

Coatings for Plastics. Dispersions of Clean Metal Particles in Polymer Matrices

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Synopsis

Oxides are frequently used to improve the mechanical properties of plastics. Here we report how oxides of zinc, lead, cadmium, and indium, when embedded in a polymer matrix, can be electrochemically reduced, resulting in a polymer-metal "composite" of high electrical conductivity. This method of preparation provides a uniform dispersion of small, clean metal particles, not obtainable by blending metal powder and polymer. The "composites" are somewhat porous, and other metals can be deposited on the "composites" from either electroplating or electroless plating solutions.

INTRODUCTION

Metal oxides are frequently added to polymers to arrive at plastics with an attractive profile of properties. Addition of oxides applies to polymers intended for molding purposes as well as to polymer solutions, dispersions, and emulsions intended for coating applications.

The general subject of coatings for plastics was recently reviewed by Brown,¹ who considered primarily coatings of a completely organic character. However, compositions containing quaternary salts, metallic pigments, or carbon black were mentioned briefly.

In this report, it will be shown that incorporation of certain oxides, for instance, zinc oxide, lead oxide, cadmium oxide, and indium oxide, in coatings for plastics, followed by electrochemical reduction of the oxide in the dry coatings, results in dispersions of clean, finely divided metal particles in polymer matrices. The electrochemical reduction of some of these oxides is practiced in the production of battery plates,² but at the present time the compositions and techniques are not applicable to coatings for plastics. Coatings obtained by the method described herein can have high electrical conductivity, and they can be further metallized by either electroplating or electroless plating from appropriate plating solutions.

It should be emphasized that the properties of the metal dispersions obtained by reduction of the oxide filler are not equivalent to those of a mixture resulting from dispersing a metal powder in a polymer matrix.

COATING COMPOSITIONS

The compositions under consideration consist of a polymer, one or more solvents, and an oxide. Each of these components has to satisfy a number of requirements.

Elastomers are generally used as the matrix material. Obviously they should be (a) soluble in a number of solvents, (b) chemically inert with respect to the oxides and the corresponding metals, and (c) stable under the conditions needed for reduction of the oxides.

The solvents for these elastomers should not dissolve or craze the plastic substrate, nor should there be a fast diffusion of the solvent into the substrate; but mild swelling of the substrate's surface promotes adhesion. At room temperature, the solvent should have a vapor pressure such that relatively short drying times can be realized. Naturally, there should be no chemical reactions between the solvent and the elastomer or the oxides.

An important requirement for the oxides is their particle size. Small particles are preferred to give smooth coatings: cadmium oxide of 1-micron particle size and zinc oxide in sizes below 1 micron, down to 0.14 micron, are commercially available.

Examples of compositions which fulfill the above requirements are given in Table I. These dispersions have been applied to plastic substrates such as Noryl (General Electric Company) thermoplastic resin, Lexan (General Electric Company) polycarbonate resin, and ABS terpolymer by dipping or by doctor blading. After drying, the layer which is approximately 2×10^{-3} to 5×10^{-3} cm thick, has the color of the particular oxide used.

From the electrochemical experiments that can be conducted on these coatings, some observations can be made regarding the structure of the dry

TABLE I
Coating Compositions

Sample no.	Ingredients	Weight, %
I	neoprene	7.0
	toluene	12.2
	monochlorobenzene	5.2
	xylene	30.3
	<i>n</i> -heptane	16.0
	zinc oxide	29.3
II	neoprene	8.7
	toluene	45.4
	benzene	18.9
	zinc oxide	27.0
III	Estane polyurethane	6.4
	1,4-dioxane	64.0
	cadmium oxide	29.6
IV	neoprene	5.7
	toluene	58.1
	lead oxide (PbO)	36.2

coatings. For instance, the oxide particles appear to be incompletely encapsulated by the matrix because complete encapsulation would prevent the oxide particles from participating in electrochemical reactions where direct contact with electrolyte solutions is required. It should be noted that the use of wetting agents in the preparation of the coating compositions in Table I leads to adverse effects in that the better wetting of the oxide particles by the polymer solution tends to result in encapsulation of the oxide particles by the polymer matrix, thus excluding them from direct contact with the electrolyte solution. Furthermore, it can be concluded that in the solid dispersions the oxides are present as networks of touching particles.

ELECTROCHEMICAL REDUCTION OF THE OXIDE PARTICLES

Electrochemical reduction of oxides to metals is a well-known process. In dry coatings obtained from the formulations in Table I, the actual reduction occurs readily provided that the electrode attached to the coating is also in contact with the electrolyte solution. If this electrode does not touch the electrolyte solution, reduction does not occur because the oxide coating is an insulator and not enough coulombs can be passed to the electrolyte solution to realize measurable reduction. However, under the correct conditions, reduction occurs readily and can be followed visually because of the color changes in the coatings. Initial reduction takes place in areas close to the electrical contact; in those areas all coatings turn

TABLE II
Volume Loss Upon Reduction

Oxide	Volume loss, %
CdO	17.5
In ₂ O ₃	18.6
PbO	22.1
ZnO	37.0

grey. Voltages from 1 to 4 V are sufficient to produce the desired reaction. There is little incentive in discussing current densities in this process because of the complete change of one of the surfaces from a poor electrical conductor to a very good conductor. Consequently, at the beginning of the experiment, the current density is very low while upon completion it may be as high as 1 A/sq in.

During the electrochemical reaction which causes the oxide to convert to the metal, there occur some physical changes in the coating as well. For instance, there is a volume loss in the filler since oxygen is removed from the oxide lattice. The size of the volume losses is given in Table II.

PROPERTIES OF THE COATINGS OBTAINED BY REDUCTION OF THE OXIDE FILLER

Due to the volume loss in the filler, the remaining metal is present as porous or spongy particles rather than as solid pieces. The volume loss also allows the polymer matrix to relieve some of its stresses.

Immediately after reduction, the metal particles are very clean, have a large surface area, and are reactive although not pyrophoric. The activity and the cleanliness of the surface of the metal are easily demonstrated when a freshly reduced sample is rinsed with distilled water to remove residual base, and dried in a stream of nitrogen under reduced pressure. Upon exposure to air, the temperature of the dry sample rises owing to re-oxidation of the metal surface.

Films obtained from the formulations in Table I show, after reduction of the oxide, a high electrical conductivity, indicating a continuous network of touching metal particles. In general, the electrical conductivity of such films is of the order of 10^2 – $10^3 \Omega^{-1} \text{ cm}^{-1}$. When smaller amounts of oxides are used, the conductivity is less than indicated here and, when the oxide content becomes smaller than the value needed for a continuous network of touching particles, the conductivity drops drastically.

Surfaces with conductivities as high as indicated can be electroplated from appropriate electroplating solutions. Thus, we have further metalized such substrates by electroplating with zinc and with copper. In addition, we have also found that the dispersed metal particles cause the deposition of copper from electroless plating solutions. Our observations on further plating of these systems will be described in another publication.³

EXPERIMENTAL

Dispersions

Neoprene AD-10, 32 parts, is dissolved in a mixture of 168 parts toluene and 70 parts benzene, and the solution is filtered to remove gel particles and other insoluble solids. To this solution is added 100 g fine-particle-size zinc oxide, and the mixture is ball-milled for 18 hr. After separation from the balls, it is ready for use. Nonsolvents for neoprene can also be added after the neoprene has first been dissolved in aromatic solvents.

Similar procedures can be used to prepare formulations containing other elastomers as well as other oxides.

Coating and Drying

Coating of flat 2 ft \times 3 in. plastic samples was done by doctor blading or by dip coating. It is recommended that the organic solvent be removed from the coating itself and also from the substrate where solvent may have penetrated by diffusion. Drying in air over night appeared adequate in most cases. Accelerated drying can be done under reduced pressure,

taking care that the rate of drying is slow enough to prevent the formation of blisters in the coating. The drying period may also be reduced by using forced warm air.

Reduction

A coated sample is made the negative electrode in a 1% KOH solution while a stainless steel strip is used as positive electrode. Contact to the coated sample is made as described above, and a voltage of 4 V is applied to the electrodes. Within 30 min, the originally white ZnO coating has turned grey over the entire surface, the current has increased to 1 A, and hydrogen gas is formed at the negative electrode.

After rinsing the sample in distilled water, it can be dried in a stream of nitrogen under reduced pressure. This drying operation is necessary only if the newly created dispersion is to be used in experiments other than further metallizing steps.

For plating purposes the water rinse is the only recommended step before subsequent plating steps; drying is unnecessary. Cross sections of the dry 1- to 2-mil-thick coating show that under these experimental conditions the oxide in the coating has been completely reduced to metal and that we do not deal with reduction of the oxide on the surface of the coating only. This is undoubtedly due to the porosity created by the reduction.

References

1. R. A. Brown, *Paint Varnish Prod.*, June 1971.
2. W. J. Schlotter, (to the Electric Storage Battery Co., N.J.) U.S. Pat. 2,738,375 (March 13, 1956); J. C. Duddy, (to the Electric Storage Battery Co., N.J.) U.S. Pat. 3,121,029 (February 11, 1964); J. C. Duddy (to the Electric Storage Battery Co., N.J.) U.S. Pat. 3,181,973 (May 4, 1965).
3. J. H. Lupinski, in preparation.

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