Coating Metal Oxide Particles via the Combustion of Deposited Polymer Precursors

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ABSTRACT: Water-swellable chelated polymers were synthesized, starting either from (1) In(III) or In(III) and Sn(II) as central ions and *N*-trimethoxysilylpropylethylenediamine or ethylenediamine each together with ethylenediaminetetraacetic acid (EDTA) as coordination ligands, or from (2) Ag(I) as the central ion and ethylene glycol (EG) and EDTA as coordination ligands, as follows: The nitrate(s) of the above metal ions together with the corresponding ligands were dissolved in water, and the solution was concentrated by heating to carry out the chelating polymerization. After cooling, the polymer was dried and ground to a fine powder, which was then mixed with a metal oxide powder by grinding in the presence of a small amount of water. A paste was thus obtained, which, after drying, was calcined at 200°C and subsequently at 750°C. The polymer became a sticky gel at 200°C, which adhered to the surface of the metal oxide particles; it was converted to an inorganic coating, In_2O_3—SnO_2—SiO_2, In_2O_3—SnO_2, SnO_2, or Ag, during the subsequent calcination at 750°C. Two metal oxide powders, namely, the electrically conductive In_2O_3 and the nonconductive SnO_2, were used as substrates. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) indicated that the substrate particles were coated after calcination by a multicomponent oxide or silver layer. Temperature-resistant electrically antistatic film could be prepared by using the metal oxide coated In_2O_3 particles as pigments and polypropylsiloxane as the binder. The Ag-coated SnO_2 powder had a conductivity $\sigma = 1.0 \times 10^{-3}$ S cm^{-1} at 8.6 vol % Ag, while the mechanically mixed powders of Ag and SnO_2 exhibited a conductivity of 2.0×10^{-7} S cm^{-1} at 16 vol %. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1891–1903, 1998

Key words: coated metal oxide powders; metal oxides and metal coatings; polymer precursors; temperature-resistant antistatic painting

INTRODUCTION

The deposition of a functional layer on the surface of individual inorganic particles constitutes an important topic in powder technology, because the generated core–shell structure can provide additional useful properties. The ex-

isting techniques involve either the deposition by precipitation of a precursor on the surface of a suspended powder[1–3] or the interfacial polymerization on the surface of a powder dispersed in a solution of a desired monomer.[4–8] The first technique was employed for coating coarse ceramic particles with a fine powder of a single component; it is, however, more difficult to control the composition of multicomponent precipitates. The second technique was used either to cover polymer microspheres that contain metal nitrate salts with a metal oxide via a sol–gel process[5,8] or to deposit a conductive organic

Table I   Compositions of the Feedstock for the Synthesis of the Polymer Precursors

Chelating Polymers (CP)	$In(NO_3)_2$ (mmol)	$Sn(OAc)_2$ (mmol)	EDTA (mmol)	TMS–PEDA (mmol)	EDA (mmol)
InSnSi–CP1	10	5	7.5	15	0
InSnSi–CP2	10	0.9	7.5	15	0
InSnSi–CP3	10	0.4	7.5	15	0
InSn–CP4	10	5	7.5	0	15
InSn–CP5	10	1.3	7.5	0	15
Sn–CP6	0	10	7.5	0	15
InSi–CP7	10	0	7.5	15	0

coating on a metal oxide powder[6,7] via an oxidative polymerization process. In the present article, an alternate method is suggested for coating an inorganic powder with a multicomponent layer, which consists of depositing a water-swellable polymer containing multi-inorganic ions on the surface of the powder, followed by combustion. In contrast to the precipitation procedure, the polymer precursor is a chelated polymer that contains various bound metal ions in close proximity. Consequently, the composition and homogeneity of the deposited layer can be more easily controlled. While such a combustion methodology was used previously by Pechini[9] to prepare multicomponent inorganic powders, this technique is employed here to deposit a fine powder of metal oxide composites (In_2O_3—SiO_2, In_2O_3—SnO_2—SiO_2 or In_2O_3—SnO_2) on In_2O_3 powders.

Further, a temperature-resistant antistatic thin film was prepared using a coated In_2O_3 powder as the conducting pigment and polypropylsiloxane as the binder. The blending was carried out by the deposition of colloidal particles of polypropylsiloxane, formed via the hydrolysis and condensation polymerization of trimethylpropylsi-
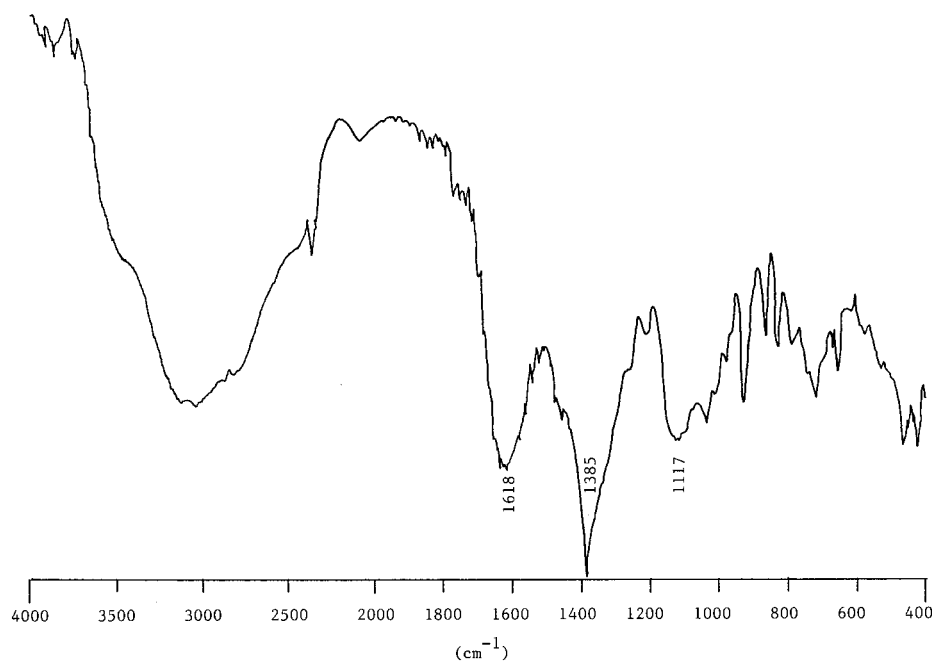
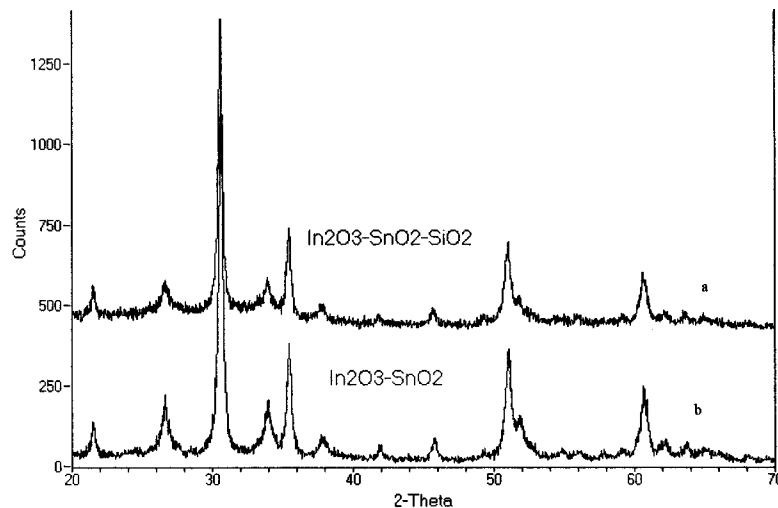**Figure 1**   Infrared spectrum of the chelated polymer InSi–CP7.

Figure 2   (a) X-ray diffraction of InSnSiO$_x$ (obtained via the combustion of InSnSi−CP1, Table I); (b) X-ray diffraction of InSnO$_x$ (obtained via the combustion of InSn−CP5, Table I).

lane (TMPS) in the presence of coated In$_2$O$_3$ powder, on the surface of the latter particles. The uncoated In$_2$O$_3$ could not be used as pigment because the polypropylsiloxane particles generated *in situ* covered too uniformly the surface of In$_2$O$_3$ particles, thus hindering the physical contacts among the latter conductive particles. In contrast, when one of the preceding oxide mixtures was deposited on the In$_2$O$_3$ particles, a conductive network could be achieved, for reasons discussed later in the article, whose conductivity was strongly affected by the composition of the coating layer. One can therefore control the conductivity of the antistatic film by selecting a suitable composition of the coating layer.

Besides the formation of metal oxide composite coatings, the method can be used to coat inorganic particles with some noble metals, such as Ag, Pd, and their alloys. In this method, the chelated polymer precursor is converted into a metal oxide during the burning of the organic component of the deposited layer and the metal oxide is decomposed further to the metal at a higher temperature. Silver-coated nonconductive SnO$_2$ powders were prepared because they are useful as SnO$_2$-based chemical sensors.[10] The silver-coated powders ex-

Table II   Compositions of the Oxide-Coated In$_2$O$_3$ Powders

No.	Symbol of the Oxide-Coated Powders	Coating Layer			Substrate (In$_2$O$_3$) Content (wt %)
		In$_2$O$_3$ Content (wt %)	SnO$_2$ Content (wt %)	SiO$_2$ Content (wt %)	
1	InSnSiO$_x$-1/In$_2$O$_3$	4.8	2.6	3.1	89.5
2a	InSnSiO$_x$-2a/In$_2$O$_3$	6.9	0.7	4.5	87.9
2b	InSnSiO$_x$-2b/In$_2$O$_3$	12.4	1.3	7.9	78.4
3	InSnSiO$_x$-3/In$_2$O$_3$	6.1	0.3	3.9	89.7
4a	InSnO$_x$-4a/In$_2$O$_3$	22.8	12.6	0	64.6
4b	InSnO$_x$-4b/In$_2$O$_3$	13.9	7.6	0	78.5
5	InSnO$_x$-5/In$_2$O$_3$	15.5	2.1	0	82.4
6a	SnO$_2$-6a/In$_2$O$_3$	0	23.4	0	76.6
6b	SnO$_2$-6b/In$_2$O$_3$	0	13.0	0	87.0
7	InSiO$_x$/In$_2$O$_3$	7.3	0	4.3	88.4

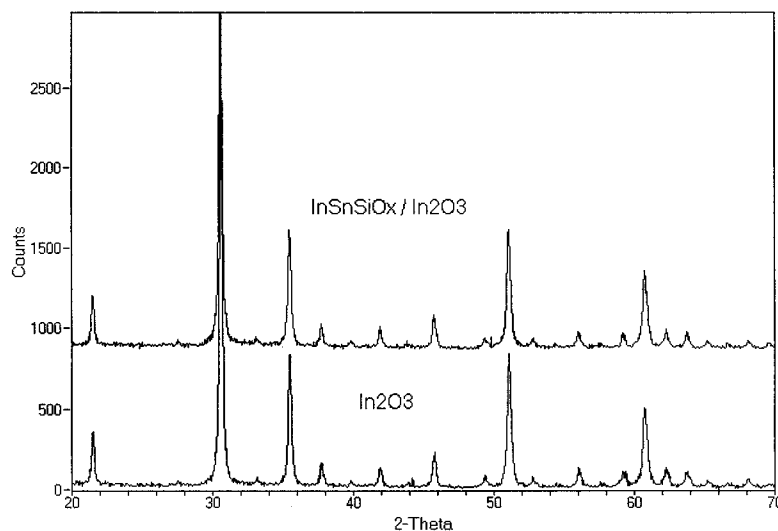**Figure 3**   (a) X-ray diffraction of the InSnSiO$_x$-1/In$_2$O$_3$ powder (Table II); (b) X-ray diffraction of In$_2$O$_3$.

hibit a conductivity percolation threshold at a much lower volume fraction of metal than that of the mechanical mixture of metal and substrate powders.

EXPERIMENTAL

Reagents

N-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMSPEDA, 90+%), ethylenediaminetetraacetic acid (EDTA, 99.5%), trimethoxypropylsilane (TMPS, 98%), indium nitrate hydrate (99.9%), tin(II) acetate, indium(III) oxide (99.99%), tin(II) oxide (99.8%), silver nitrate (99+%), ethylenediamine (EDA), ethylene glycol (EG, 99+%), benzoyl peroxide (97%), and ammonium hydroxide (20–30% NH$_3$) were purchased from Aldrich and used without further purification.

Chelating and Condensation Polymerizations of TMSPEDA and EDTA

An EDTA powder (2.2 g, 7.5 mmol) was introduced with magnetic stirring in 15 mL H$_2$O placed in a 100-mL beaker. An aqueous ammonia solution was then added dropwise to neutralize EDTA, which was thus converted into a water-soluble ammonium salt. The resulting solution had a pH of about 6.5. After another water-soluble chelating agent, TMSPEDA (3.3 g, 15 mmol),

was introduced into the aqueous solution, In-(NO$_3$)$_3 \cdot x$H$_2$O (3 g, 10 mmol) and Sn(OAc)$_2$ (0.22 g, 0.94 mmol) were added with magnetic stirring, at room temperature. A white suspension was obtained, which changed gradually into a homogeneous and highly viscous gel under stirring on a hot plate at about 200°C. When cooled, the gel became a solid, which was no longer soluble, but highly swellable in water. This solid could be easily ground into a powder, which contained In-(III)—Sn(II)—Si(IV).

Chelating Polymerizations of EDA and EDTA

The synthesis was performed as in the preceding section, except that EDA replaced TMSPEDA, and in some cases, only Sn(OAc)$_2$ was used as the central ion.

Coating In$_2$O$_3$ Particles with In$_2$O$_3$—SnO$_2$—SiO$_2$ or In$_2$O$_3$—SnO$_2$ or SnO$_2$ Fine Particles

The polymer precursor powder (1.6 g), In$_2$O$_3$ powder (1.2 g), and water (about 2 mL) were introduced into a mortar, where, after absorbing the water, the polymer became either a gel, when based on TMSPEDA, or a paste when based on EDA. A uniform mixing of the In$_2$O$_3$ powder with the gel or paste could be easily achieved by grinding. The obtained paste was heated to 200°C, temperature at which it was kept 30 min to let the softened
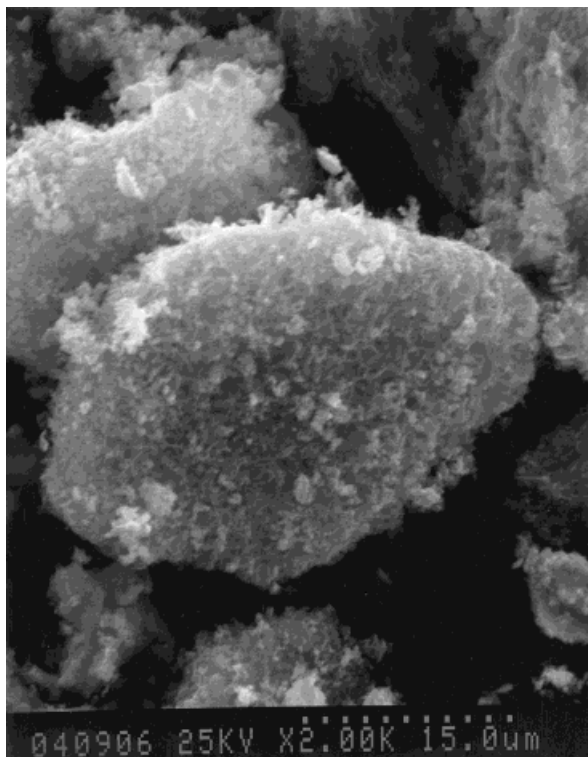
Figure 4 Scanning electron micrograph of the In-SnSiO$_x$-1/In$_2$O$_3$ powder (Table II).

polymer to flow and to stick to the indium oxide particles. Subsequently, the temperature was increased to 750°C (about 5°C/min), where it was kept 30 min in order to convert the polymer precursor to the composite oxide coating containing In$_2$O$_3$—SnO$_2$—SiO$_2$, In$_2$O$_3$—SnO$_2$, or SnO$_2$. The first coated particles are denoted InSnSiO$_x$/In$_2$O$_3$; the second, InSnO$_x$/In$_2$O$_3$, and the third, SnO$_2$/In$_2$O$_3$.

Deposition of Polypropylsiloxane on Coated Indium Oxide Particles

In a 100-mL round-bottom flask, a suspension consisting of either InSnSiO$_x$/In$_2$O$_3$ or InSnO$_x$/In$_2$O$_3$ powder (0.8 g), TMPS (0.8 g), and 20 mL deionized water was stirred at 65–70°C until the powder was transformed into sticky agglomerates that precipitated onto the bottom of the flask (about 3 h). These sticky agglomerates were washed twice with water and, after drying, were dispersed in 2-propanol to obtain a paint (1.5 mL 2-propanol was used to disperse 0.5 g of the solid).

Painting an Antistatic Thin Film on a Ceramic Plate

The paint prepared by the above procedure, in which the initiator benzoyl peroxide (2×10^{-3} g) was dissolved, was applied to a dense alumina plate by brushing several times. After drying in air, the coating was cured on a hot plate at 200°C for 1 h. During curing, the initiator stimulated the crosslinking of the binder. An elastic coating film with a thickness of about 0.15 mm was thus obtained.

Synthesis of the Ag(I)-Containing Polymer

To a 100-mL beaker containing AgNO$_3$ (5.6 g, 33 mmol) in 5 mL water, EDTA (2.92 g, 10 mmol) and EG (2.48 g, 20 mmol) were added. This aqueous solution was heated on a hot plate (200°C) until it became a brown gel. After cooling, it became a paste, containing the EDTA–EG–Ag(I) polymer and unreacted EG.

Preparation of the Ag-Coated SnO$_2$ Powder

A black SnO powder was converted via calcination in air at 750°C into a white SnO$_2$ powder. Subsequently, 1.02 g of the SnO$_2$ powder was blended with 1.36 g of the Ag(I)-EDTA–EG paste by grinding in a mortar and the mixture was heated up to 200°C, where it was kept 30 min to let the polymer stick to the SnO$_2$ particles. The mixture was calcined at 600°C for 0.5 h, and a brown powder (1.35 g) was obtained. The powder was ground
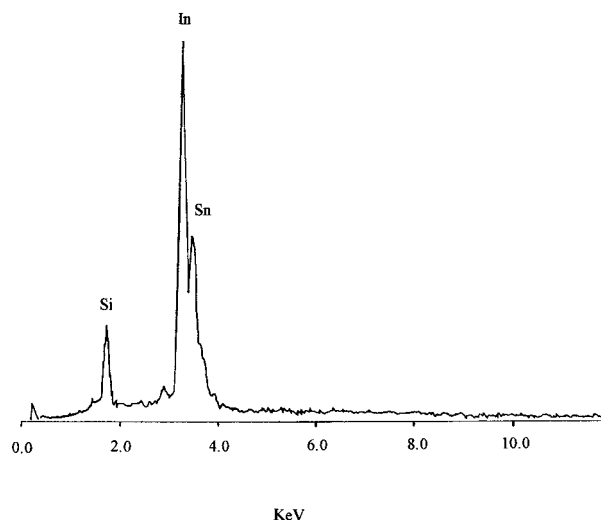

Figure 5 Energy dispersive spectrum of the surface of the particle presented in Figure 4.

Table III Composite Films, Consisting of Coated In_2O_3 Powder and Polypropylsiloxane on Alumina Plates

No.[a]	Powder−Binder Composite Films on the Alumina Substrate[b]	Weight Ratio of the Powder to the Binder[c]	Electric Conductivity $(S\ cm^{-1})$
1	$InSnSiO_x$-1/In_2O_3−$(SiOPr)_n$	1.4/1	2.3×10^{-6}
2a	$InSnSiO_x$-2a/In_2O_3−$(SiOPr)_n$	1.4/1	2.5×10^{-3}
2b	$InSnSiO_x$-2b/In_2O_3−$(SiOPr)_n$	1.4/1	1.7×10^{-6}
3	$InSnSiO_x$-3/In_2O_3−$(SiOPr)_n$	1.4/1	2.4×10^{-4}
4a	$InSnO_x$-4a/In_2O_3−$(SiOPr)_n$	1.4/1	2.1×10^{-2}
4b	$InSnO_x$-4b/In_2O_3−$(SiOPr)_n$	1.4/1	0.1
5	$InSnO_x$-5/In_2O_3−$(SiOPr)_n$	1.4/1	0.1
6a	SnO_2-6a/In_2O_3−$(SiOPr)_n$	1.4/1	1.9×10^{-2}
6b	SnO_2-6b/In_2O_3−$(SiOPr)_n$	1.4/1	0.3
7	$InSiO_x$/In_2O_3−$(SiOPr)_n$	1.4/1	9.5×10^{-4}
8	In_2O_3−$(SiOPr)_n$	1.4/1	Insulator

[a] The sample numbers correspond to those used for the coated powders in Table II.
[b] The thickness of the film is in the range of 50–200 μm.
[c] It is assumed that the precursor TMPS converted quantitatively to polypropylsiloxane, which is denoted as $(SiOPr)_n$.

and pressed in a die under a pressure of about 1700 atm. A disc (diameter = 12.7 mm and thickness $\approx$ 1 mm) with a metal luster was obtained and employed to determine the conductivity. For comparison, SnO_2 and silver powders (Degussa, mean particle size = 5 μm) were mixed by grinding, and after a disc was prepared, the conductivity was measured.

Instrumental

The conductivity of the $InSnSiO_x$/In_2O_3−polypropylsiloxane film was measured at room temperature by the four-point technique, and the conductivity of the silver-coated SnO_2 powder was measured at room temperature by the two-point technique, with a multimeter (HP-3478A) instrument. The infrared absorption spectra of the polymer precursors were determined with a Perkin−Elmer (1720) FTIR instrument and the X-ray diffraction analysis of the powders was performed with a Rigaku diffractometer provided with a CuKα source (30 kV, 10 mA). Scanning electron microscopy (SEM) micrographs of the coated particles and of the pigment−binder composites were obtained with a Hitachi S-800 instrument, and the energy-dispersive spectroscopy (EDS) elemental analysis of the surface was performed using a PGT/IMIX field emission electron microscopy instrument. The particle-size distributions of SnO_2 and Ag-coated SnO_2 were determined with a HORIBA laser scattering particle-size distribution analyzer (LA-900).

RESULTS AND DISCUSSION

Synthesis of Polymer Precursors

N-[3-(Trimethoxysilyl)propyl]ethylenediamine (TMSPEDA) is a coordination ligand because of its EDA moiety and a monomer of silicone polymers due to its trimethoxysilyl moiety. TMSPEDA and EDTA, which possess strong coordination abilities for most of metal cations, were mixed with In(III) nitrate and Sn(II) ace-
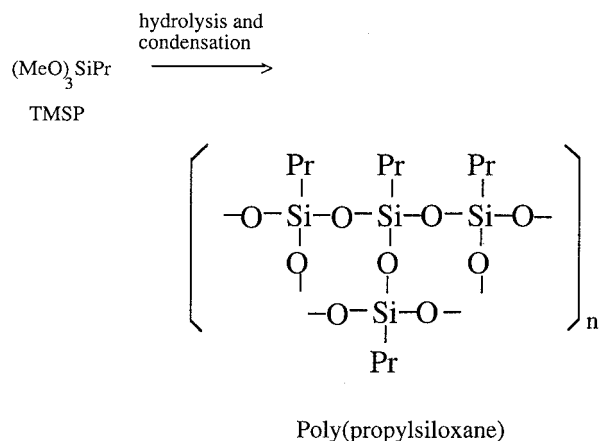

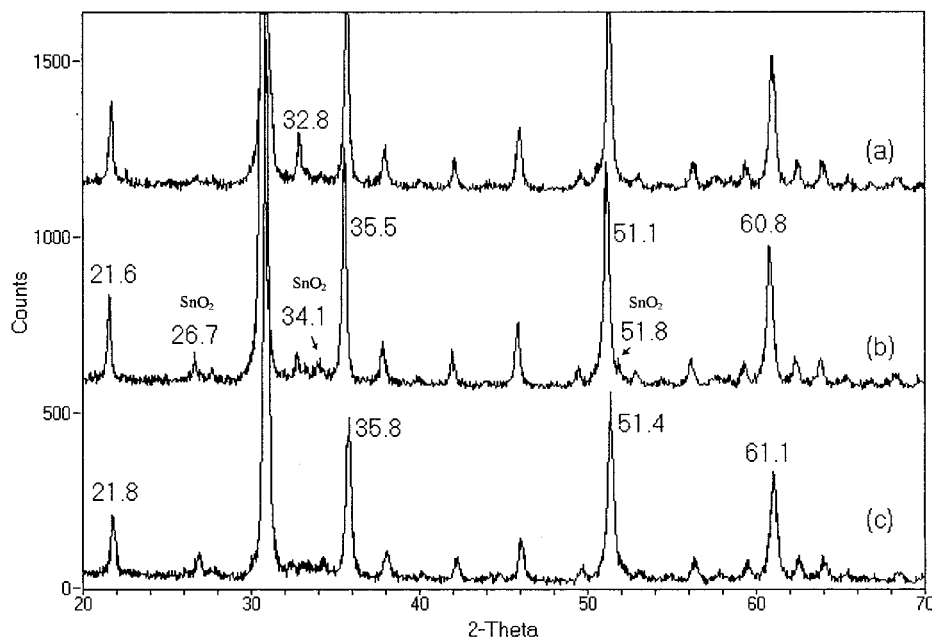**Figure 6** Schematic structure of the polypropylsiloxane gel.

Figure 7 (a) X-ray diffraction of the $InSnO_x$-4b/In_2O_3 powder, SnO_2 = 7.6 wt %; (b) X-ray diffraction of the $InSnO_x$-4a/In_2O_3 powder, SnO_2 = 12.6 wt %; (c) X-ray diffraction of the SnO_2-6b/In_2O_3 powder, SnO_2 = 13 wt %.

tate in an aqueous medium. Concentrated by heating, the mixture transformed into a crosslinked matrix, because of the coordination of the two cations by the ligands and the formation of a silicone network via the hydrolysis and condensation polymerization of the trimethoxysilyl moieties of TMSPEDA. The two metal ions trapped in the polymer matrix and Si atoms were thus brought into the proximity of each other. Due to the double crosslinking (coordination and condensation polymerization), the polymer precursors became insoluble but swellable in water.

To synthesize Si free polymer precursors, EDA and EDTA were mixed with $In(NO_3)_3$ and $Sn(OAc)_2$ in an aqueous medium as described in the Experimental section. Because no silicone network consisting of $\equiv Si-O-Si\equiv$ was present in this polymer precursor, the material obtained was brittle. It could be easily suspended in water to form a concentrated colloidal dispersion.

Various polymers with different compositions, listed in Table I, were synthesized. Figure 1 presents the FTIR spectrum of the polymer InSi–CP7. It shows that the stretching absorption band of the carbonyl groups $\nu_{C=O}$ of EDTA was shifted from 1691 cm^{-1} (noncoordinated) to 1618 cm^{-1} (coordinated), because the carboxylate groups

were coordinated with In^{3+} ions. It also shows that the stretching absorption frequency of EDA groups ν_{N-H} of TMSPEDA was shifted from 1460 cm^{-1} (noncoordinated) to 1385 cm^{-1}, due to the chelation of the two β-amine groups to the In^{3+} ions. In addition, the absorption at 1117 cm^{-1}, due to the Si—O bond stretching vibration, indicates the presence of the $\equiv Si-O-Si\equiv$ silicone structure.

X-ray diffraction (Fig. 2) revealed that the inorganic oxide powders obtained via the combustion at 750°C of the polymer precursors InSnSi–CP1 and InSn–CP5 have identical XRD patterns. The peaks at 2θ = 26.7, 34.1, and 51.8 are due to SnO_2, while the other ones, to In_2O_3. The SiO_2 peaks are missing in Figure 2(a), probably because SiO_2 is in an amorphous state. It is, indeed, known that the calcination of a silicone precursor at a low temperature (750°C in the present case) leads to amorphous silica.[11]

Preparation of an Electrically Conducting Film Using Coated In_2O_3 Powder as Pigment and Polypropylsiloxane as Binder

As described in the Experimental section, the process of coating In_2O_3 powder with an oxide composite layer consists of two steps: (1) The
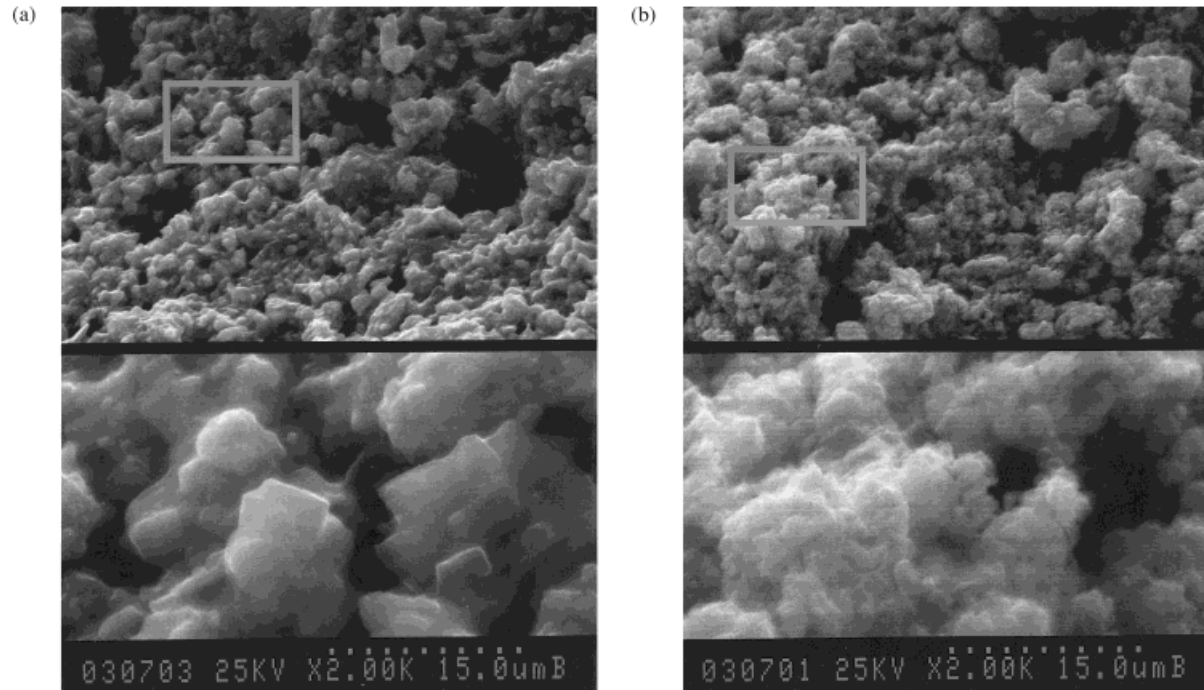
(a)

(b)

030703 25KV X2.00K 15.0umB

030701 25KV X2.00K 15.0umB

Figure 8   (a) Scanning electron micrograph of the specimen $InSnSiO_x$-1/In_2O_3—(SiOPr)$_n$; (b) Scanning electron micrograph of the specimen $InSiO_x$/In_2O_3—(SiOPr)$_n$.

grinding of the mixture of In_2O_3 and the polymer precursor powders in the presence of a small amount of water. In this step, the polymer swollen by water acquires higher lubricating and adhesive abilities and covers more uniformly the surface of the indium oxide powder. (2) The calcination of the mixture, first at 200°C and then at 750°C in air. In this step, the polymer precursor can flow at 200°C, becoming stickier and adhering to the In_2O_3 particles; subse-
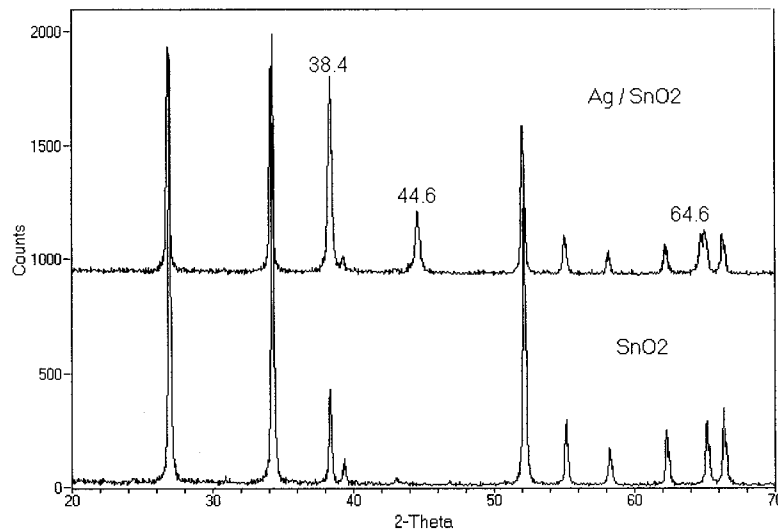

Figure 9   X-ray diffraction of the Ag-coated SnO_2 powder; the three peaks $2\theta = 38.4$, 44.6, and 64.8 are due to Ag and the other ones to SnO_2.
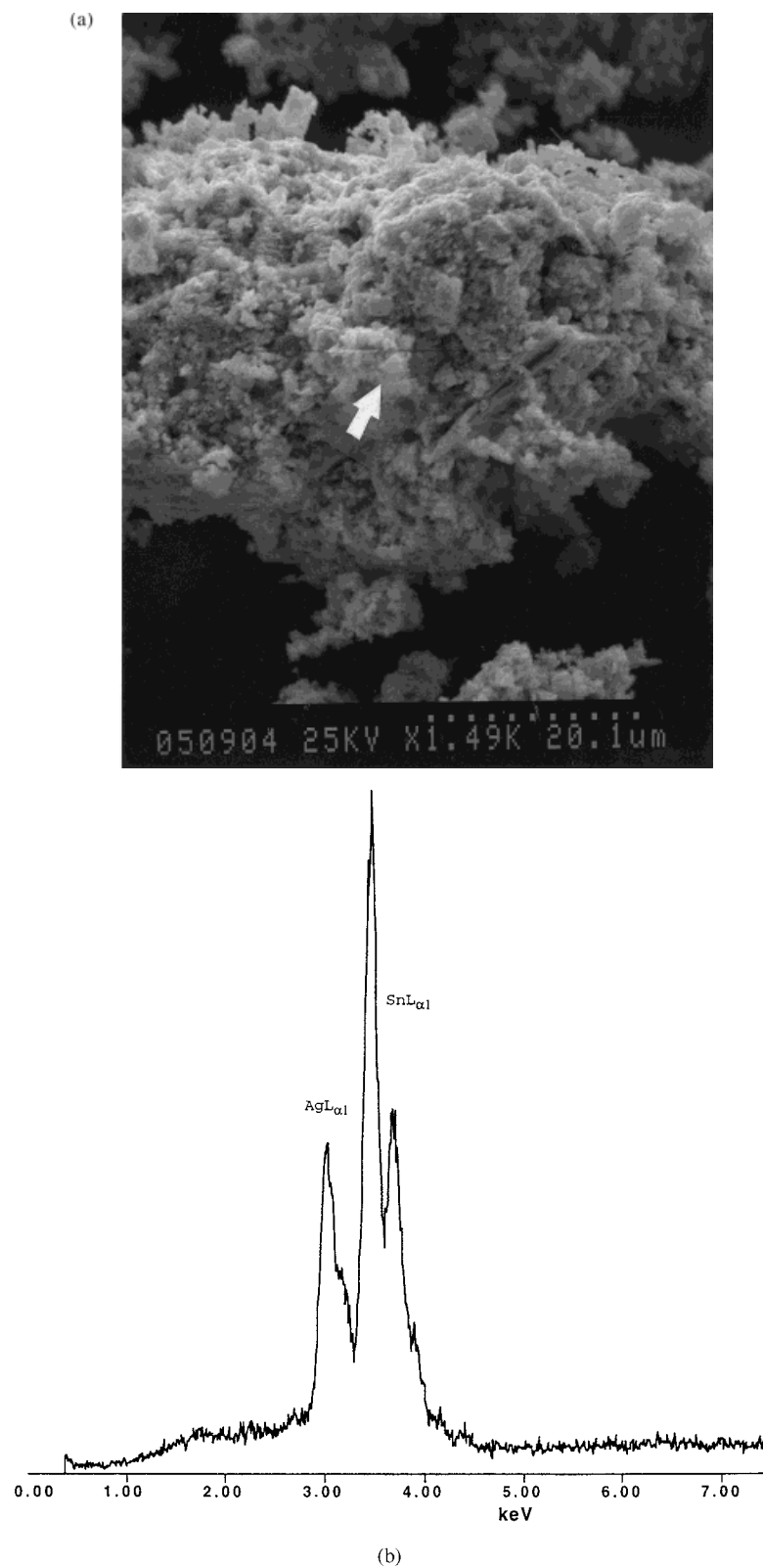
(a)

(b)

Figure 10 (a) Scanning electron micrograph of the Ag-coated SnO_2 particle; the arrow indicates the Ag coating. (b) Energy dispersive spectrum of the surface of the particle presented in (a).
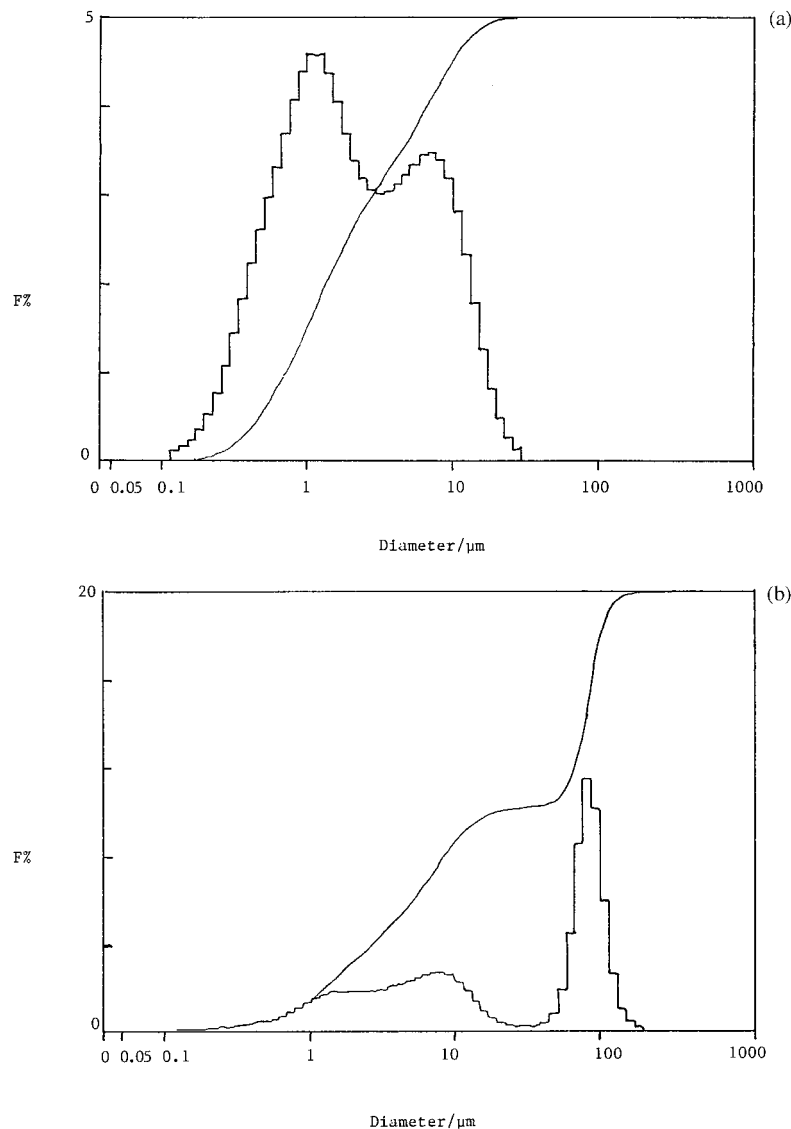
Figure 11   (a) Particle-size distribution of the SnO_2 powder; (b) particle-size distribution of the Ag-coated SnO_2 powder.

quently, at 750°C, the organic material is burned out, and the resulting fine oxide particles, which have irregular shapes, remain bound to the In_2O_3 particles, forming a coating layer.

Ten coated In_2O_3 powders, which are listed in Table II, were prepared. The XRD patterns of the coated powder $InSnSiO_x$-1/In_2O_3 are identical to those of In_2O_3 (Fig. 3), because the SnO_2 content was too low to be detected (Table II). The SEM micrographs (one of them is presented in Fig. 4) revealed that the $InSnSiO_x$-1/In_2O_3 particles have a rough surface and that the In_2O_3 particles are not completely covered by

the oxide composite. The EDS (Fig. 5) of the particle presented in Figure 4 indicates that the ratios of the peak intensities of In to Si and Sn are higher than those of the oxide coating alone. This implies that the In_2O_3 particles are not completely covered by the oxide composite. In addition, it is worth noting that the combustion of the chelated polymer precursor free of In_2O_3 particles led to cellular structures,[12] which can also be observed in the scanning electron micrograph (Fig. 4) on the surface of the coated In_2O_3 particles. This indicates that the oxide composite is indeed present on the surface of In_2O_3.
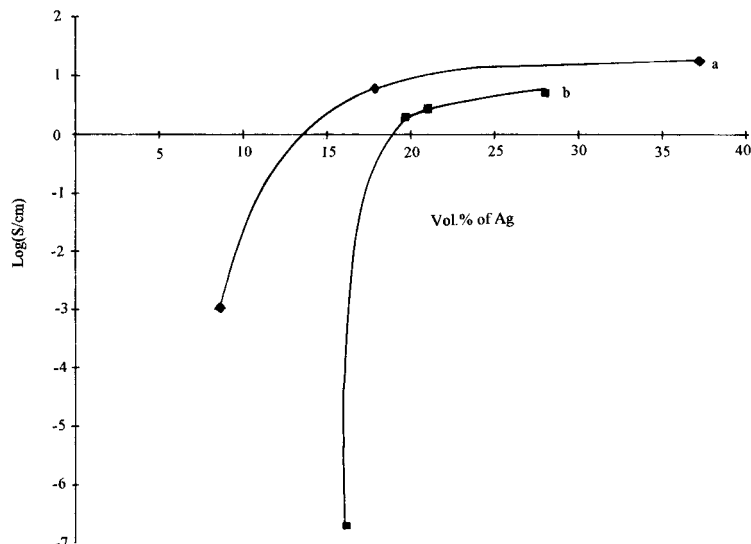
Figure 12   The electrical conductivities of the discs prepared from (a) Ag-coated SnO_2 powder and (b) mechanically mixed powders of Ag and SnO_2.

The coated In_2O_3 powders were used as electrically conducting pigments and polypropylsiloxane as the binder to prepare temperature-resistant antistatic films. The composition of the coating layer strongly affected the conductivity of the antistatic films (Table III).

The blending of the coated In_2O_3 powder with polypropylsiloxane was carried out in a water-based suspension of coated In_2O_3 powder and the monomer trimethoxypropylsilane (TMPS), which is the precursor of the binder polypropylsiloxane. During the sol–gel process, the formed sol particles (nanometer size) deposited on the surface of the coated In_2O_3 particles (5–15 μm), generating a gel. Figure 6 provides a possible chemical structure of the gel. We found that polypropylsiloxane can cover very uniformly the pure In_2O_3 particles. However, in this case, a nonconductive uniform film of In_2O_3—$(SiOPr)_n$ on the alumina plate (No. 8, Table III) was obtained after curing, because the binder hindered the physical contact among the In_2O_3 particles. When, instead of In_2O_3 powders, the coated In_2O_3 powders were employed as pigments, the films exhibited various conductivities depending on their compositions (Table III). When the coating consisted of $InSiO_x$, the sample had a conductivity as large as 10^{-3} S cm^{-1} (No. 7, Table III). This probably happens because of the formation of Si—O—Si bonds between the SiO_2 sites of the coating and the

siloxane groups of the binder and because, according to Figure 4, the oxide composite did not cover completely the In_2O_3 particles. Therefore, when the coated In_2O_3 particles were forced by the binder to approach each other, the uncoated areas on their surfaces had a high probability to contact physically and thus to generate a conducting network.

The XRD of $InSnO_x/In_2O_3$ powders with SnO_2 contents of 7.6 wt % (No. 4b, Table II) and 12.6 wt % (No. 4a, Table II) revealed that (a) for a SnO_2 content of 7.6 wt % the peaks of SnO_2 are missing, and, in addition to the peaks of In_2O_3, a new peak at $2\theta = 32.8$ is present [Fig. 7(a)], which is characteristic of the Sn(IV)-doped In_2O_3 structure.[13] (b) For a SnO_2 content of 12.6 wt %, the peak at $2\theta = 32.8$ becomes weaker, but the three characteristic peaks of SnO_2 at $2\theta = 26.7, 34.1$, and 51.8 are present. The film with 7.6 wt % SnO_2 (4b of Table III) has a high conductivity, while that with 12.6 wt %, a somewhat lower one (4a of Table III). The likely explanation is that, in the pigment of the former film, SnO_2 doped the In_2O_3 substrate during calcination, while in the pigment of the latter film, only a fraction of SnO_2 doped In_2O_3 and the remaining SnO_2, being nonconducting, hindered the conductivity.

When the coating consisted of SnO_2 alone (6a and 6b of Table II), the content of SnO_2 affected the conductivity of the film. The film SnO_2-6b/

In_2O_3—$(SiOPr)_n$, which contains in the pigment 13 wt % SnO_2 (6b, Table III), exhibited a higher conductivity than that which contains 23.4 wt % (6a, Table III). The XRD of the SnO_2-6b/In_2O_3 powder [Fig. 7(c)] is similar to that of $InSnO_x$-4a/In_2O_3 [Fig. 7(b)], which has approximately the same SnO_2 content. The major peaks are, however, shifted to higher d-spacings, and the peak at $2\theta = 32.8°$, characteristic of the Sn(IV)-doped In_2O_3 structure, is absent. We are tempted to consider that another solid solution of SnO_2 and In_2O_3 was generated, which is also electrically conductive. The only argument which we have is that the powder of SnO_2-6b/In_2O_3 has a deep green color, while the powder of $InSnO_x$-4a/In_2O_3, a different yellow–green one. The different colors may indicate that different reactions between the substrate and coating have occurred during calcination. The lower conductivity at 23.4 wt % SnO_2 is perhaps due to an excess of the nonconductive SnO_2 present.

The SnO_2 content affected the conductivity of the $InSnSiO_x$/In_2O_3—$(SiOPr)_n$ as well. We found that the binder covered the coated In_2O_3 particles more uniformly when the coating contained SnO_2. Indeed, the SEM micrographs [Fig. 8(a,b)] show that film 1 (No. 1, Table III) which contains SnO_2 has a smoother binder layer than has film 7 (No. 7, Table III), which is free of SnO_2. It has also a smaller conductivity than has film 7. Similarly, film 2a with a lower SnO_2 content than film 1 has a higher conductivity. It is likely that this happens because (1) SnO_2 reacts with SiO_2[14] and fewer SiO_2 sites remain to anchor the binder, and (2) the higher uniformity of the binder layer hinders the contacts between the uncoated areas of the In_2O_3 particles. A thicker coating layer is expected to decrease the conductivity (compare films 2a and 2b).

SnO_2 behaves very differently in the presence of SiO_2 than in its absence. In the latter case, Sn(IV) is a dopant (in the low content range) and increases the conductivity, while in the former, it interacts with silica and decreases the conductivity. In summary, it is possible to design the composition of the coating layer so as to achieve the desired conductivity of the antistatic film.

Coating SnO_2 Particles with Silver

Another application of the technique is the silver coating of tin(IV) oxide particles. EG and EDTA were employed to coordinate Ag(I) ions and to obtain the polymer precursor (see Experimental). Both ligands had to be employed, because neither of them alone could generate the chelated polymer precursor. During combustion, the Ag(I) compound was converted to Ag metal (as indicated by XRD [Fig. 9]). (In this sample, the weight content of Ag was 24%.) The Ag-coated SnO_2 particles were investigated by SEM and EDS [Fig. 10(a,b)]. Figure 10(a) shows that the silver coating is adherent to the SnO_2 particles. Additional evidence for the coating is the change in the particle-size distribution after coating [Fig. 11(a,b)]. One can note that while most of the SnO_2 particles have sizes below 10 μm the Ag-coated particles have two peaks at 10 and 90 μm. The larger particles are most likely a result of the agglomeration of Ag-covered particles.

The electrical conductivity of the discs prepared from the Ag-coated SnO_2 powders displayed a conducting percolation threshold at a lower volume fraction of Ag than when SnO_2 and Ag were mechanically mixed (Fig. 12). The former has a conductivity of 1.0×10^{-3} S cm^{-1} at 8.6 vol % and the latter a conductivity of 1.9×10^{-7} S cm^{-1} at 16 vol % of Ag.

CONCLUSION

The main novelty of the proposed technique lies in the coating of an inorganic powder with a multicomponent inorganic oxide or metal (when its oxide decomposes to metal during calcination). The precursor of the coating is a water-swellable metal-chelated polymer. A two-step process is employed: The first consists of the deposition of the precursor on an inorganic oxide powder, and the second, in the calcination of the deposit. Two kinds of coated powders were prepared: (1) a multioxide-coated In_2O_3 powder, and (2) a silver-coated SnO_2 powder. The multioxide-coated powder can be used as an electrically conductive pigment. Combined, via a sol–gel process, with polypropylsiloxane as the binder, a temperature-resistant antistatic film was prepared. Ag-coated SnO_2 particles displayed a conducting percolation threshold at a lower volume fraction of silver than did the mechanical mixture of the two powders.

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