

Effects of the loadings and type of copper powder on the electrical resistivity of copper powder–polymer paint films

K. MORI, Y. OKAI, H. YAMADA,* Y. KASHIWABA*

*Department of Applied Chemistry, and *Department of Electrical Engineering, Faculty of Engineering, Iwate University, Ueda, Morioka 020, Japan*

Conductive behaviour in copper powder-filled paint films was subdivided into three regions, I, II, and III, with copper loading. Paint films were insulators in Region I. In Region II, resistivity decreased linearly in proportion to the cube root of the volume concentration, V , of the copper powders, reaching a minimum value at a certain V , which is the critical volume concentration, V_c , of copper powders. V_c increased linearly in proportion to the bulk density of branched copper powders. This suggests that conductivity in the region is dependent upon the packing state of the copper particles. V_c and resistivity at V_c decreased with decrease in the grain size of isotropic branched and spherical copper powders, although they increased for flake copper powders. In Region III, resistivity increased with increase in copper loading. The increase in resistivity was due to the decrease in the apparent density of dry paint films.

1. Introduction

Carbon black and metal powder-filled conductive paints are widely known for their application in many fields, such as resistors, antistatic protection of sensitive devices, electromagnetic radiation shielding, and solder substitute products for fixing electrode terminals [1–4]. In addition, recent conductive paint films require very high conductivity for use as circuit-forming materials in integrated circuits [1, 2]. However, attention and interest thus far have been mainly paid to conductive mechanisms [5–9] in dry paint films and the type of conductive fillers [4, 10], in studies of conductive powder-filled paint films. Little is known of the various factors which enhance the conductivity of dry paint films. To prepare dry paint films with high conductivity, it is not only necessary to make a clear conductive mechanism in the paint film and select fillers with high conductivity [11], but it is also important to understand in detail the effects of various factors on conductivity and to control these factors.

In the present paper, the effects of the type and shape of copper powders on the electrical resistivity of dry conductive paint films have been investigated for the critical volume concentration of copper powder loading and its generation mechanism as a function of copper loading.

2. Experimental procedure

2.1. Preparation of paints and paint films

Copper powders used are listed in Table I. Each copper powder was dispersed in acrylic paint containing 6 g acrylic resin (MW = 110 000) and 20 ml

methylethylketone (MEK) in a 200 ml tall beaker (diameter of 4 cm). Paints with various weight concentrations of copper powders varying between 1.5 and 54 g were prepared by dispersing the powders with a disperser rotating at 3000 r.p.m. for 10 min. The copper powder-filled paints were coated on base sheet (PET film) with a thickness of 80 μm using an applicator after deaeration under a reduced pressure. The coated paints were dried by maintaining for 24 h at 20°C and 50% relative humidity. Prior to the measurement, all samples were kept in a desiccator with sodium sulphate anhydride.

The volume concentration, V , and weight loading of copper powders in a dry paint film were calculated from Equations 1 and 2

$$V = \frac{W_P/W_B}{W_P/W_B + D_P/D_B} \times 100 \quad (1)$$

$$\text{copper loading} = \frac{W_P}{W_P + W_B} \times 100 \quad (2)$$

where W_P and W_B are the weight of the copper powder and acrylic resin used, and D_P and D_B are the densities of copper (8.93 g cm^{-3}) and acrylic resin (1.15 g cm^{-3})

2.2. Measurements

The surface electrical resistivity was measured with a digital multimeter TR6861 (Advantest Co. Ltd) equipped with 1 cm^2 cross-section electrodes spaced 1 cm apart in dry air at 20°C by means of a four-probe technique. At least three measurements were taken for each sample, and their average was recorded. The

TABLE I Characterization of copper powders

No	Shape	Grain size (μm)	BSG ^a (g cm^{-3})	Surface area ^b ($\text{cm}^2 \text{g}^{-1}$)
1B	Branched	2.2	0.83	5800
2B	Branched	2.5	0.88	5000
3B	Branched	2.9	0.94	4200
4B	Branched	4.5	0.90	4000
5B	Branched	7.0	1.28	3200
6B	Branched	8.7	1.65	2100
7B	Branched	13.6	1.77	1300
8S	Spherical	0.8	1.15	15300
9S	Spherical	2.2	2.55	6200
10F	Flaked	-	0.91	10000
11F	Flaked	-	0.94	6800
12F	Flaked	-	0.98	4900

^a BSG, bulk specific gravity.

^b Surface area: BET method.

volume resistivity was obtained by multiplying the surface resistivity by the average film thickness: the relation between the surface resistivity, R_s , and the volume resistivity, R_v , is as follows [3]:

$$R_v = tR_s \quad (3)$$

where t is the thickness of the paint film ($\sim 80 \mu\text{m}$).

To determine the specific volume of paint films, the area of coated substrates, A , was measured with an accuracy of 0.01 mm^2 . The film thickness, t , was determined with a micrometer ($1 \mu\text{m}$ accuracy). The apparent density of paint films, D_f , was determined from $D_f = At/W$, where W is weight of the film. The surface microstructure of conductive paint films was observed by scanning electron micrographs (Nippon Denshi Co. Ltd, JSM-330A).

3. Results and discussion

3.1. Conductive behaviour

It is very important to understand the conductive behaviour of paint films as a function of filler loading. Fig. 1 shows the relation between electrical resistivity and copper powder loading in paint films. Three regions, I, II and III, were distinguished in the relation between resistivity and powder loading. In Region I, at low powder loading, the film behaved as a dielectric medium or an insulator. At a certain powder loading, electrical resistivity started to decrease rapidly with increases in powder loading. This is often called the percolation threshold [10, 12, 13]. Region II is thus the percolation region. In this region, electrical resistivity decreased rapidly and reached a certain constant value. Conductivity is possible in the region by tunnelling or percolation of electrons. A small portion of the stream of electrons penetrates potential barriers under a given electric field. The electric current thus generated increases as an exponential function of the barrier width, as follows [4, 10, 14]:

$$\text{resistivity } (\rho) = \exp(a/V)^b \quad (3)$$

where V is the volume concentration of the copper powder in the dry paint film, and a and b are constants, with b generally $1/3$.

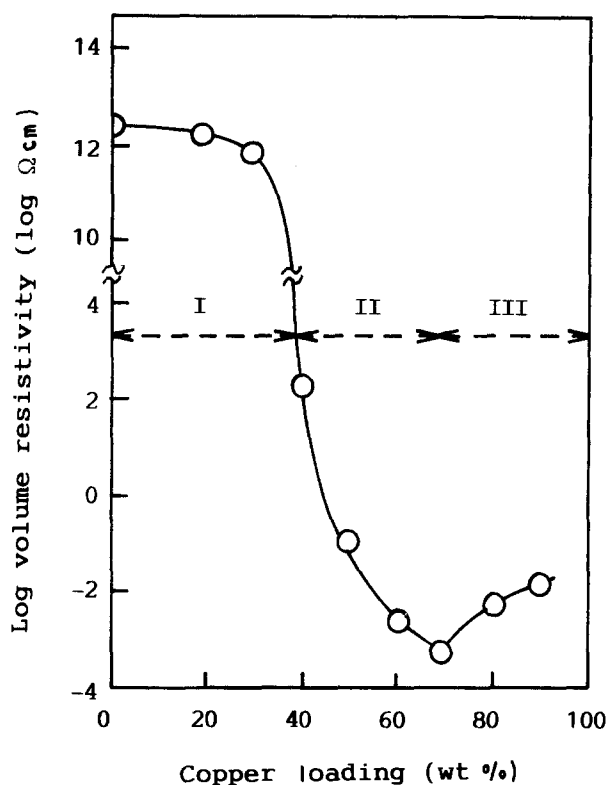


Figure 1 Relation between volume resistivity and copper loading in paint films. Copper powder: 2B.

In paint films, the interaggregate gap filled by dielectric acrylic resin serves as a potential barrier between adjacent conductive agglomerates acting as electrodes. Narrowing of the gap width was achieved by increasing the copper powder loading. The conductivity of copper powder-filled paint films increased with increases in copper powder loading in the paint films and reached a constant value at a certain copper powder loading. At this copper loading, dry paint films have the best conductivity attainable by copper powder fillers. There is an optimum copper powder loading which is defined as the critical copper loading or volume concentration, V_c . At this loading, the interaggregate gap becomes so small that a network of conductive paths is established.

As the copper powder is further increased, electrical resistivity increased reversely. The conductive behaviour at a high loading area of copper powder is shown in Region III. It is considered that V_c is the volume concentration at which the acrylic resin just fills the voids between the packed copper powder aggregates, leading to a minimal interaggregate gap [4]. At this time, the acrylic resin exhibits the best binder effect between particles. As the voids increase with copper powder loading, the polymer becomes too short to create a binder effect sufficient to fix between particles. Consequently, the interaggregate gap between particles in paint films increases with copper powder loading and resistivity increases [15].

3.2. Effect of copper loading and shape

Thus far, there has been great interest in the filler loading where the resistivity of films decreases suddenly and discontinuously to propose conductive mo-

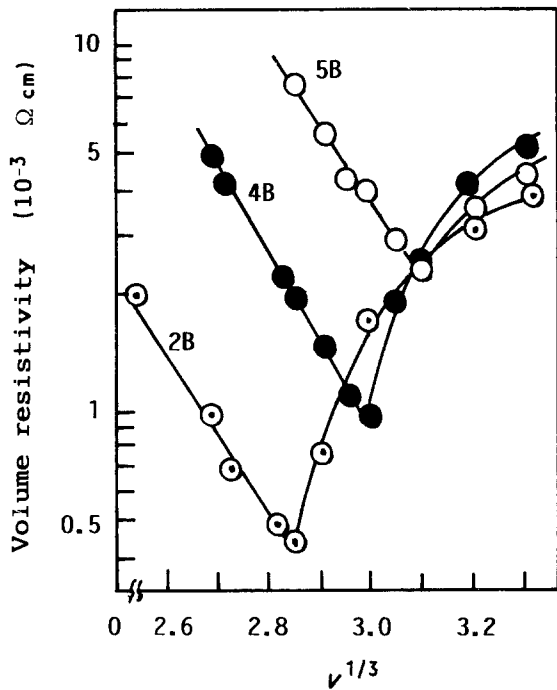


Figure 2 Relation between volume resistivity and the cube root of volume concentration ($V_c^{1/3}$) of branched copper powders (2B, 4B, and 5B) in paint films.

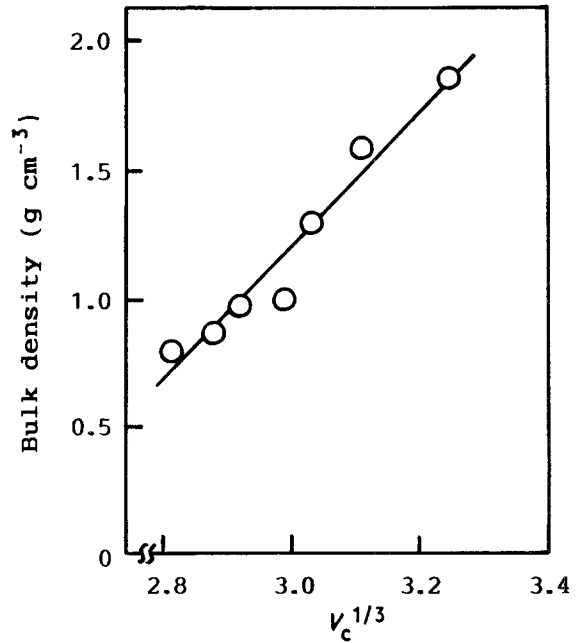


Figure 3 Relation between the bulk densities of branched powders and the cube root of critical volume concentration ($V_c^{1/3}$) in paint films.

dels for conductive phenomena [4]. However, to prepare the optimum paint films for conductivity, the effects of overall filler loading on the conductive behaviour between Regions I and II should be fully understood.

The relation between the $V_c^{1/3}$ of branched copper powders and volume resistivity in acrylic resin is shown in Fig. 2. Branched copper powders are manufactured with an electrolytic powdering machine. The powders have many branches on the surface and are isotropic in shape and conductivity. The branches on the surface serve to narrow the interaggregate gap between particles. The electrical resistivity of paint films decreased in inverse proportion to $V_c^{1/3}$ in Region II. This shows that the interaggregate gap between branched particles decreases with increases in the volume concentration of copper powder and the network of conductive paths increases simultaneously. The slope of linear decrease was roughly the same regardless of the grain size of the branched powder. At a certain $V_c^{1/3}$, the resistivity of paint films reached a minimum value and then increased over $V_c^{1/3}$. The copper volume concentration at the minimum resistivity is defined as the critical volume concentration, V_c . The minimum resistivity increased with increases in the grain size of copper powders. This is because the network of conductive paths decreases with increases in the grain size. The V_c increased with increases in the grain size of a powder. Fig. 3 shows the relation between V_c and the bulk density of copper powders indicating the packing state of powder interaggregates. $V_c^{1/3}$ increased linearly in proportion to the bulk density of copper powders. That is, the packing state of powders in dry paint films is reflected by the inherent properties of the powder. The packing state of the powder determines the rough V_c in dry paint films.

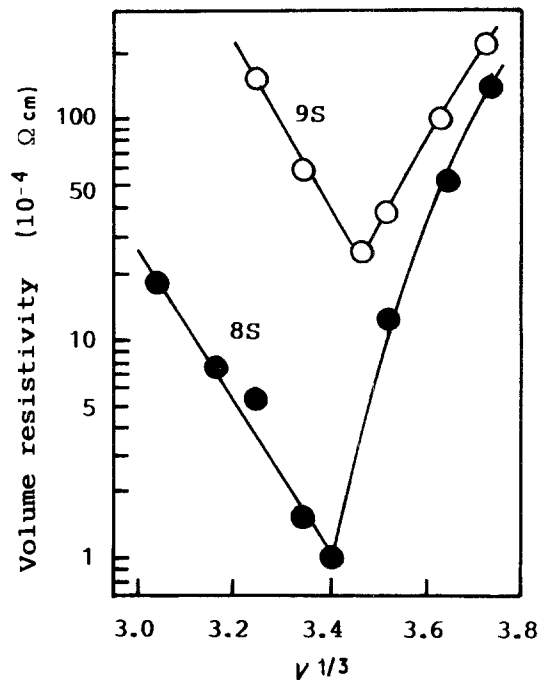


Figure 4 Relation between volume resistivity and the cube root of volume concentration ($V_c^{1/3}$) of spherical copper powders (8S and 9S) in paint films.

Fig. 4 shows the relation between $V_c^{1/3}$ of spherical copper powders and the volume resistivity in dry paint films. Spherical copper powders are also isotropic in shape and conductivity. When the spherical powders are theoretically packed with a regular hexahedral structure, the powders have three touch points per particle in the aggregates. Spherical copper powders exhibited a similar conductive behaviour to branched copper powders. The V_c in spherical powders was higher than that in branched powders. This is because the porosity or voids in the close packed structure of

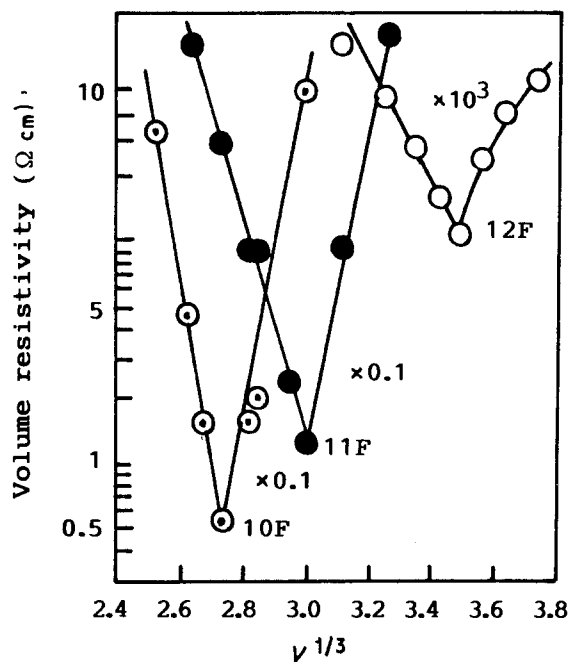


Figure 5 Relation between volume resistivity and the cube root of volume concentration ($V^{1/3}$) of flaked copper powders (10F, 11F and 12F) in paint films.

spherical powders is smaller than in branched powders. The maximum conductivity of paint films with spherical powders was lower than that in branched powders as understood from the comparison of 1B and 9S powders. This is because branched powders have more contact points between particles in paint films than spherical powders. The contact points are dependent upon the shape of the powder. The network of conductive paths in paint films increases with the contact points between particles. Therefore, the slope of the line in spherical powders becomes higher than in branched powders.

Fig. 5 shows the relation between the $V^{1/3}$ of flaked copper powders and the electrical resistivity in paint films. Flaked powders are manufactured with a mechanical crusher machine and are tropic in shape and conductivity which is different from branched and spherical copper powders. The aggregates of the powders are essentially able to touch with three points per particle in a cross-packed structure. It has been generally considered that the grain size of flaked powders increases with decreases in surface area although we have no data on grain sizes. In the conductive behaviour of paint films with various copper concentrations, there was no difference between tropic and isotropic powders. However, the V_c in flaked powders decreased with decreases in the surface area of flaked powders, i.e. with increases in the grain size. The lowest resistivity at V_c also decreased with increases in the grain size. The two results are the reverse of those for branched and spherical powders. This is a difference between tropic and isotropic powders, and is due to the difference in contact or the network structure between particles in paint films, as shown in Fig. 6. Isotropic powders, such as branched and spherical powders, contact at a point between particles, while the tropic powders, such as flaked powders contact on the surface between particles. With isotropic powders, the

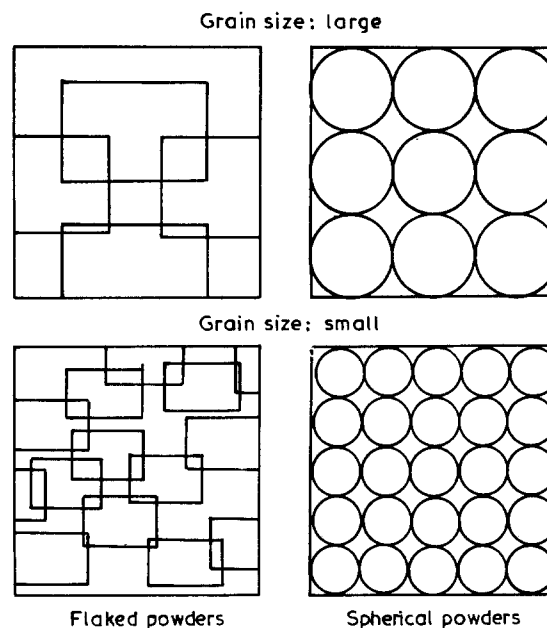


Figure 6 Contact structures between particles in isotropic (spherical powders) and tropic (flaked powders) powder aggregates per unit volume.

conductivity increases with increases in the contact points per volume. The contact points increase with increases in the number of particles per volume, i.e. with decreases in the grain size. On the other hand, with tropic powders, the conductivity increases with the contact area between particles in paint films, because flaked powders contact at the surface. The contact area increases with increases in the surface area or grain size.

Flaked powders imparted considerably lower conductivity at V_c to paint films than branched and spherical powders, as seen from the comparison of flaked and branched powders with similar surface areas. This is due to the difference in the interaggregate gap between particles in paint films. The higher interaggregate gap in flaked powder aggregates than in branched and spherical powder aggregates in paint films is dependent upon the lack of binder effect of acrylic resin. In this case, the acrylic resin does not have a binder effect sufficient to fix the surface contacts between particles in paint films.

3.3. Density of paint films

To clarify the decreases in conductivity over V_c , SEM photographs of the surfaces of paint films were observed. As shown in Fig. 7, the surface morphology changed with the copper loading. At a 60 wt % copper loading ($V = 16.2\%$, $V^{1/3} = 2.53$), copper powder appeared to some extent on the surface of the films, but the contact points of the copper particles in acrylic resin seem to be small even though the paint films have resistivity over $0.0020 \Omega \text{ m}$. With increases in copper loading, copper particles which appear on the surface increase, and it can be assumed that the contact points between the particles increases. At a 71 wt % copper loading ($V = V_c = 24\%$, $V^{1/3} = 2.88$) which gives the highest conductivity of dry paint films,

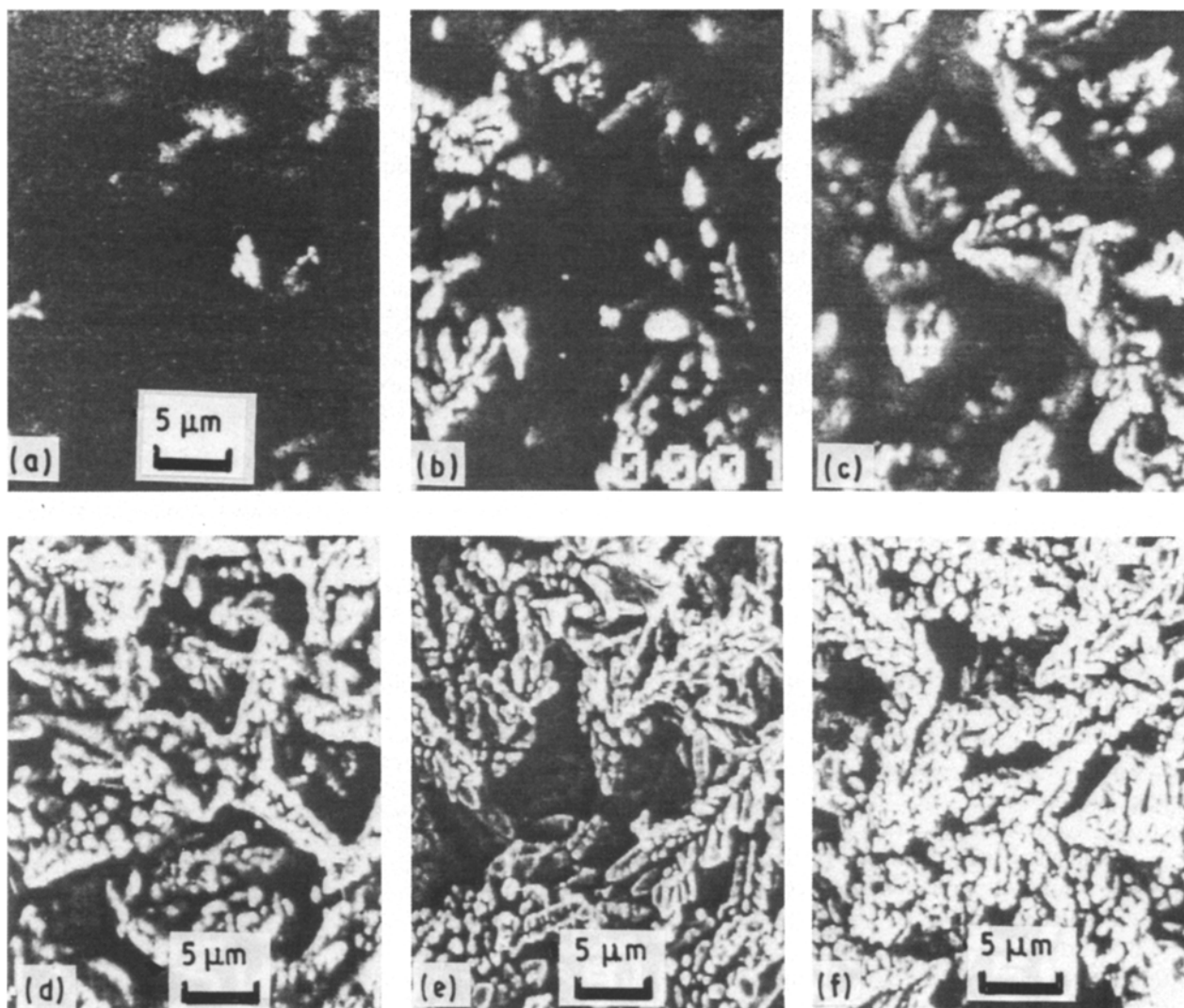


Figure 7 Surface morphology in dry paint films with various copper loadings (2B) in acrylic resin. (a) 60%, (b) 67%, (c) 71%, (d) 73%, (e) 75%, (f) 80%.

the copper particles seem to be packed very closely in acrylic resin and are tightly bound by acrylic polymer to each other. However, at a 73 wt % copper loading ($V = 25.1\%$, $V^{1/3} = 2.95$), which is over the V_c , the surface of the paint films is not filled by acrylic resin. Some holes and voids appear on the surface. The acrylic polymer does not bind between the copper particles. Although at a 73 wt % copper loading, acrylic resin adsorbed on branched powders distinctly appears, the polymer is no longer recognized on the surface over 75 wt % ($V = 27.9\%$, $V^{1/3} = 3.03$). At these loadings, acrylic resin no longer exhibits a binder effect in paint films, and the marked morphological changes on the surface suggest a change in the density of dry paint films.

Fig. 8 shows the relation between the apparent density and calculated density in paint films. The calculated density was determined using the densities of copper and acrylic resin as 8.93 and 1.15 g cm^{-3} , respectively. At low copper loading, the apparent density of paint films agrees roughly with the calculated density, although it is very slight, and increased linearly in proportion to the copper loading up to

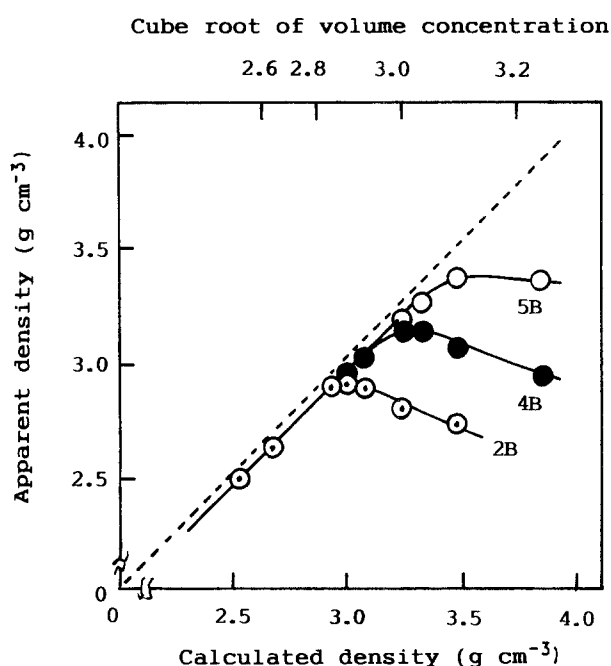


Figure 8 Relation between the apparent density and calculated density in dry paint films with various copper loadings.

around V_c . However, over V_c , the apparent density become considerably smaller than the calculated density. The volume concentration at which the apparent density starts to decrease below the calculated density agrees considerably with V_c . This shows that the generation of V_c in dry paint films is dependent upon the change in density of the paint films. The conductivity of paint films increases with increases in the density under the same copper loading. Therefore, the decrease of conductivity with copper loading over V_c is due to the decrease in the density of the dry paint films. The rapid decrease in density of dry paint films over V_c is due to the decrease in the binder effect of the polymer. The binder effect will be described in the next paper.

4. Conclusions

In copper powder-filled conductive paints, the relation between conductivity and copper loading has been investigated for various types and shapes of copper powders.

1. The relation between resistivity and copper loading is distinguished by three Regions, I, II and III, which show different conductive behaviour.

2. There is a critical volume concentration, V_c , of copper powder which gives the maximum conductivity to dry paint films.

3. V_c increased with increases in the grain size of isotropic branched and spherical copper powders, although the conductivity at V_c decreased.

4. With tropic flaked copper powders, V_c decreased with increases in the grain size, although the conductivity at V_c increased.

5. The conductivity of dry paint films increased in the order flaked powders < spherical powders < branched powder at a given grain size.

6. Region III was generated by a rapid drop in density of the dry paint films, which is due to the decrease in the binder effect of the resin.

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