

Conductive Coating Films Based on Low Density In_2O_3 Powders and Polymer Latexes

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SYNOPSIS

Several kinds of conductive coating films were prepared from a low-density indium(III) oxide powder (which was employed because it provides a much higher volume for the same weight) and polymer latexes. The low-density In_2O_3 , which is an electrically conductive pigment, was prepared by pyrolysis followed by the combustion of water-swellable polymer microspheres imbibed with $\text{In}(\text{NO}_3)_3$, the precursor of In_2O_3 . Either acrylamide/*N,N'*-methylenebisacrylamide or poly(vinylalcohol)/glutaric dialdehyde was used to generate spherical hydrogel particles. The polymer latexes with which the In_2O_3 was mixed had a soft core and a hard shell structure to ensure that the coating film has suitable mechanical properties in addition to conductivity. Acrylonitrile/butadiene/styrene copolymer ABS or acrylonitrile/butylacrylate/styrene copolymer ABAS latexes were used as binders for the conductive pigment. The powder coating followed by hot pressing, the water-borne coating consisting of low-density In_2O_3 and polymer latexes followed by curing, or the colloidal dispersion coating was used to deposit flexible conductive coating films on polyester sheets. The conductive pigment density and the polymer latexes' size and flowability are the factors that affect the characteristics of the film. We found that the colloidal suspension coating procedure based on ABAS latexes achieves better electrical and mechanical properties for the coating films. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The electrically conductive films of doped and undoped indium oxides constitute interesting materials because they exhibit high visible transmission, fairly good electrical conductivity, and high infrared reflectivity.¹⁻³ One of the applications is as antistatic coating on the surface of spacecrafts. However, it has been found that the usual tin-doped indium oxide coatings crack and peel in the hostile environment of the low earth orbit. In order to overcome this difficulty, it was suggested that In_2O_3 microspheres be dispersed in a polymer matrix⁴ to generate a flexible antistatic film. Spherical In_2O_3 particles 0.5–2 μm in size were generated by spraying a solution of indium acetate into a heated chamber. The oxide microspheres thus obtained can be dispersed in a suitable polymer matrix to form a conductive composite. It is possible to achieve a conductive per-

colation threshold at a lower In_2O_3 loading by using porous instead of nonporous indium oxide particles. This paper proposes a method of producing porous indium oxide particles. First, water-swellable polymer microspheres were imbibed with an aqueous solution of $\text{In}(\text{NO}_3)_3$; then the microspheres were pyrolyzed in air and subjected to combustion to decompose indium nitrate to In_2O_3 and to destroy the polymer network. The low-apparent-density In_2O_3 powder thus obtained was used as the conductive component of the composite. Two kinds of thermoplastic polymer latexes, namely acrylonitrile (AN)/butadiene/styrene (ST) copolymer ABS and AN/butylacrylate (BA)/ST copolymer ABAS, were used as binders in the composites.

EXPERIMENTAL

Chemicals

Most chemicals were purchased from Aldrich. Indium(III) nitrate hydrate (99.9%), indium oxide

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Table I The Apparent Density of Porous In_2O_3 Particles Prepared by using Hydrogel Networks as Porogens

Various Indium Oxide Powders	Weight Ratio of Indium Nitrate Hydrate to the Hydrogels	Apparent Density (g/cm^3)
In_2O_3 -I	$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}/\text{AM-MBAM} = 6/7.2-1.6$	0.55
In_2O_3 -II	$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}/\text{AM-MBAM} = 4/10.8-2.5$	0.29
In_2O_3 -III	$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}/\text{AM-MBAM} = 3/15-3.2$	0.15
In_2O_3 -IV	$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}/\text{PVA-GDA} = 2/2.1-0.9$	0.71
In_2O_3 -V	$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}/\text{PVA-GDA} = 2/3.6-1.4$	0.54
In_2O_3 -VI	$\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}/\text{PVA-GDA} = 2/5.7-2.3$	0.46
In_2O_3 -A	Commercial (Aldrich)	1.0

(99.99%), acrylamide (99+%) (AM), *N,N'*-methylenebisacrylamide (99%) (MBAM), poly(vinyl alcohol) (80% hydrolyzed, $M_w = 9,000-10,000$) (PVA), and glutaric dialdehyde (50 wt % in water) (GDA) were used as received. AN (99+%), BA (99.9%), and ST (99.9%) were passed through an inhibitor-removal column before use. AN/butadiene/ST block copolymer ABS, ethylene/vinylacetate copolymer (vinylacetate content 9%) (PEVA), and poly(ethyl methacrylate) (PEMA) were purchased from Polymer Science Co.

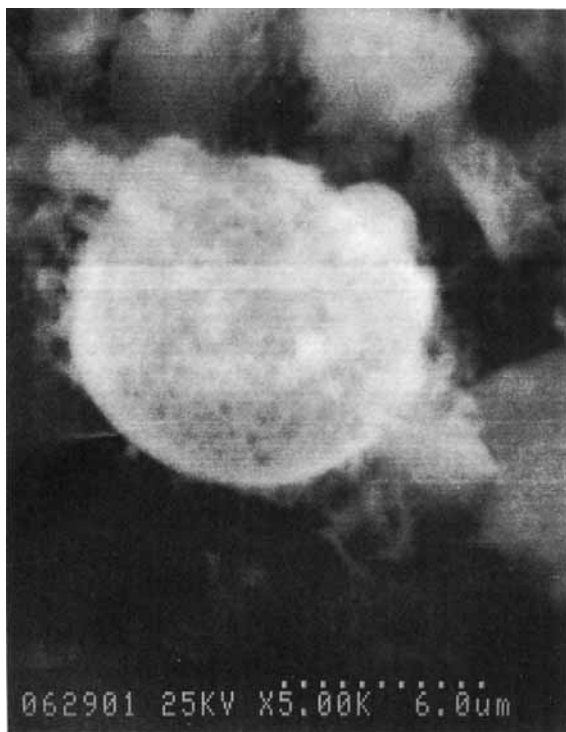


Figure 1 The backscattered electron image of carbon-indium oxide composite spheres prepared by pyrolysis at 250°C for 15 h of P(AM-MBAM) spheres imbibed with $\text{In}(\text{NO}_3)_3$. The weight ratio of the indium nitrate to the polymer is given in the second row of Table I.

Preparation of Low-Density In_2O_3 Powders

Procedure A

In a 100-mL round-bottom flask, indium nitrate (4 g), AM (7.2 g), the crosslinker MBAM (1.54 g), and the initiator $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.10 g) were dissolved in water (20 mL). Toluene (20 mL) and Span-80 (2 g) were then introduced, and the flask was sealed with a septum and purged with nitrogen for a few minutes. An emulsion of the aqueous solution in toluene was generated by magnetic stirring. The polymerization was carried out by heating the flask in an oil bath ($\sim 65^\circ\text{C}$) until the emulsion transformed into a suspended powder (about 4 h). After cooling

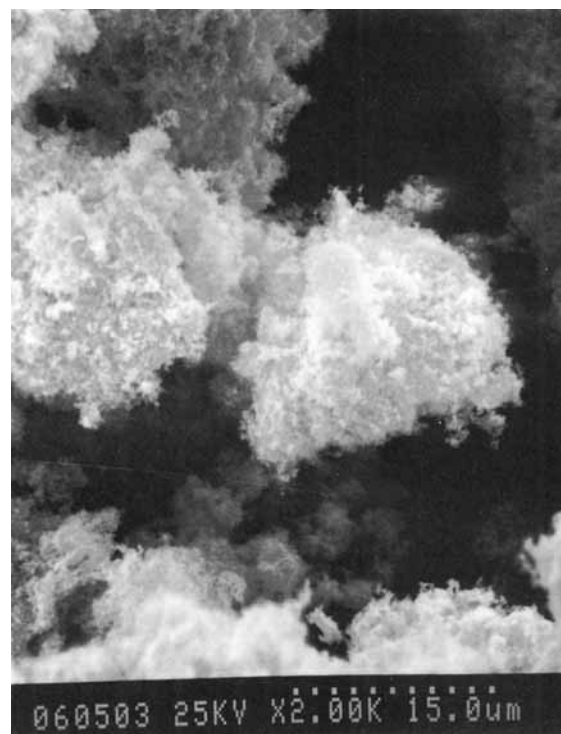
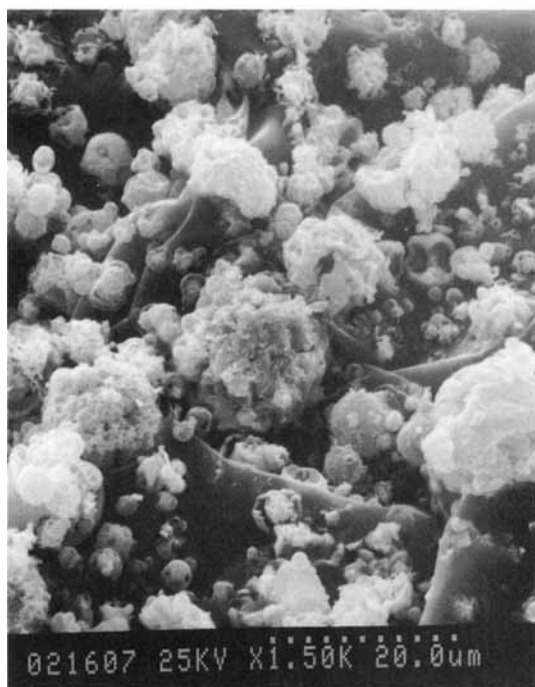
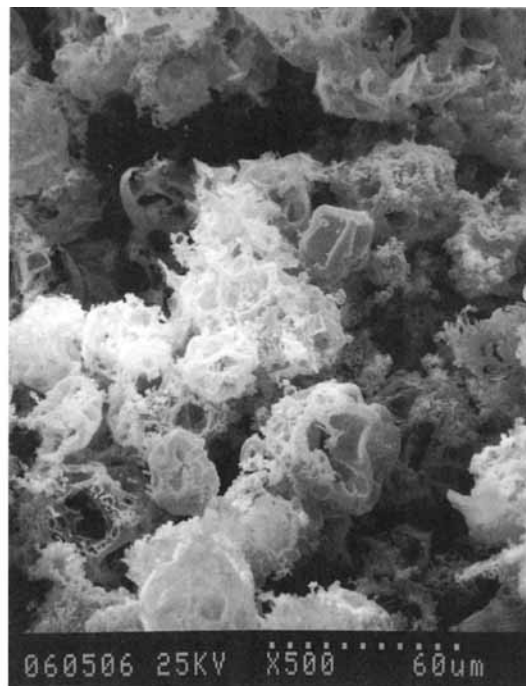


Figure 2 Scanning electron micrograph of the In_2O_3 -IV particles (see Table I).



(a)



(b)



(c)

Figure 3 Scanning electron micrographs of (a) $\text{In}_2\text{O}_3\text{-I}$; (b) $\text{In}_2\text{O}_3\text{-II}$; and (c) $\text{In}_2\text{O}_3\text{-III}$ (see Table I).

to room temperature, 30 to 40 mL acetone was added to the flask to extract the water from the powder. After filtering and drying, the powder was transferred to a small ceramic pot. Pyrolysis was carried

out in a furnace, in air, at 250–300°C to decompose the indium nitrate and carbonize the polymer; this was followed by combustion at 600°C to remove the carbon.



a. Porous structure

b. Star-like fibrous structure

Figure 4 Schematic of the (a) cavitylike and (b) starlike morphologies.

Procedure B

In a 250-mL round-bottom flask, an aqueous solution of PVA (60 g, 10 wt %) and an aqueous solution of the crosslinker GDA (5 g, 50 wt %) were introduced. Cyclohexane (40 mL) and Span-80 (2 g) were then added. The two-liquid-phase system was transformed into an emulsion by mechanical stirring, then 2 mL of acetic acid (as catalyst for crosslinking) was injected into the emulsion. The system was heated at 50°C with stirring overnight for the crosslinking to occur. The generated crosslinked powder was washed with 2-propanol and filtered. Finally, about 8.2 g of dry polymer powder was obtained. To load the precursor $\text{In}(\text{NO}_3)_3$ into the polymer network, 8 g of polymer powder was introduced into an aqueous solution of 2 g $\text{In}(\text{NO}_3)_3$ in 8 mL water with stirring. The water was allowed to evaporate in a fume hood; this was followed by pyrolysis and combustion as in procedure A.

Synthesis of the Core-Shell Polymer Latexes of ABAS

In a 100-mL round-bottom flask, an organic liquid containing BA (6.0 g), ST (1.25 g), and the initiator AIBN (40–50 mg) was dispersed with magnetic stirring in 35 mL aqueous solution containing 1.5 wt % PVA as dispersant. The flask was purged of air with N_2 and sealed. The suspension was stirred at 60°C for 4 h. During this time about 20–25% of the monomers polymerized, generating incipient latexes; then a mixture of ST (1.25 g) and AN (1.5 g) was injected into the partially polymerized suspension and the polymerization continued for another 20 h. The incipient latexes were thus completely polymerized, forming the core of the latexes; the injected monomers polymerized as a shell around the core. A colloidal dispersion of ABAS latexes in a PVA aqueous solution was generated. The adsorption of PVA upon the surface of the latexes ensures, via steric repulsion, the stability of the colloidal dispersion. This dispersion can be transformed in a transparent film after the water is evaporated at room temperature.

Coating via Hot-Pressing a Powder Mixture of In_2O_3 and ABS on a Polyester Substrate

Procedure A

In_2O_3 (0.1 g) and ABS (0.2 g, > 120 mesh) powders were mixed by grinding and located as a layer on a horizontal polyester sheet. Hot-pressing the system for a few minutes at 150°C generated a yellowish film of In_2O_3 -ABS composite on the polyester sheet.

Procedure B

In_2O_3 (0.1 g) and ABS (0.2 g, > 120 mesh) powders were mixed by grinding, and a 10 wt % aqueous solution (0.7–0.8 g) of PVA was added. A yellow paint was thus formed after stirring. The paint was applied to a polyester sheet and remained adherent to the sheet after the water was evaporated. The system was cured for a few minutes by hot-pressing at 150°C.

ABAS Colloidal Dispersion Coating

In_2O_3 powder (0.1 g) was suspended in a latex dispersion of ABAS in water in a small test tube using a shaking mixer. The suspension was then spread over a polyester sheet. The water was allowed to evaporate in a fume hood, and the deposited film was subjected to hot-pressing at 90°C in order to smooth the surface.

Instruments

The conductivity of the films of In_2O_3 -ABS or -ABAS composites was measured at room temperature by the four-point technique with a multimeter (HP-3478A) instrument. The X-ray diffraction analysis of the In_2O_3 powder was performed using a Nicolet powder diffractometer equipped with a $\text{CuK}\alpha$ source. Scanning electron microscopy (SEM) micrographs of the In_2O_3 particles and ABAS latex films were obtained with a Hitachi S-800 instrument. The distribution of the In_2O_3 particles in the polymer matrix was investigated with PGT/TMIX field emission microscopy equipment using the secondary electron-scattering image and the back-scattered electron image techniques. The infrared spectra of the ABAS latex film were obtained with an FTIR instrument (Perkin-Elmer 400) using a KBr cell. The adhesive strength of ABS and ABAS to the surface of the polyester substrate was measured at room temperature using an Instron Testing Instrument (Model 1000).

Table II Various Polymer Binders used for the Preparation of In_2O_3 -A/Polymer Composite Films

In_2O_3 -Polymer Composites	Hot-pressing Temperature ($^{\circ}\text{C}$)	Weight Ratio of In_2O_3 -A to Polymer	Adhesion Strength of Polymer to the Polyester sheet (Kg/cm^2)	Electrical Conductivity (S/cm)
In_2O_3 -A/PEVA	75	1/0.5		Insulator
In_2O_3 -A/PEMA	150	1/1	4.5	$(4.0\text{--}5.5) \times 10^{-4}$
In_2O_3 -A/PVCVA	95	1/1		$(7.3\text{--}8.5) \times 10^{-5}$
In_2O_3 -A/ABS	150	1/1	22.4	$(3.2\text{--}5.3) \times 10^{-5}$

RESULTS AND DISCUSSION

Preparation of the Highly Porous Indium Oxide

Compared to the fine In_2O_3 particles, the highly porous ones which have a low apparent density exhibit a conductive percolation threshold at a lower pigment loading of the composite. The low-density particles were prepared by pyrolysis followed by the combustion of water-swallowable polymer microspheres imbibed with an aqueous indium nitrate solution (Table I). Two kinds of hydrogel microspheres were prepared by the inverted suspension polymerization method, namely PAM crosslinked with MBAM and PVA crosslinked with GDA. The use of a polymer as porogen to prepare highly porous structures requires, however, that the decomposition of the indium nitrate occur at a temperature lower than or close to that needed for the charring of the polymer network. Usually, in the pyrolysis of a polymer network, a carbonization first occurs at a relatively low temperature. If the indium nitrate decomposes at a temperature lower than that of carbonization, the In_2O_3 framework will be intermingled with that of carbon. A back-scattered electron image of indium in the carbonized sample was taken (Fig. 1). Since $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ decomposes at about 100°C and PAM-MBAM carbonizes at about 250°C , the sample was treated at 250°C for 15 h. The fact that the white area covers the entire particle indicates that the indium oxide is uniformly distributed as a network in the carbon network (Fig. 1). When the In_2O_3 -carbon composite was subjected to a higher temperature to remove the carbon (combustion), porous In_2O_3 spheres were generated (see the discussion later in the paper).

The network of PAM-MBAM has a higher temperature resistance than PVA-GDA. Since PVA-GDA is easily burned off during the decomposition of the nitrate, the oxide formed has the tendency to agglomerate; hence the porosity will be lower. Indeed, Table I shows that although the weight ratio of the precursor $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ to hydrogel is al-

most the same in cases I and IV, the density is lower in case I, which is based on PAM-MBAM. The SEM micrographs [Figs. 2 and 3(a)] show that they possess different morphologies, case I [Fig. 3(a)] being less closely packed than case IV (Fig. 2). The same conclusion can be reached by comparing cases II and III with cases V and VI of Table I, respectively.

Two kinds of pores are generated in the low-density particles: cavity-like and star-like (Fig. 4). We observed a cavitylike morphology when the weight ratio of the precursor indium nitrate hydrate to the PAM-MBAM was relatively large [cases I (Fig. 3(a)) and II (Fig. 3(b))]. A starlike morphology occurred when the ratio was low [case III (Fig. 3(c))]. The powder X-ray diffraction patterns of In_2O_3 -II, In_2O_3 -V, and In_2O_3 -A prepared via the three methods (see Table I) indicated the same crystallinity.

Preparation of In_2O_3 -ABS Conductive Films via Powder Coating

Several kinds of polymer latexes were used to prepare In_2O_3 -polymer composite films (Table II). When ethylene-vinylacetate copolymer PEVA latexes were employed the conductivity was negligible, even for high weight ratios of oxide to latexes. This happens because, during the hot-pressing, the flowability of PEVA chains is high and, as a result, the contacts among the In_2O_3 particles are interrupted. When poly(ethyl methacrylate) (PEMA) was employed as binder, a conductive film could be generated but the film was brittle, because the PEMA chains have low flexibility. The vinylchloride-vinylacetate copolymer (PVCVA) was not a good binder because it is thermally unstable and reacts easily with In_2O_3 . The AN/butadiene/ST block copolymer ABS was found to be an appropriate binder due to its core-shell structure. The AN-ST copolymer blocks constitute the shell of the latex, and the butadiene-ST copolymer its core. It is likely that the AN segments of the shell restrict the flowability of the ST during hot-pressing to such an extent that few gaps are generated among the In_2O_3 particles. The soft core of the latexes provides

Table III Electrical Conductivities of In₂O₃-ABS Composite Films Based on the Powder Coating Process

In ₂ O ₃ -ABS Composites ^a	Weight Ratio of In ₂ O ₃ to ABS	Apparent Density of In ₂ O ₃ (g/cm ³)	Electrical Conductivity (S/cm)
(1)			
In ₂ O ₃ -I/ABS	1/1	0.55	(1.2-2.7) × 10 ⁻⁴
In ₂ O ₃ -I/ABS	1/2	As above	(4.5-4.9) × 10 ⁻⁵
In ₂ O ₃ -I/ABS	1/4	As above	Insulator
(2)			
In ₂ O ₃ -II/ABS	1/1	0.29	(1.8-4.5) × 10 ⁻³
In ₂ O ₃ -II/ABS	1/2	As above	(1.8-6.7) × 10 ⁻⁵
In ₂ O ₃ -II/ABS	1/4	As above	Insulator
(3)			
In ₂ O ₃ -III/ABS	1/1	0.15	(1.7-3.5) × 10 ⁻³
In ₂ O ₃ -III/ABS	1/2	As above	(1.9-8.4) × 10 ⁻⁵
(4)			
In ₂ O ₃ -IV/ABS	1/1	0.71	Insulator
In ₂ O ₃ -V/ABS	1/1	0.54	(1.1-2.6) × 10 ⁻⁵
In ₂ O ₃ -VI/ABS	1/1	0.46	(7.8-8.2) × 10 ⁻⁴
(5)			
In ₂ O ₃ -A/ABS	1/1	1.0	(3.2-5.3) × 10 ⁻⁵
In ₂ O ₃ -A/ABS	1/2	1.0	Insulator

Powder coating process described in procedure A of the Experimental section.

^a Indium oxide of groups (1) to (3) was prepared by using PAM-MBAM as porogen; of group (4) was prepared by using PVA-GDA as porogen; and of group (5) was obtained from Aldrich.

the film with flexibility. In addition, the adhesion strength of ABS film to the polyester sheet after hot-pressing at about 150°C is as high as 22.4 Kg/cm².

Combining the ABS binder with any of the indium oxides (based on PAM-MBAM or PVA-GDA as porogens or on dense indium oxide), coating films on polyester substrates were prepared via hot-pressing (Table III). The secondary electron image (Fig. 5) of In₂O₃-II/ABS (Table I) provides an example of a conductive network of indium oxide (the white region) in the film. The experimental results listed in Table III have been divided into five groups. The indium oxide powders in the composites of groups (1) to (3) were prepared by using PAM-MBAM hydrogel as porogen, and have apparent densities in the sequence: I > II > III. It is noted that when the weight ratio of In₂O₃ to ABS is unity, II and III exhibit higher conductivities than I. However, when the ratio reduces to half, all three exhibit comparable conductivities. It is clear that the composites of group (5), which are based on nonporous In₂O₃-A, exhibit much lower conductivities than those of groups (1) to (3). This occurs because the commercial indium oxide has a higher density and therefore a stronger tendency for ag-

gregation of particles. As a result, the volume fraction of the pigment is lower and the distribution of particles in the coating film is nonuniform. The composites of group (4), prepared by using PVA-GDA as porogen, also increase their conductivity as the density of In₂O₃ decreases.

For practical purposes, the waterborne powder coating method is usually more convenient than that in which the powder is directly applied on the substrate. The data in Table IV are for coating films prepared by (1) brushing a paint, which is a suspension of In₂O₃-ABS powder in an aqueous solution of PVA, on a polyester sheet; and (2) hot-pressing the deposited layer. Compared to the conductivities of the corresponding coating films of Table III, the conductivities of the coating films in Table IV are sometimes higher by about one order of magnitude. The reason might be that the PVA molecules diminish the agglomeration tendency of the oxide particles.

Preparation of In₂O₃-ABAS Latex Film via Colloidal Dispersion Coating

As noted above, polymer latexes with core-shell structure are particularly suitable as polymer binders

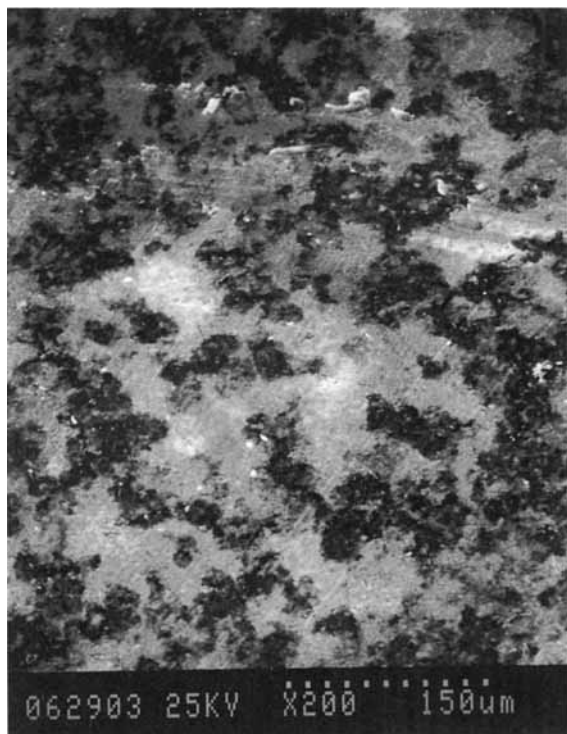


Figure 5 The secondary electron image of the composite $\text{In}_2\text{O}_3\text{-II/ABS}$ film; the bright spots indicate the indium oxide network.

for the pigment-polymer composites films. For this reason a new polymer latex, ABAS, which has a core-shell structure analogous to that of ABS, was synthesized by replacing the soft butadiene-ST copolymer in ABS with the soft BA-ST copolymer. We found that when PVA was used as emulsifier, the dispersion obtained after polymerization could be transformed via brushing on a substrate into a film after it was dried at ambient temperature. It is important to emphasize that the colloidal dispersion obtained after polymerization was stable because the adsorption of the PVA on the surface of the latexes stabilizes the system. The SEM micrograph of the film (Fig. 6) shows that the film is generated by the partial aggregation of polymer latexes. The FTIR spectrum of an ABAS latex film is presented in Figure 7. It exhibits three types of characteristic absorptions: ν_{CO} of the BA units; ν_{CN} of the AN units; and ν_{Ph} of the ST units. Because of the two-step synthesis procedure (see Experimental section), one can consider that most of the latex particles possess a core-shell structure. The adhesion strength of the ABAS film to the polyester sheet after hot-pressing at 150°C was 20.5 Kg/cm^2 .

The simplest way to prepare an $\text{In}_2\text{O}_3\text{-ABAS}$ conductive film is to suspend the indium oxide particles into the dispersion, and then to spread the

Table IV Electrical Conductivities of $\text{In}_2\text{O}_3\text{-ABS}$ Composite Films Based on the Water-borne Coating Process

$\text{In}_2\text{O}_3\text{-ABS}$ Composites	Weight Ratio of In_2O_3 to ABS	Electrical Conductivity (S/cm)
$\text{In}_2\text{O}_3\text{-II/ABS}$	1/1	$(3.1\text{--}3.4) \times 10^{-3}$
$\text{In}_2\text{O}_3\text{-II/ABS}$	1/2	$(3.3\text{--}4.3) \times 10^{-3}$
$\text{In}_2\text{O}_3\text{-II/ABS}$	1/4	Insulator
$\text{In}_2\text{O}_3\text{-A/ABS}$	1/1	$(1.4\text{--}3.3) \times 10^{-4}$
$\text{In}_2\text{O}_3\text{-A/ABS}$	1/2	Insulator

Waterborne coating process described in procedure B of the Experiment section.

suspension over a polyester sheet. A composite film will form on the substrate after drying. However, this approach requires that the density of indium oxide be sufficiently low, otherwise the sedimentation of the oxide particles during drying will make the upper face of the film nonconductive. When the nonporous commercial indium oxide $\text{In}_2\text{O}_3\text{-A}$ was used, the surface of the film indeed became insulating, while the bottom face of the film became conductive (Table V). In addition, two more observations can be made on the basis of the data listed in Table V: (1) The AN content affects the conductiv-

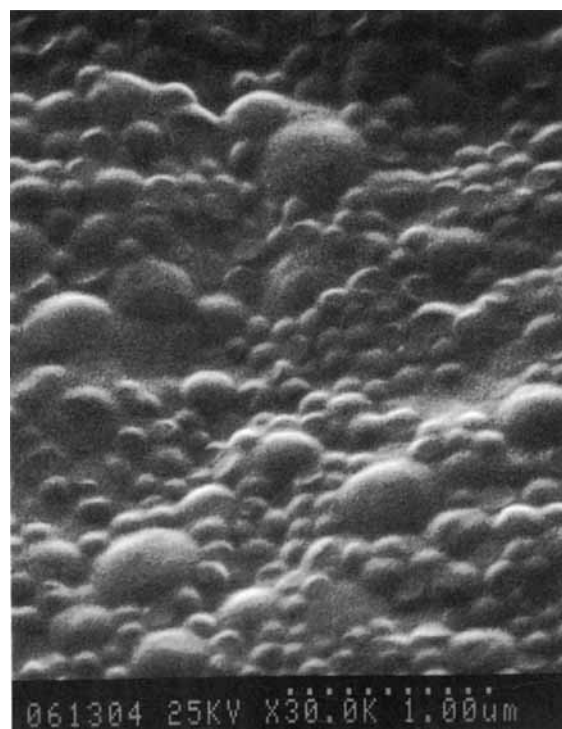


Figure 6 Scanning electron micrograph of ABAS-#2 polymer latex film (see also Table V).

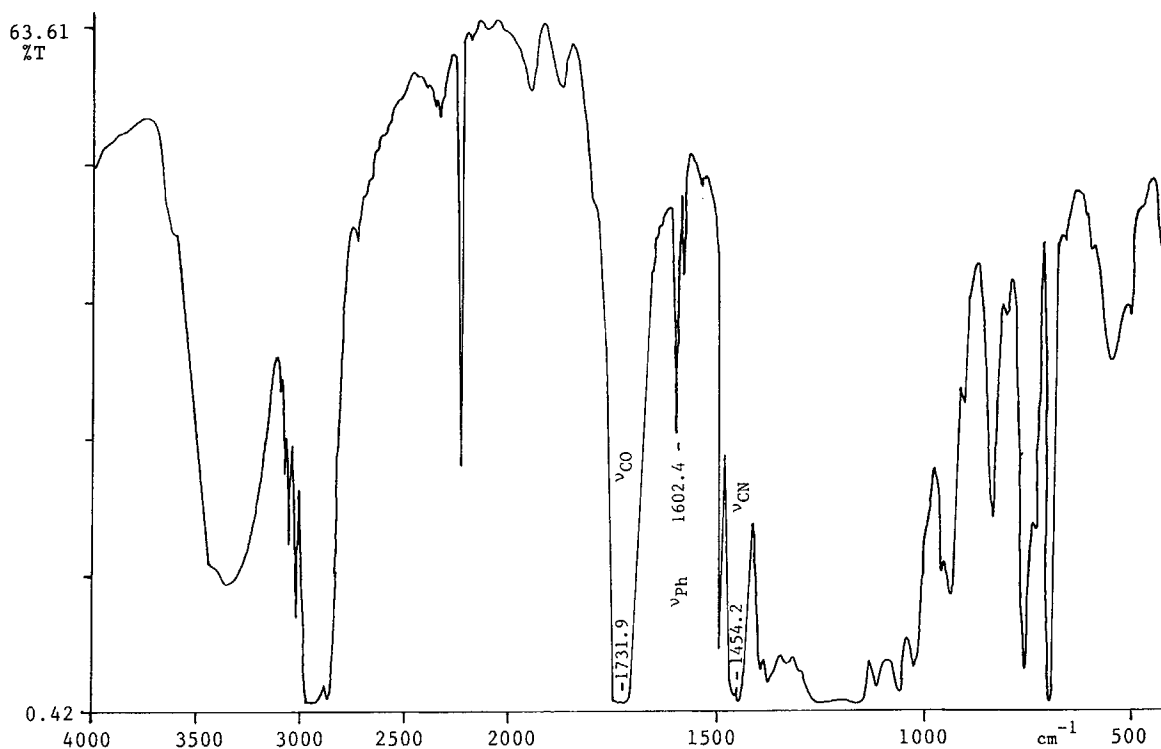


Figure 7 FTIR spectrum of ABAS-#2 (see Table V).

ity; indeed, the film in the second row of the table has a conductivity by more than one order of magnitude higher than that of the first row. The only difference between ABAS #2 and ABAS #1 is the AN content, which is double in the former case. This probably happens because a higher content of AN decreases the flowability of ST and BA blocks, and hence decreases the number of gaps among the indium oxide particles. (2) Compared to the conductivities of the coating films based on low-density $\text{In}_2\text{O}_3\text{-II}$ powder and ABS binder (Tables III and IV), the conductivities of the coating films with the

same low-density oxide as pigment but with the ABAS binder (Table V) are much larger. This advantage seems to occur because the conductive film of $\text{In}_2\text{O}_3\text{-II}/\text{ABAS}$ is formed at room temperature during drying. Hence the consequences arising from the decrease in the interparticle contacts of indium oxide, caused by the high temperature flow of the polymer binder during the hot-pressing, are avoided. The small size of the ABAS particles and the presence of the stabilizer ensure the stability of the colloidal dispersion. For the above reasons, the colloidal-dispersion coating process at room temperature

Table V Electrical Conductivities of $\text{In}_2\text{O}_3\text{-ABAS}$ Composite Films Based on the Colloidal Dispersion Coating

$\text{In}_2\text{O}_3\text{-ABAS}$ Composites	Weights of Components in ABAS Colloidal Dispersion (AN/BA/ST/PVA/ H_2O)	Weight Ratio of $\text{In}_2\text{O}_3/\text{ABAS}$	Electrical Conductivity (S/cm)
$\text{In}_2\text{O}_3\text{-II}/\text{ABAS}$ #1	0.75/6.0/2.5/0.5/34	0.1/0.12	$(7.7\text{-}8.3) \times 10^{-3}$
$\text{In}_2\text{O}_3\text{-II}/\text{ABAS}$ #2	1.5/6.0/2.5/0.5/34	0.1/0.12	$(1.4\text{-}2.1) \times 10^{-1}$
$\text{In}_2\text{O}_3\text{-II}/\text{ABAS}$ #2	As above	0.05/0.12	$(8.4\text{-}8.9) \times 10^{-3}$
$\text{In}_2\text{O}_3\text{-II}/\text{ABAS}$ #2	As above	0.03/0.12	$(1.4\text{-}3.1) \times 10^{-3}$
$\text{In}_2\text{O}_3\text{-II}/\text{ABAS}$ #3	1.5/6.0/2.5/0.9/34	0.1/0.12	$(2.9\text{-}3.5) \times 10^{-3}$
$\text{In}_2\text{O}_3\text{-A}/\text{ABAS}$ #2	1.5/6.0/2.5/0.5/34	0.1/0.12	Insulator at the Upper Face
$\text{In}_2\text{O}_3\text{-A}/\text{ABAS}$ #2	As above	0.1/0.12	$(0.7\text{-}1.9) \times 10^{-4}$ At the Bottom Surface

constitutes a most suitable method for the preparation of a conductive film.

CONCLUSION

Three main issues regarding the preparation of a conductive coating film of indium oxide-polymer composite have been presented: (1) The preparation of low-density and high-porosity indium oxide using water-swallowable polymer networks as porogens. This technique consists of two steps: First, microspheres of hydrogels are imbibed with indium nitrate, the precursor of In_2O_3 . This is followed by the pyrolysis and combustion of the microspheres. (2) The preparation of the In_2O_3 -polymer coating films via the hot-pressing of a powder mixture of In_2O_3 and polymer latexes. We found that the apparent density of indium oxide and the flowability of the polymer binder when heated are the key factors that affect the conductivity of the composite film. A waterborne system consisting of low-density In_2O_3 , a polymer latex binder, which has a core-shell structure (ABS, AN/butadiene/ST triblock copolymer), and an aqueous solution of PVA, which functions as dis-

persion medium, provides better results than the powder-mixture method. (3) Preparation of In_2O_3 -polymer films via a colloidal-dispersion coating process. In this case, an ABAS (AN/BA/ST copolymer) dispersion is first synthesized by suspension polymerization and a low-density In_2O_3 powder is added to the system. The conductive composite film is generated simply by drying at room temperature. This method is especially effective because the overflow of polymer during hot-pressing, which reduced the physical contacts between the pigment particles, no longer occurs.

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