

Studies on graphite based conductive paint coatings

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Abstract

Electrically conductive coatings are mainly required for static charge dissipation and electromagnetic/radio frequency interference (EMI/RFI) shielding. Electrically conductive coatings are prepared by the incorporation of the metallic pigments/graphite onto the binder. In the present investigation graphite is used as the conductive filler and epoxy polymer as binder. Optimization of the solid content and pigment volume concentration (PVC) of the coating is done by varying the composition of the binder and pigment volume. To get the minimum resistivity value offered by the coating. The resistivity of the coating was measured by means of the four-probe resistivity method. The effect of inclusion of carbon black as additional pigment is also studied. The results are presented and discussed in this paper.

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1. Introduction

Paints are inherently non-conducting and would provide no shielding effect. To produce a paint, which is conductive, it is necessary to incorporate conductive pigments into the system [1].

Electrically conductive coatings are required for a variety of applications such as static charge dissipation and electromagnetic/radio frequency interference (EMI/RFI) shielding. They are also used in the production of antistatic coatings, space heating, and in various electrical applications [2–4]. The amount of dc conductivity required is dependent upon the specific application. Tribo electric charge buildup by dielectric substrates, such as fiberglass structures in frictional contact with other materials, can result in very large static voltages that may lead to dangerous discharge sparks. The amount of surface resistance required effectively to bleed off this charge and prevent sparking, is usually rather low 10^{-6} to $10^{-9} \Omega \text{ cm}^2$. At the other extreme, near metal like conductivity is required for directing large current such as those experienced in lightning strikes on composite aircraft structures. Currently, there are no organic coatings enough to provide complete lightning protection, but some can reduce or minimize damage to local areas [5]. The amount of ac conductivity required for striking applications is more complex since

attenuation can result from absorption, scattering or reflection of electromagnetic radiation and specific methods are preferred upon the coating function. External EMI/RFI from either natural (e.g. electrical storms) or synthetic (e.g. transmitters) sources can cause electronic equipment failure, memory erasure, and navigational errors and jammed radio reception.

Conceptually, there are three methods possible to design conductive coatings.

- (1) Utilize conductive polymers as the continuous matrix.
- (2) Incorporate conductive pigments as sufficient pigment volume concentration.
- (3) Combination of both methods.

While there have been many recent advances in conductive polymer technology, these materials have been limited use due to loss of conductivity upon environmental exposure (e.g. oxidation) and poor processability and solubility. Hence, incorporating pigments such as conductive carbon blacks and metal flakes into a polymeric matrix that has desirable physical/chemical properties produces most of high conducting coatings [6].

To enlarge the available resistivity range, the use of graphite/carbon black combinations were investigated in the present work. The advantage of graphite as pigment is due to its high conductivity with low surface area, enhancing relatively high loading without affecting the rheological properties of the paint to the material structure. The objective of the present work

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therefore was to determine the optimal graphite/carbon black combination, in terms of conductivity, in a conductive paint and to suggest an explanation of the improvement in conductivity achieved over the graphite loaded paint [7].

2. Experimental

2.1. Materials

The binder used in the present work was, a poly sulphide modified epoxy resin having 100% solids. It was cured with a polyethylene polyamine, diluted to application consistency with measured quantities of mixed solvents (*iso*-propyl alcohol:methyl *iso*-butyl ketone:Cellulosolve).

The graphite filler used was lamellar structured graphite. Its carbon content is 98–99%, typical particle size is up to 50 μm and its density is 2.26 g/cc (SD fine chemicals). Volumetric oil absorption was determined according to ASTM D 285–94 and was found to be 0.4 ml oil to ml of graphite, i.e. 40%. The graphite used was a conductive grade. Carbon black used was a commercial one.

2.2. Preparation and paint application method

Paint formulations with various combinations of graphite and carbon black and epoxy binder in appropriate amounts. The resistivity of the formulated paints was measured using the four-probe resistance method. In this method current is applied across the outer probes and the voltage is measured across the two inner probes. Fig. 1 shows the experimental set-up used for the resistivity measurements. From the resistivity measured, the specific volumetric electrical resistance (ΩM) is calculated as per ASTM D-4496-87. The coating composition, which had the minimum specific volumetric electrical resistance, was concluded as the optimized composition. The optimized pigment content is 55%. The optimized mix ratio between graphite and carbon black was 85:15. The paint base was dispersed well using a dispersing agent, dibutyl phthalate, the paint was applied over a solvent



Fig. 1. Experimental setup.

cleaned glass plates at different thickness. The surface resistivity of films has been made for:

- (i) optimization of solid content (Vs);
- (ii) optimization of pigment content (PVC);
- (iii) optimization of mix ratio between graphite and carbon black.

3. Results and discussion

3.1. Optimization of solid content

To know the effect of amount of binder on the resistivity of dry paint films, the solid content of the paint was varied from 30 to 100% the PVC was kept at a constant volume, i.e. 55%. Fig. 2 shows the variation of resistivity of the film with volume solids. When the pigment particles are closely packed then it gave a particle-to-particle contact which at 100% the resistivity was around $3.7 \times 10^{-2} \Omega\text{M}$. When the solid content was reduced to 60% the resistivity was suddenly decreased to $4.3 \times 10^{-3} \Omega\text{M}$. This decrease in resistivity was due to the close packing of the pigment particles, that is, the particle-to-particle contact of the pigment would be more in 60% than in 100%. The particle-to-particle contact of the pigments would be increased when the solid content of the paint was further reduced. Hence, the resistivity would be reduced at the low solid content. When the solid content was further reduced to 55% the resistivity was $1.3 \times 10^{-3} \Omega\text{M}$ and the solid content was further reduced to 50 and 40%, the resistivity was reduced to 8.6×10^{-4} and $6.3 \times 10^{-5} \Omega\text{M}$. Below 40% poor hiding problem occurs due to the low binder content in the paint. At the 40% solids the particle-to-particle contact was maximum and thus the resistivity was at minimum value of $6.3 \times 10^{-5} \Omega\text{M}$.

3.2. Optimization of pigment volume concentration (PVC)

Similar to the binder optimization, the PVC, which had the low resistivity value, would be considered as optimized PVC. The PVC was varied from 30 to 60%. The PVC was optimized at the optimized binder volume, i.e. 40%. Fig. 3 shows the nature

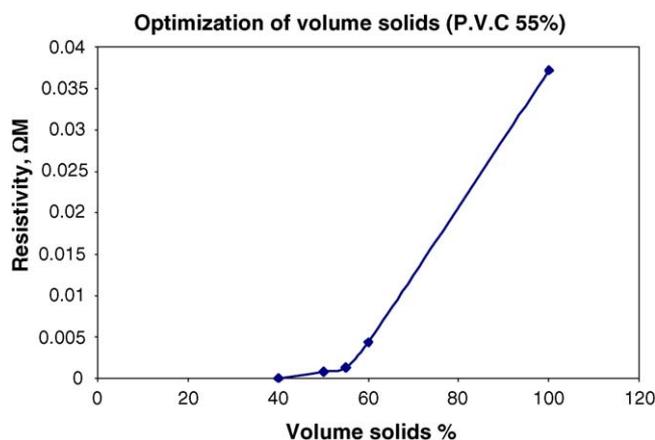


Fig. 2. Optimization of volume solids.

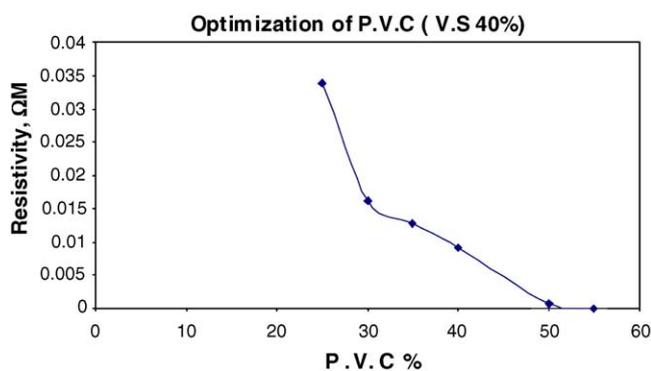


Fig. 3. Optimization of PVC.

of variation of resistivity and PVC. At 25%, the resistivity is above $3.3 \times 10^{-2} \Omega M$. Upon increasing the pigment volume, the resistivity was found to reduce. The increase in the pigment content would increase the amount of the pigment particles in the binder hence it causes the closer packing of the particles and thus make the particle-to-particle contact, which in turn resulted in minimum resistivity. At 30%, the resistivity was reduced to $1.6 \times 10^{-2} \Omega M$. At 40% PVC, the resistivity was further reduced to $9.1 \times 10^{-3} \Omega M$. Upon increasing PVC to 50% the resistivity was $6.7 \times 10^{-4} \Omega M$. At 55% PVC, the resistivity reached a minimum value of $6 \times 10^{-5} \Omega M$. This is due to the tight packing of the pigment particles so that every particle is in contact with the other, hence results in minimum resistivity. Above 55% the dispersion of pigment was too difficult.

3.3. Optimization of graphite and carbon black mix ratio

In order to reduce the resistivity further, carbon black is added as the additional pigment. The advantage of the use of carbon black as additional pigment is due to its low density and large dimensions of particles, relative to regular grades, resulting in low resistivity at low weight loading. The carbon black particles would occupy the interstitial positions and so that the particle-to-particle contact can be made evenly throughout the dried paint film, which can result in the minimum resistivity value. The carbon black was added to graphite at various mix ratios such as 90:10, 87:13, 85:15, 83:17, 80:20, 75:25, 60:40, and their resistivities were measured. The variation of resistivity with various mix ratios of graphite and carbon black is given in Figs. 4 and 5. From the resistivity values it is observed that the resistivity is reduced to $4 \times 10^{-5} \Omega M$ at 90:10 mix ratio and the resistivity is further reduced with increasing the carbon black ratio. This reduction in the resistivity is due the incorporation of the carbon black particles in the interstitial position between the graphite particles. The minimum resistivity value ($2 \times 10^{-5} \Omega M$) was observed at 85:15 mix ratio. When carbon black content is increased above 15% there is no decrease in resistivity. Hence, the ratio 85:15, which has the low resistivity value is considered as the optimized mix ratio. The carbon black content is varied as 10, 20, 25, and 40%. From the resistivity values observed it is found that 20% of carbon black inclusion gives the minimum resistivity. To know the exact mix ratio between

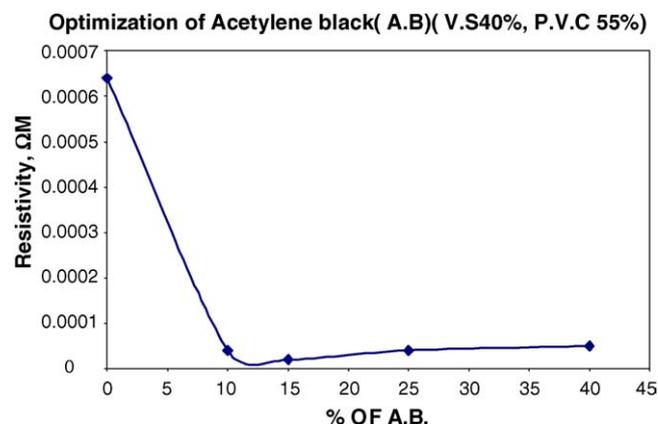


Fig. 4. Optimization of carbon black content.

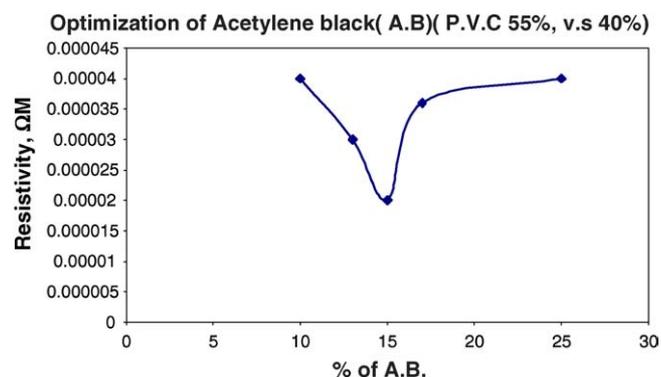


Fig. 5. Optimization of carbon black content.

the graphite and carbon black, the carbon black mix ratio was further narrowed in between from 10 to 20%, as 10, 13, 15, 17 and 20%. From the resistivity values it is found that 15% mix ratio of the carbon black has the minimum resistivity (Fig. 5).

4. Conclusion

Graphite and carbon black has assumed a highly important role in the formulation of conductive organic-based coatings for use in electromagnetic and radio frequency shielding applications. This is due to the fact that these coatings have a unique combination of properties like electrical conductivity, oxidation and corrosion resistance. The conductive paint composition was optimized by various mix ratios of binder pigment and solvent. The optimized composition having the minimum resistivity in the range of $2 \times 10^{-5} \Omega M$ with volume solids (Vs) 40%, and pigment volume concentration (PVC) 55%. In the pigment content the graphite occupies the major portion of 85%, and remaining portion is carbon black so as to reduce the resistivity of the paint further.

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