolymer of bisphenol A and epichlorhydrin and commercially known as "Phenoxy" plastic, was cleaned by abrasive blasting, immersed into an ultrasonically agitated solution of a commercial detergent at 160° F., then rinsed with water, dried, and exposed for five minutes to air vapors containing caproamide, then placed in a gas plating chamber having transparent walls. The gas plating chamber was purged free from air by admitting argon gas, the synthetic resin object heated to 180° F. by infrared radiation, and plating gases consisting of argon gas mixed with 10% of stannane admitted. After exposure for five minutes to the plating gases, a coating of tin was deposited on the synthetic resin object. Heating was then discontinued and the plating gas was purged from the plating chamber by the admission of argon. The coated article was then removed and electroplated with nickel, and tested for adhesion of the coated film to the synthetic resin object. Tests of the coated film gave results similar to those reported for Examples I–III above.

The gas-plated synthetic resin coated surfaces prepared as described in Examples I–IV inclusive are particularly suitable for electroplating by any of the conventional electroplating methods. When electroplating is to be employed only a relatively thin coating of metal need be applied by gas-plating in order to obtain electroplates which are strongly adherent to the synthetic resin materials.

What is claimed is:

1. In a process for the gas plating of synthetic resin surfaces produced from injection-moldable resins having high strength and impact resistance, the steps which consist of subjecting the synthetic resin surface to treatment with vapors of a high boiling organic acid having a vapor pressure of less than 0.1 mm. at ambient temperatures and then gas plating.

2. In a process for the gas plating of synthetic resin surfaces produced from injection-moldable resins having high strength and impact resistance, the steps which comprise, subjecting a synthetic resin surface to abrasive blasting with a fine abrasive, followed by treatment with vapors of a high boiling organic acid having a vapor pressure of less than 0.1 mm. at ambient temperatures and then gas plating.

3. In a process for the gas plating of synthetic resin surfaces produced from injection-moldable resins having high strength and impact resistance, the steps which comprise subjecting a synthetic resin surface to blasting with a fine abrasive, treating said blasted surface with a hot detergent solution, and subjecting said detergent-washed material to treatment with vapors of a high boiling organic acid having a vapor pressure of less than 0.1 mm. at ambient temperatures and then gas plating.

4. The process which comprises gas plating a synthetic resin surface produced from injection-moldable resins having high strength and impact resistance which has been treated with a high boiling organic acid having a vapor pressure of less than 0.1 mm. at ambient temperatures.

5. The process of claim **1** wherein the synthetic resin surface is treated with vapors of paratoluene sulfonic acid.

6. The process of claim **1** wherein the synthetic resin surface is treated with the vapors of ethylhexanoic acid.

7. The process of claim **1** wherein the synthetic resin surface treated is composed of acetal resin.

8. The process of claim **1** wherein the synthetic resin surface treated in composed acrylonitrile-butadiene-styrene copolymer.

9. The process of claim **1** wherein the synthetic resin surface treated is composed of a copolymer of bisphenol A and epichlorhydrin.

10. The process of claim **4** wherein the synthetic resin surface is subjected to blasting with a fine abrasive, treating said blasted surface with a hot detergent solution, followed by treatment with vapors of a high boiling organic acid having a vapor pressure of less than 0.1 mm. at ambient temperatures.

11. A process for the metal coating of synthetic resin surfaces produced from injection-moldable resins having high strength and impact resistance, which comprises subjecting the synthetic resin surface to be coated to blasting with a fine abrasive, treating said blasted surface with a hot detergent solution, washing with water to remove detergent, subjecting said treated surface to the action of vapors of a high-boiling organic acid having a vapor pressure of less than 0.1 mm. Hg at ambient temperatures, subjecting the resulting treated surface to gas plating at temperatures ranging from 180 to 425° F. with compounds of metals decomposable to metal by the action of heat at said temperatures, and subjecting to electroplating the resulting gas-plated surface.

12. In a process for electroplating a synthetic resin surface produced from injection-moldable resins having high strength and impact resistance, the steps which comprise subjecting the synthetic resin surface to be coated to sand blasting with a fine abrasive, treating said blasted surface with a hot detergent solution, subjecting said treated surface to the action of the vapors of a high-boiling organic acid having a vapor pressure of less than 0.1 mm. Hg at ambient temperatures, subjecting the resultant treated surface to gas plating at temperatures ranging from 180 to 425° F. with compounds of metals decomposable to metal by the action of heat at said temperatures, and subjecting to electroplating the resulting gas-plated surface.

13. In a process for electroplating a synthetic resin surface produced from injection-moldable resins having high strength and impact resistance, the steps which comprise subjecting the synthetic resin surface to be coated to the action of vapors of a high-boiling organic acid having a vapor pressure of less than 0.1 mm. Hg at ambient temperatures, subjecting the resulting treated surface to gas plating at temperatures ranging from 180 to 425° F. with compounds of metals decomposable to metal by the action of heat at said temperatures, and subjecting the resulting gas-plated surface to electroplating.

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