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Electric Conductive ZnO Particles Microcapsulated with Carbon Film

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A new method has been developed for imparting electric conductivity to ZnO particles. The conductive particles are obtained by treating pure ZnO particles with a hydrocarbon at a temperature of- or higher than 500 ℃ and depositing a 1 nm thick film of carbon. Resulting products are comparable regarding conductivity, particle size, and whiteness with the Sb-doped conductive SnO_2 particles currently in market. In addition, they are advantageous in that they can be produced at a much lower cost due to the simplifie production process and lower material costs.

Recently, in electronic industry, the role of antistatic agents is of increasing interest for the protection of electronic machinery from disturbance by static electricity occurring in plastic and rubber materials. For this purpose,metal oxides are commercially available such as, for example, Al doped ZnO, Sb-doped SnO_2 and TiO (titanium black).1) Their conductivity, particle size, whiteness and price must, however, be improved.

In contrast with the conventional technique by which conductivity is imparted by increasing the nonstoichiometry of the metal oxide, or by doping a different kind of metal to increase the carrier concentration, ours is a very simplified method and consists of just treating pure ZnO particles with a hydrocarbon gas at a temperature of- or higher than 500 ℃ so as to deposit carbonfilm which gives an electric conductivity. In comparison with the conventional technique of Al doping to ZnO, this new technique is advantageous in that the conductivity is achievable while the particles remain small in size , because the heat treatment time is very short and sintering or grain growth does not occur. Further, such particles can be produced at costs much lower than Sb-doped SnO_2 particles. This paper treats the new method of producing the electric conductive particles and several properties of the thus obtained product.

Figure 1 shows an arrangement for depositing carbon film by treating with

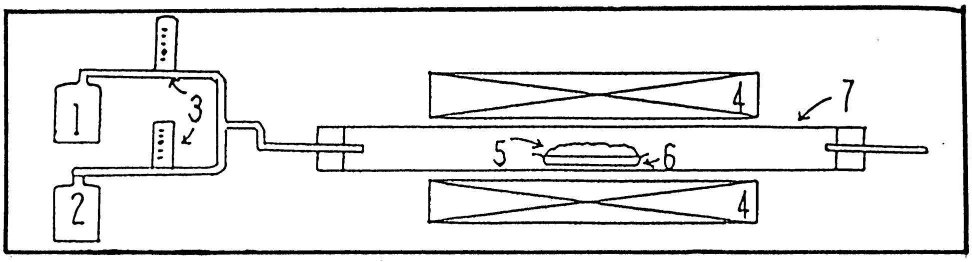

Fig. 1. Schematic presentaiton of the reaction arrangement.
1: C_3H_6 gas, 2: N_2 gas, 3: Flow meter, 4; Heater
5: ZnO powder, 6: Boat, 7: Reaction tube (alumina)

propylene on ZnO particles. A ceramic boat is loaded of ZnO powder and placed at the right end of a reaction tube which is surrounded and heatable with a furnace, while nitrogen gas is introduced until the oxygen content in the tube has been replaced; then propylene is passed in a flow ratio N_2 / C_3H_6 of 4 to 1. The boat is moved to the center heated in advance to 650 °C , where it is held at the temperature for a period which varies from 10 seconds to several minutes and, then, to the left end quickly, where it is cooled to room temperature. The recovered product is a grayish-white powder exhibiting conductivity. The mass of the carbon deposit on the ZnO powder was determined with a CN corder. The resistivity was measured by placing 2.0 grams of the powder in an 11.3 mm I.D. cylinder and squeezing with a steel electrode from each end at a pressure of 100 kg·cm^{-2}.

Figure 2 shows SEM images of the surface of the ZnO particles with a specific surface area of 3.8 m^2 g^{-1} before (a) and after the propylene treatment to a carbon content of 4.9 wt.% (b). As seen here, the untreated particles have a smooth surface (a) , while, the treated ones are covered with a film, scattered with projections (b).

Figure 3 shows the resistivity vs. the carbon content for a ZnO powder of a specific surface area of 46.5 m^2 g^{-1}(a Sumitomo Metal Mining product) as

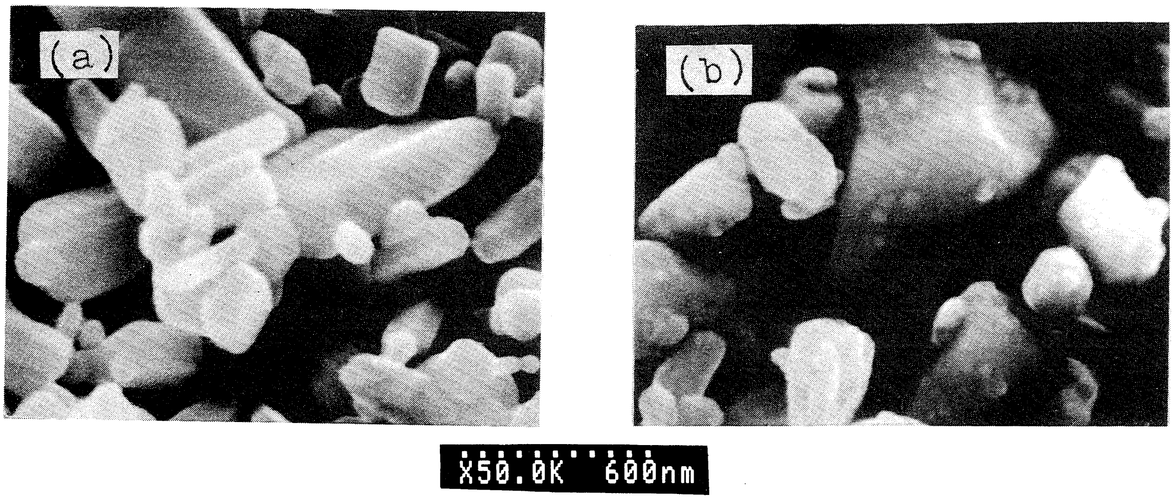

Fig. 2. SEM images of propylene treated ZnO particles.
(a) untreated, (b) propylene treated

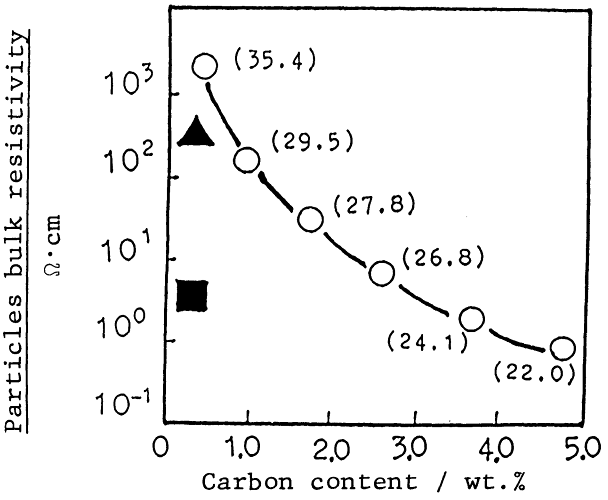

Fig. 3. Dependence of the bulk resistivity on the carbon content of propylene treated ZnO particles. The values in parentheses represent the specific surface areas (m^2 g^{-1}).

▲ : particles bulk resistivity of Al-doped ZnO (s.s.a. 1.5 m^2 g^{-1}), Honjo Chemical product;

■ : particles bulk resistivity of Sb-doped SnO_2 (s.s.a. 32 m^2 g^{-1}), Mitsubishi Metal product.

propylene treated. The values in parentheses represent the respective specific surface areas. The carbon content of the deposit on the treated particles was 97.4 wt.% C as determined by thermogravimetry and with the CN coder. The resistivity levels are marked on the figure for both commercial products of Al-doped ZnO (from Honjo Chemical Co.; specific surface area: 1.5 m^2 g^{-1}) and Sb-doped SnO_2 (Mitsubishi Metal Corporation; specific surface area: 32 m^2 g^{-1}) for the purpose of a comparison.

Table 1 compares the reflective density of this Sb-doped SnO_2 and a ZnO (with a carbon content of 3.8 wt.%) exhibiting a comparable resistivity for component colors as determind with a Macbeth reflective densitometer. The results for the component black demonstrated that they had comparable whiteness levels. Regarding the hue, it was observed that the Sb-doped SnO_2 was higher in the cyan level than the propylene treated ZnO.

Table 1. Reflective density of paper coated with the conductive ZnO particles (mixed with acrylate resin at a particle concentration 50%, coat thickness 100 μm)

	Reflective Density for Component Colors			
Specimen	Black	Cyan	Magenta	Yellow
ZnO-Carbon	0.91	0.95	0.90	0.83
Sb-doped SnO_2	0.88	1.01	0.84	0.74
Base paper	0.08	0.06	0.10	0.11

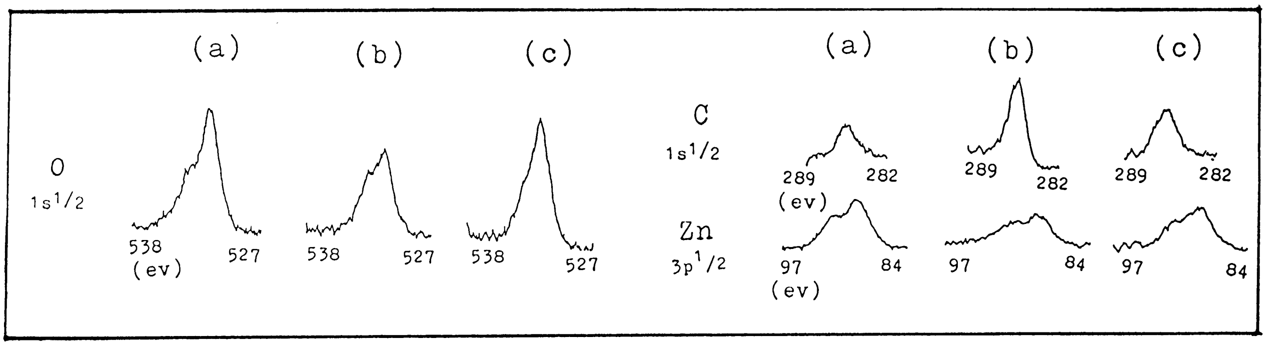

Fig. 4. Transition of ESCA spectra by propylene treatment and Ar^+ sputtering: (a) as untreated, (b) propylene treated and (c) sputtered.

Figure 4 shows ESCA spectra for O $1s^{\frac{1}{2}}$, C $1s^{\frac{1}{2}}$, and Zn $3p^{\frac{1}{2}}$, indicating the surface state of a coarse ZnO powder with a specific surface area of 0.8 m^2g^{-1}as untreated (a), propylene treated to a 0.5 wt.% C content (b) and further etched by 10 nm on the (b) surface by Ar^+ sputtering (c). As propylene treated (b), it can be seen that the Zn and O peaks reduce while the C peak increases; as Ar^+ sputtered (c), the O and Zn peaks increase again, while the C peak decreases.

Such conductive ZnO powder can be also obtained by similarly treating with another hydrocarbon gas such as propane and acetylene.

It may be possible that in the propylene treatment a reduction reaction could take place on the surface of ZnO particles such that lattice oxygen atoms are removed and, at the same time, organic compounds form such as hexadiene, benzene, acetone etc.,$^{2)}$ but our IR spectroscopic analysis of particles and soot deposit on the reaction tube failed to point out any such compounds. It is thus estimated that the carbide forming reaction should take place in preference to the redox reaction at such elevated temperatures.

It may be thus considered that electric conductivity is achieved by forming a thin film of carbon on ZnO particles in the propylene treatment. Assuming that the carbon deposit on the particles is regular and homogeneous, the thickness may be calculated as follows for an example where the carbon content is 3.8 wt.%. Being amorphous, the carbon exhibits a density of the order of 2.0 $g \cdot cm^{-3}$, so 1.000 grams of the conductive particles have a volume of $0.038g / 2.0g \cdot cm^{-3} = 0.019\ cm^{-3}$. As the particulate ZnO substrate has a collective surface area of $24.1 \times (1.000 - 0.038)\ m^2\ g^{-1}$ so the thickness will be: $0.019\ cm^3 / 24.1 \times (1.000 - 0.038) \times 10^4\ cm = 0.82 \times 10^{-7}\ cm = 0.82\ nm$.

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