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PROCESS FOR THE NON-ELECTROLYTIC METALLIZING OF NON-CONDUCTORS

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ABSTRACT OF THE DISCLOSURE

Improved process for applying adherent metal coatings to non-conductors by the non-electrolytic deposition of an electric conductive metal layer from an aqueous metal salt solution containing a reducing agent and a metal for catalyzing the deposition of the metal from the salt solution wherein the non-conductor to be metallized has incorporated therein a finely divided filler having functional groups capable of chemically binding the catalytic metal and of imparting the degree of roughness to the non-conductor surface required for the metallization.

This application is a continuation of application Ser. No. 593,736, filed Nov. 14, 1966, now abandoned.

The invention relates to a process for the adherent metallizing of non-conductors, especially synthetic resins and rubber, by the non-electrolytic deposition of an electrically conductive metal layer from a predominantly aqueous metal salt solution in the presence of metals catalysing the deposit of the metals which is easy to carry out. Further metal layers can, if desired, be deposited galvanically over such electrically conductive layer for technical or decorative purposes.

It is known that metal layers can be appled to non-conductors by non-electrolytic methods by chemical deposition or by deposition by vaporization.

The non-electrolytic chemical deposition of metals on non-conducting materials depends upon the reduction of a metal salt solution which wets the object to be metallized with a reducing agent to a metal or to a metal phosphide or boride when hypophosphites, boranates or borazanes are used.

Metal salt solutions are used as metallizing baths in which the metal is bound in a complex. For this purpose a complex is formed, that is, a compound containing amino, hydroxyl and/or carboxyl groups is added to an aqueous solution of a metal salt to form the corresponding metal complex salt. The concentration of free metal ions is considerably reduced in the solution of the complex salt so that when the reducing agent is added to the bath no metal deposit occurs either on the object to be metallized or in the solution.

Such baths therefore are relatively stable and are suited for longer periods of use. This stability of the baths, which can still be increased by the use of stabilizing agents, however, is undesired at the surface of the object to be metallized so that the surface of such object must be activated in order that when such object is dipped into the metallizing bath a regulated deposit of metal can take place thereon.

Such activation can be effected by pretreatment of the object to be metallized which is essentially carried out in two steps. The object is first sensitized with a solution which contains a reducing agent, for instance, tin II chloride, and then activated by treatment with a metal salt solution, preferably, a noble metal salt solution (silver nitrate, palladium II chloride) from which nuclei of the corresponding metal are deposited by reduction.

Such metal nuclei in view of the catalysing effect upon the metal deposit effected when the object is subsequently introduced into the actual metallizing bath causes a uniform metallizing of the object so that the object can then be coated with a metal layer for decorative or technical purposes in a subsequent galvanic process.

In metallizing materials which per se have rough surfaces as in ceramic objects, wood and the like, the metallizing can be effected in its individual phases after thorough degreasing and activation of the materials, without any further pretreatment. However, with objects having smooth surfaces, especially, those of synthetic resins, a roughening treatment either mechanical or chemical is absolutely necessary.

As the mechanical roughening of synthetic resins on one hand leads to an undesired change in the surface characteristics thereof which render it difficult to obtain smooth metal deposits thereover or, on the other hand, requires costly additional process steps, other methods have been sought after to ensure the firm anchoring of the metal layers which are to be applied. Certain graft polymers, known as ABS resins (acrylonitrile-butadiene-styrene resins), appeared promising for this purpose as with them a mechanical roughening can be replaced by a chemical pretreatment.

However, the chemical pretreatment for roughening the ABS resins which is based on an oxidative etching with chrome sulfuric acid is rather difficult to carry out for, if the etching is too light, the desired effect is not attained and it is also again lost by over etching. In addition, the ABS graft polymers are relatively expensive so that their practical application is limited.

The object of the invention is to provide a process for the adherent metallizing of non-conductors, especially synthetic resins and rubber, by the non-electrolytic deposit of an electrically conductive layer from a predominantly aqueous metal salt solution containing a reducing agent in the presence of metal deposit catalysing metals which is easy to perform on the most varied types of synthetic resins, such as, for example, polyvinyl chloride, polyethylene, polypropylene and the like, as well as rubber, for instance, hard rubber.

The essence of the invention resides in that the synthetic resin or rubber is prepared with a filler which on one hand has functional groups which are capable of chemically binding the catalyst and on the other hand provide the necessary roughness on the synthetic resin or rubber surface. The filler employed for the preparation can already contain the catalyst in chemically bound form or it is also possible first to prepare the synthetic resin or rubber with the filler and then treating the thus prepared resin or rubber with a solution of the catalyst, preferably, ammoniacal, to bind the catalyst on the filler. Following this the pretreated article is subjected to a known chemical metallizing treatment. It is rather surprising that a successful adherent metalizing could be attained on synthetic resins using a previous preparation of the article to be metallized with fillers, as, according to the teachings of the prior art, pigmented synthetic resins were considered unsuited for metallizing.

It has been found expedient to employ a filler, the secondary particle size of which is about 0.1μ to about 150μ, preferably, about 1.0 to about 5μ, so that the degree of roughness of the resin surface can be adjusted depending upon the particle size of the filler. In order to bind the metal ions serving as catalyst, fillers are employed which preferably contain free OH groups, for example, about 1 to about 10 wt. percent so that Ag ions or Pd ions can be bound from an ammoniacal solution. This effect can be strengthened by the use of modified fillers. Silicas containing SiH bonds which possess reducing properties are especially suited for this purpose. The binding of the activation ions manifests itself by the more or less brown coloration of the filler or respectively the resin. The synthetic resin or rubber is prepared depending upon the type of filler employed, with about 10 to 50 wt. percent, preferably, up to 35 wt. percent of filler.

Finely divided precipitated or pyrogenic metal or metalloid oxides in the form of single oxides, mixed oxides or oxide mixtures have proved especially advantageous as fillers. The precipitated fillers include all fillers (having the prerequisite functional groups for chemical bonding of the catalyst) which are prepared by wet processes, during which they may also be charged with catalytic metal ions.

The pyrogenic fillers are produced from volatile metal or metalloid compounds by vapor phase hydrolysis or oxidation in a flame. In the flame hydrolysis a homogeneous mixture of, for example, a volatile metal or metalloid halide, such as, silicon tetrachloride in the vapor phase and a gas forming water on combustion and air or oxygen and, if desired, an inert gas is converted to the oxide and hydrochloric acid in a flame. When vaporized mixtures of several metal halides, such as, silicon tetrachloride and aluminum chloride are employed in place of a single halide, so-called mixed oxides can be obtained in which each primary particle already consists of the oxides. The joint coagulation of separately prepared oxide aerosols gives unseparable oxide mixtures of the type of "co-coagulates." It, however, is also possible to emply mechanical mixtures of separately prepared oxide aerogels which are separable "mixtures of oxides." The individual oxide type used depends upon the synthetic resin to be metallized.

Advantageously, the filler particles at the surface of the synthetic resin or rubber article prepared with the filler according to the invention can be dissolved out, for example, by an alkaline treatment prior to the metallization thereof. In this instance the bonding of the catalyst is effected on the lower lying filler particles after the alkaline pretreatment.

The charging of the filler with the catalytic active ions, for example, can be effected by treatment with an ammoniacal metal salt solution which can be carried out before the filler is incorporated in or applied to the synthetic resin or rubber which is to be prepared therewith or after the synthetic resin has already been prepared with said filler.

After such pretreatment, the synthetic resin or rubber is washed thoroughly with water and then introduced into the metallizing bath which, as is known, generally essentially consists of a salt of the metal to be deposited, a complex former, a stabilizer and a reducing agent, such as, for example, a hypophosphite, borazane, boranate or formaldehyde.

The process according to the invention can also be carried out in that the non-conductor is prepared with a dispersion of the filler, preferably, an aqueous dispersion, which is already charged with the catalytically active ions and which contains an anchoring agent known per se which contains a cationically active material and after drying to leave a film of the activation filler thereon, subjected to the metallizing process. This procedure is especially applicable for metallizing clear synthetic glass materials which are only to be metallized and galvanized on one side. Such procedure, for example, is also particularly suited for preparing cellulose hydrate films for metallizing as such films can be charged with catalytically

active ions at the same time an antiblocking agent is applied thereto by treatment, for example, with a stable silica suspension.

According to an advantageous embodiment, the process according to the invention can also be used in instances where it is desired to protect the decorative effect of a metallic coating on a shaped metal base, such as, iron or aluminum against corrosion, such as, for example, in the case of automobile bumpers. For this purpose, the rough metal base is first provided with a protective coating of a filler containing synthetic resin in which the filler is charged with the catalytically active ions and such coating provided with the conductive metal coating over which a thicker coating of decorative metal (chrome or nickel) is applied galvanically. Metal bases coated in this way are protected against corrosive attack even when the decorative metal coating is damaged and also prevents the formation of local cells.

The advantages of the process according to the invention reside in that mechanical roughening of the surfaces of the article to be metallized is not required and also aside from the possible leaching out of the upper layers of the filler chemical roughening need not be carried out. In addition, sensitization with SnH or the like becomes entirely unnecessary. In the instance where the filler already charged with active ions (Pd^{++}, Ag^{+}) is incorporated in the article to be metallized separate activation is not necessary. The process according to the invention therefore is a substantially simplified metallizing process especially as the incorporation of fillers in synthetic resins and especially rubber in many instances renders it possible to provide other advantageous properties therein. A further advantage of the process according to the invention resides in the optimum adherence of the metallizing coating obtained in view of the chemical bond over the activators which are chemically bonded to the filler. The degree of roughness can be controlled by suitable selection of the particle size of the filler employed.

Adherence tests according to the known peeling test could not be carried out with reproducible results as even the spot wise loosening often only occurred with destruction of the synthetic resin base. The adherence even exceeded that of a galvanically applied copper coating 20μ thick.

In addition to the fillers mentioned above, other fillers, provided they have the necessary functional groups for chemically binding the catalyst required for the electroless metallization, can be used for the purposes of the invention. For instance, alkali metal silicates, alkaline earth metal silicates or their mixed silicates, as well as aluminum silicates, can be used in an analogous manner to the wet precipitated silica employed in Example 1, which follows, with analogous results. The process of the invention also is not limited to the use of the so-called light fillers as active carbon blacks can also be used alone or in conjunction with the light filters for the preparation of the synthetic resins or rubber to be metallized. In the case of the active carbons they cannot be used in an "aged" state (by vulcanization or other heat treatment).

The fillers employed according to the invention, as indicated above, have secondary particle sizes of 0.5 to 100μ, preferably 5 to 30μ. The secondary particles thereof are agglomerates of primary particles of a much smaller size, namely, for example, about 2 $m\mu$ to 500 $m\mu$, preferably, 5 $m\mu$ to 30 $m\mu$. Especially suited are the finely divided wet precipitated silicas and silicates and pyrogenic silicas which can be essentially pure silicas or in the form of "mixed oxides" or co-coagulates of silica with, for instance, 0.5 to 1.5 wt. percent of Al_2O_3 which are commercially available as various grades of Aerosil which have BET surface areas ranging from about 60 to about 380 $m.^2/g$. Suitable finely divided precipitated silicas, for instance, are commercially available as Ultrasil VN 2 and Ultrasil VN 3 (having other oxide contents below 1 wt. percent) as well as Durosil (having an Na_2O content of about 2 wt. percent). Such precipitated silicas upon calcination suffer a weight loss of about 12%. Both the pyrogenic and the wet precipitated silicas employed according to the invention can be hydrophobized, for example, by treatment with methyl chlorosilanes to provide products containing about 1–3% of bound carbon. Suitable finely divided precipitated silicates, for instance, are the commercial product Calsil containing about 69–70 wt. percent of SiO_2 and about 10–11 wt. percent of CaO and calcium silicates DS 53 and DS 54 containing about 47 to 50 wt. percent of SiO_2 and about 34 to 35.5 wt. percent of CaO, as well as aluminum silicates P 820 and Silteg As 7 containing about 71–72 wt. percent of SiO_2 and about 8–9 wt. percent of Al_2O_3. The surface areas of the finely divided fillers employed according to the invention can, for instance, range between about 10 m.^{2}/g. and 400 m.^{2}/g.

The metallizing of the pretreated synthetic resins and rubber according to the invention can be carried out with good results with the well known metallizing baths under the usual conditions, such as, for example, are illustrated in Metalloberfläche, No. 8, pages B133–B138 (1965), and in Metal Finishing, Electroless Plating Today, Dr. Edward B. Saubestre, June 1962, pages 67–73, July 1962, pages 49–53, August 1962, pages 45–49 and September 1962, pages 59–63.

The following examples will serve to illustrate the process according to the invention.

EXAMPLE 1

Wet precipitated silica with a 6 wt. percent content of silanol groups having a secondary particle size of 1–5μ and a primary particle size of 16 mμ was worked into three batches of high pressure polyethylene on mixing rollers to provide a silica content of 10 wt. percent, 20 wt. percent and 30 wt. percent in the respective batches. Plates 2 mm. thick were molded from each of the batches as well as from the unfilled high pressure polyethylene.

(a) A plate of each of such batches (0 wt. percent, 10 wt. percent, 20 wt. percent and 30 wt. percent filler content) was introduced for 15 minutes in a hot bath (50° C.) of chrome sulfuric acid, then rinsed with hot water (60° C.) and then introduced for 10 minutes in an ammoniacal solution of PdCl (2 g./liter) and subsequently rinsed several times with water. The treatment with chrome sulfuric acid served to degrease the plates.

The thus pretreated plates were then treated in an aqueous metallizing bath of the following composition at 20–30° C.:

34 g./l. Rochelle salt (potassium sodium tartrate)
10 g./l. NaOH
7 g./l. $CuSO_4 \cdot 5H_2O$
6 g./l. Na_2CO_3
50 ml./l. formaldehyde (40%).

The metallization of the plates was increasingly more rapid, more uniform and more adherent with increasing filler content. The results after 45 minutes' treatment were:

Plate with
- 0 wt. percent—No metallization
- 10 wt. percent—Spot wise metallization, low adherence
- 20 wt. percent—Far reaching metallization, adherent, only several defective spots
- 30 wt. percent—Good adherent metallization

Filler

(b) The procedure described under (a) was followed except that after the degreasing with the chrome sulfuric acid, the plates were given an intermediate alkaline treatment for 15 minutes in an aqueous bath containing 30 wt. percent of NaOH at 50° C. followed by a water rinse and a short dip in half concentrated HCl before activation with the $PdCl_2$ solution.

After such pretreatment the metallization proceeded a little more slowly than in (a) but in this instance sufficient adherence was already attained with a 10 wt. percent filler content. The unfilled plate was not metallized. Similar results are obtainable with other reducing agents, such as sodium hypophosphite, N-diethyl borazane and sodium borohydride.

EXAMPLE 2

Three batches of unplasticized polyvinyl chloride powder were mixed with quantities of silica of a secondary particle size of 8–28μ and a primary particle size of 16 mμ which had been treated with silicochloroform to charge it with Si-H groups, such as to provide silica contents of 10 wt. percent, 20 wt. percent and 30 wt. percent. The resulting mixtures were then processed to form bands in an extruder which were cut into plates. These plates and an unfilled polyvinyl chloride plate were then metallized as described in Example 1(a).

It was found that the plates with increasing filler content already were colored dark brown in the activating bath and also were coated extraordinarily rapidly with an adherent conductive coating in the metallizing bath. The unfilled plate was not metallized.

EXAMPLE 3

Mixtures of polypropylene with 10 wt. percent, 20 wt. percent and 30 wt. percent of a pyrogenic silica of a secondary particle size of 10–40 mμ which had previously been charged with Ag^+ ions from an ammoniacal solution containing 0.5 g./l. of $AgNO_3$ were prepared on mixing rollers. Plates 2 mm. thick were molded from such mixtures and hung together with an unfilled polypropylene plate for 15 minutes in a chrome sulfuric acid bath at 50° C., then washed with hot water (60° C.) and then introduced into a metallization bath of the composition given in Example 1 without further activation.

With increasing filler content, well adherent and uniform conductive coatings are obtained with this simple method. The unfilled plate was not metallized. The metallized plates were subsequently galvanically coated with copper, bright copper, bright nickel and bright chromium without any trouble.

What is claimed is:

1. A process for metallizing a non-conductor wherein a base of synthetic resin or rubber is metallized by nonelectrolytic deposition thereon of a metal, the said process comprising the steps of distributing a silica filler throughout said resin or rubber prior to molding; then molding the resin or rubber to the desired shape to form said base; then applying a metal catalyst for the deposition of the metallizing metal to said base, the metal catalyst being in the form of a solution of a salt of the catalyst metal, and the catalytically active ions of said metal salt being chemically bound to said filler through free OH groups present on the surface of the filler, the amount of said filler being at least 10% by weight of said resin or rubber and the said amount of filler being sufficient to provide for a strong bond with said catalyst; and then subjecting the thus prepared base to treatment with an aqueous solution of the salt of the metallizing metal in the presence of a reducing agent for the latter metal salt so as to cause formation of a catalytically promoted firmly adhering deposit of the metallizing metal on said base.

2. The process of claim **1**, wherein the metal salt catalyst is applied in the form of an ammoniacal solution of a palladium or silver salt.

3. The process of claim **1**, in which the silica filler has a secondary particle size between about 0.1μ to about 150μ.

4. The process of claim **1**, in which the particles of the filler present at the surface of the said base are dissolved out prior to the metallization.

5. The process of claim 1, in which the filler is silica containing SiH bonds enabling the filler to effect a reduction of said catalytic metal salt to the metal.

References Cited

UNITED STATES PATENTS

2,690,403	9/1954	Gutzeit	117—160
3,014,818	12/1961	Campbell	117—160 R
3,259,559	7/1966	Schneble et al.	

OTHER REFERENCES

Lewis, J. R., College Chemistry, 8th ed. N.Y., Barnes and Noble, 1965; p. 175.

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