Improving the Electrical and Mechanical Behavior of Electrically Conductive Paint by Partial Replacement of Silver by Carbon Black

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Partial replacement of silver particles by carbon black (low cost) in electrically conductive paint was found to decrease the electrical resistivity and increase the scratch resistance of the resulting thick film, which is for use in electrical interconnections. An effective carbon black content is 0.055 of the total filler volume. By using a total solid volume fraction of 0.1969 and a silane-propanol (1:1 by weight) solution as the vehicle, a paint that gives a thick film with resistivity 2×10^{-3} Ω·cm has been attained.

Key words: Electrically conductive paint, silver, carbon black, electrical resistance, mechanical, thick film

INTRODUCTION

Electrically conductive paints are widely used for electrical interconnections in electronics.[1–5] They are in the form of a dispersion of electrically conductive particles, such as silver. It is desirable for the coating (i.e., thick film) resulting from the paint to be high in electrical conductivity and good in mechanical integrity (such as scratch resistance). By the use of a mechanically strong and adhering polymer, such as epoxy, as the vehicle or binder in the paint, the mechanical integrity can be improved. However, the presence of the polymer between adjacent conductive particles reduces the conductivity of the coating. On the other hand, the use of a volatile vehicle, such as ethanol, allows the conductive particles in the resulting coating to contact one another after the volatilization of the vehicle, thus resulting in high conductivity but poor mechanical integrity (such as scratch resistance). In general, for any vehicle, the higher is the binder content, the lower is the conductivity and the better is the mechanical integrity. Therefore, the attainment of both high conductivity and good mechanical integrity has been challenging.

This work uses an innovative method for the attainment of both high conductivity and good mechanical integrity in coatings resulting from paints. This method involves the combined use of silver and carbon black as conductive fillers. Silver particles have been widely used in conductive paints, due to the high electrical conductivity of silver. Although carbon black is conductive, it is lower in conductivity than metals by a few orders of magnitude. Thus, carbon black is only used in applications that do not require very high conductivity, such as antistatic applications. In this work, it was found that the partial replacement of silver by a minor amount of carbon black (e.g., 0.05 of the total filler volume or 0.01 of the total filler weight) results in a coating that is more conductive and more scratch resistant than the counterpart without the carbon black replacement. The low cost of carbon black is also attractive.

The effectiveness of carbon black is due to its being in the form of porous agglomerates of nanoparticles (30-nm size in this work). This microstructure results in a high degree of compressibility, and hence conformability.[6,7] Its ability to conform allows it to fill the microscopic space between adjacent silver particles in the resulting coating. The filling of the space helps both the conductivity and the mechanical integrity.

Due to its conformability, carbon black dispersions have been previously found to be effective for use as interface materials in pressure electrical contacts[8] and in pressure thermal contacts.[6,7] The pressure enables the conformability to be manifested. Conformability allows the filling of the valleys in the surface topography of the mating surfaces, thereby displacing air, which is insulating, from the valleys.

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Carbon black has been used as an electrically conductive additive in electrochemical electrodes, such as MnO_2, which by itself is not conductive.[9] Carbon black is even more effective than carbon nanofiber for this application,[9] due to its ability to conform to the shape of the MnO_2 surfaces between which it resides.

In spite of the above applications, carbon black has not been used previously in paints that are required to exhibit very high conductivity—whether electrical or thermal conductivity. The conductivity in this context refers to the conductivity within the coating, rather than the conductance across the surfaces that sandwich the coating. In particular, this work focuses on the electrical conductivity in the plane of the coating.

The primary objective of this paper is to investigate the effectiveness of carbon black as a partial replacement for silver in electrically conductive paint for improving both the electrical and mechanical performance. The secondary objective is to compare the performance of paints obtained in this work with that of commercial silver paints.

EXPERIMENTAL METHODS

The silver (99.9%, metal basis) particles were spherical in shape, with sizes ranging from 0.5 μm to 1.0 μm, as obtained from Alfa Aesar (Ward Hill, MA).

The carbon black was Vulcan XC72R GP-3820 from Cabot Corp. (Billerica, MA). It was a powder with particle size 30 nm, a nitrogen specific surface area 254 m^2/g, maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm^3.

The vehicle used was silane (Dow Corning Corp., Midland, MI, Z-6020, $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$). This particular silane had been previously used for coating ceramic particles for the purpose of improving the bond between the particles and the epoxy matrix.[10] Silane has long been used as an adhesion promoter in coatings.[11–16]

The organic solvent used in combination with silane in a weight ratio of 1:1 (unless noted otherwise) was 1-methoxy-2-propanol ($C_4H_{10}O_2$), 99.5+%, as obtained from Aldrich Chemical Company (Milwaukee, WI). The combined use of silane and alcohol as a solution is common for improving flow and adhesion.[17] For the sake of comparison, this study includes a composition in which the silane vehicle does not contain the propanol.

For the sake of comparison, this study includes two commercial silver paints, namely, those provided by Ernest F. Fullam (Latham, NY, Product 14,810) and Metech (a Lord Company, Elverson, PA, Product 6103A). These commercial silver paints do not contain carbon black. In addition, this study includes two compositions obtained by adding different proportions of carbon black to the Fullam silver paint. The density of the Fullam silver paint (without carbon black) is 1.37 g/cm^3.

The ingredients of any of the paints of this work were combined by manual mixing in order to form a workable paste. The uniformity of each paste was confirmed by testing multiple specimens obtained from each batch.

Commercial alumina substrate (96% Al_2O_3) cut to a size of 25 mm × 7 mm × 0.6 mm was used. The pastes were applied on alumina substrates manually by using a steel spatula and were allowed to dry in air at room temperature. They took only about 1 min to dry. Nevertheless, the time allowed for drying was 24 h. The pastes could have been applied by screen printing instead.

The direct-current volume electrical resistivity of the film after drying was measured using the four-probe method. This method involved the use of four electrical contacts. The outer two contacts (20 mm apart) were for passing current, while the inner two contacts (14 mm apart) were for voltage measurement. The volume resistivity was calculated from the measured resistance and thickness; both quantities were separately measured for each specimen. The four electrical contacts were made by laying copper wire of diameter 0.15 mm on the substrate (in contact with the substrate) prior to paint application. The film thickness was measured using an optical microscope. Three specimens were tested for each composition.

The sheet resistivity (a commonly used attribute for thick films) was obtained as R·W/L, where R is the resistance measured by using the four-probe method, as mentioned above, W is the width of the thick film, and L is the length in the direction of resistance measurement.

Scratch testing of the thick films, as described in Ref. 18, was conducted using a 502 shear/scratch tester, which was manufactured by Teledyne Taber (North Tonawanda, NY). The specimen was mounted on a horizontally rotatable plate. A diamond scratching tool in the shape of a cone was used. The tool was attached to a finely balanced scale beam calibrated in grams. The load was 500 g. The scratch width was measured by scanning electron microscopy (SEM). The scratch morphology was also observed by SEM. In this work, the scratch was not deep enough to cause substrate exposure. Nevertheless, the smaller the scratch width, the higher is the shear strength, which relates to both the bond strength of the thick film to the substrate and the shear strength within the thick film. Three specimens with at least one scratch per specimen were measured for each composition.

RESULTS AND DISCUSSION

Table I shows that partial replacement of silver by up to 0.00714 weight fraction carbon black (weight relative to that of the dispersion) decreases the volume resistivity and improves the scratch resistance. Along with these improvements in properties is the enhanced workability, which was clearly observed during the application of the dispersions on the substrate. The largest improvement occurs at 0.00357 weight fraction carbon black for both the electrical and mechanical behavior. Further replacement of

Table I. Electrical and Mechanical Properties of Thick Films with Various Proportions of Silver to Carbon Black, Such That the Total Solid Weight Fraction is Fixed at 0.7143 and the Vehicle Weight Fraction (before Any Drying) is Fixed at 0.2857; CB = Carbon Black

Weight fraction Ag	0.7143	0.7107	0.7071	0.7036	0.7000
Weight fraction CB	0	0.00357	0.00714	0.0107	0.0143
Total solid weight fraction	0.7143	0.7143	0.7143	0.7143	0.7143
Volume fraction Ag	0.1882	0.1864	0.1846	0.1829	0.1811
Volume fraction CB	0	0.0055	0.0109	0.0162	0.0215
Total solid volume fraction	0.1882	0.1919	0.1955	0.1991	0.2026
Thickness (μm)	53 ± 4	52 ± 4	48 ± 3	50 ± 3	50 ± 4
Sheet resistance (Ω)	1.47 ± 0.04	0.63 ± 0.04	0.43 ± 0.02	0.525 ± 0.03	0.605 ± 0.04
Volume resistivity (10^{-3} Ω·cm)	7.57 ± 0.63	3.20 ± 0.43	2.18 ± 0.38	2.67 ± 0.41	3.07 ± 0.42
Scratch width (μm)	50 ± 2	47 ± 2	47 ± 2	47 ± 2	47 ± 2

Table II. Electrical and Mechanical Properties of Thick Films with Various Proportions of Silver to Carbon Black, Such That the Total Solid Volume Fraction is Fixed at 0.1882 (or 0.1883) and the Vehicle Volume Fraction (before Any Drying) is Fixed at 0.8118; CB = Carbon Black

Weight fraction Ag	0.7143	0.6729
Weight fraction CB	0	0.0071
Total solid weight fraction	0.7143	0.6800
Volume fraction Ag	0.1882	0.1774
Volume fraction CB	0	0.0109
Total solid volume fraction	0.1882	0.1883
Thickness (μm)	53 ± 4	51 ± 4
Sheet resistance (Ω)	1.47 ± 0.04	0.66 ± 0.04
Volume resistivity (10^{-3} Ω·cm)	7.57 ± 0.63	3.35 ± 0.44
Scratch width (μm)	50 ± 2	48 ± 2

silver up to 0.00714 weight fraction carbon black gives incremental improvement. However, still further replacement of silver beyond 0.00714 weight fraction carbon black causes the resistivity to increase, though the scratch resistance remains unchanged. Thus, among the compositions in Table I, the optimum carbon black content is the intermediate weight fraction of 0.00714, i.e., 0.0558 of the total filler volume, or 0.0100 of the total filler weight.

Table II shows that at the same total solid volume fraction of 0.1882 (or 0.1883), partial replacement of silver results in a decrease in the resistivity and improvement in the scratch resistance. This occurs in spite of the decrease in the total solid weight fraction from 0.7143 to 0.6800. The amount of carbon black used to replace silver partially is 0.0579 of the total filler volume, or 0.0104 of the total filler weight.

The decrease in resistivity and improvement in scratch resistance upon partial replacement of silver by up to 0.00714 weight fraction carbon black in Table I is not due to the increase in the total solid volume fraction from 0.1882 to 0.1955. Even at a fixed value of the total solid volume fraction, partial replacement of silver by carbon black decreases the resistivity and improves the scratch resistance, as shown by Table II.

The positive effect of carbon black is due to the improvement of the electrical and physical connectivity, as made possible by the compressibility of carbon black between adjacent silver particles. However, an excessive amount of carbon black is detrimental, as shown in Table I. This is expected because carbon black is itself not as conductive as silver.

Table III shows that, with the ratio of silver to carbon black fixed, a decrease of the total solid weight fraction from 0.7163 (a value close to the value of 0.7143 in Table I) to values below it increases the resistivity (as expected). The increase is significant when this fraction is decreased from 0.7163 to 0.6966, but is slight when this fraction is further decreased. The effect on the scratch resistance is small and unclear.

The design of a silver-carbon paint involves selection of the total solid content as well as the proportion of silver to carbon black. Though a number of selected compositions have been investigated in this work, the work performed is not sufficient for arriving at the optimum composition. Nevertheless, the best performance attained in this work corresponds to the composition in the last column of Table III. The resistivity for this composition is lower than

Table III. Electrical and Mechanical Properties of Thick Films with a Fixed Weight Proportion of 100:1 for Silver to Carbon Black, but for Different Total Solid Weight Fractions; the Total Volume Fraction is Fixed at 0.1969; the Silver Volume Fraction is Fixed at 0.01861; the Carbon Black Volume Fraction is Fixed at 0.0108 (CB = Carbon Black)

	Total Solid Weight Fraction				
	0.6433	**0.6779**	**0.6871**	**0.6966**	**0.7163**
Thickness (μm)	48 ± 3	53 ± 4	63 ± 4	51 ± 4	47 ± 3
Sheet resistance (Ω)	0.740 ± 0.030	0.655 ± 0.030	0.520 ± 0.020	0.630 ± 0.020	0.370 ± 0.020
Volume resistivity (10^{-3} Ω·cm)	3.87 ± 0.54	3.37 ± 0.44	3.44 ± 0.39	3.25 ± 0.33	1.88 ± 0.25
Scratch width (μm)	45 ± 2	47 ± 2	48 ± 2	47 ± 2	47 ± 2

that for the best composition in Table I because of the higher total solid content for the former.

For the sake of comparison, the thickness of the films of this work (excluding those made from commercial paints) is around 50 μm. However, the thickness could have been much less (such as 20 μm). Due to the improved workability of the paint in the presence of carbon black, films can be much thinner in the presence of carbon black.

Table IV shows that the absence of the propanol in the silane vehicle results in high resistivity and poor scratch resistance. The resistivity increase due to the absence of propanol occurs in spite of the increase in total solid volume fraction. Figure 1 shows the poor scratch morphology for the case without propanol; extensive plowing and peeling were observed. Thus, the use of silane without the propanol is ineffective, due to the poor adhesion of the vehicle. Figure 1a (for the case with propanol) is similar to the photographs of the films with a carbon black weight fraction of 0.00357 or 0.00714 (Table I).

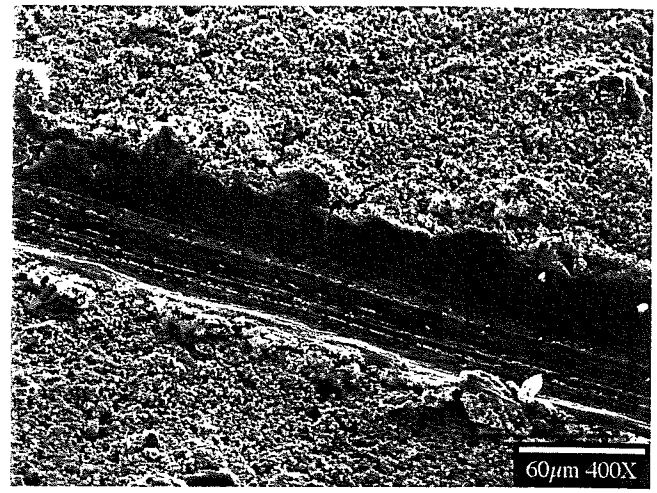
Better adhesion was attained with the presence of propanol because of the hydrolysis of silane with the aqueous alcohol solution (1-methoxy-2-propanol with 0.10% of water). Reactive silanols (compounds containing silicon atoms to which hydroxyl substituents bond directly) are known to form from the hydrolysis. Reaction between silanols form oligomeric polymers, which possess the siloxane (Si-O-Si) backbone. Reaction between silanols and an inorganic substrate also forms a siloxane backbone. The siloxane backbone is mechanically strong. Therefore, the addition of propanol to silane enhances the bonding within the paint and also the adhesion of the resulting coating on the alumina substrate.

Table V shows the corresponding results for two commercial silver paints. The Fullam silver paint is superior to the Metech silver paint in both the electrical and mechanical properties. However, comparison of Tables I and V shows that the silver-carbon paint with 0.00714 weight fraction carbon black is much superior to both commercial paints in the scratch resistance, though the resistivity is between the values of the Fullam and Metech products. This is because carbon black acts as a binder that enhances the connectivity between silver particles, thereby enhancing the scratch resistance. However, the addition of carbon black causes the viscosity to increase, thereby leading to a decrease in workability and an increase in electrical resistivity.

Table VI shows that the modification of the Fullam silver paint by addition of carbon black by up to 0.00755 volume fraction increases resistivity slightly, due to the low resistivity of the unmodified

Table IV. Electrical and Mechanical Properties of Thick Films with and without Propanol in the Silane Vehicle; Each Film was Made from a Paint That Contained 0.7092 Weight Fraction Silver, 0.00709 Weight Fraction Carbon Black, and 0.2837 Weight Fraction Vehicle (CB = Carbon Black)

	With Propanol	Without Propanol
Volume fraction Ag	0.1862	0.1948
Volume fraction CB	0.0108	0.0114
Total solid volume fraction	0.1970	0.2062
Thickness (μm)	47 ± 3	49 ± 3
Sheet resistance (Ω)	0.370 ± 0.020	3.100 ± 0.030
Volume resistivity (10^{-3} Ω·cm)	1.88 ± 0.25	16.87 ± 1.13
Scratch width (μm)	47 ± 2	50 ± 2



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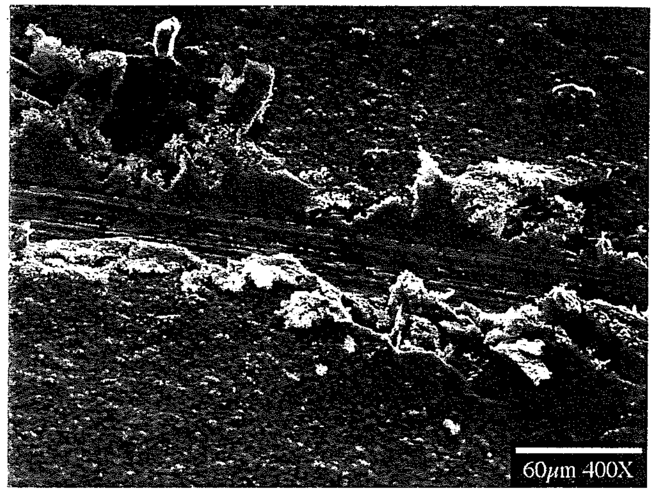

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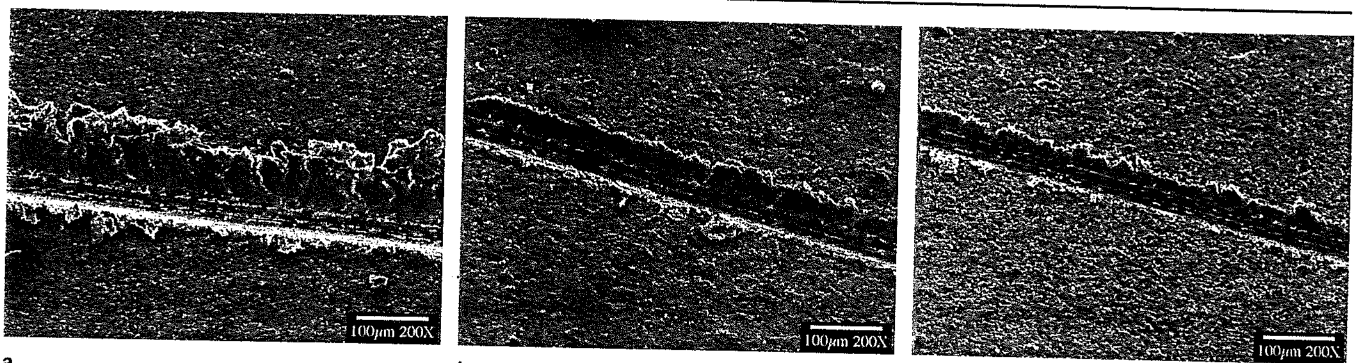
Fig. 1. SEM photographs of the scratches on the films containing silver (0.7092 weight fraction), carbon black (0.00709 weight fraction), and silane vehicle (balance) (a) with the propanol in the vehicle and (b) without the propanol in the vehicle.

Table V. Electrical and Mechanical Properties of Thick Films Made from Commercial Silver Paints

	Fullam	Metech
Thickness (μm)	25 ± 2	48 ± 3
Sheet resistance (Ω)	0.405 ± 0.010	0.55 ± 0.02
Volume resistivity (10^{-3} Ω·cm)	1.10 ± 0.15	2.80 ± 0.40
Scratch width (μm)	58 ± 2	60 ± 2

Table VI. Electrical and Mechanical Properties of Thick Films with Various Proportions of Carbon Black in Fullam Silver Paint; CB = Carbon Black

Weight fraction CB	0	0.00538	0.01000
Volume fraction CB	0	0.00408	0.00755
Thickness (μm)	25 ± 2	28 ± 2	27 ± 2
Sheet resistance (Ω)	0.405 ± 0.010	0.460 ± 0.020	0.580 ± 0.030
Volume resistivity (10^{-3} Ω·cm)	1.10 ± 0.15	1.25 ± 0.21	1.64 ± 0.29
Scratch width (μm)	58 ± 2	57 ± 2	55 ± 2



a b c

Fig. 2. SEM photographs of the scratches on the films obtained from the Fullam silver paint containing (a) 0, (b) 0.00538, and (c) 0.01000 weight fraction carbon black.

Fullam silver paint (Table V). Nevertheless, the carbon black addition decreases the scratch width. Figure 2 shows the scratch morphology. The higher is the carbon black content, the less is the extent of plowing.

CONCLUSIONS

Partial replacement of silver by carbon black in electrically conductive paint results in a decrease in the volume electrical resistivity and improvement of the scratch resistance, provided that the carbon black content is not excessive. An effective carbon black content is 0.055 of the total filler volume, or 0.010 of the total filler weight. Beyond this carbon black content, the resistivity increases slightly, though the scratch resistance does not change. The positive effect of carbon black is probably due to the compressibility of the carbon black and the consequent improved connectivity of silver particles. However, excessive use of carbon black increases the resistivity, due to the low conductivity of carbon compared to silver and the reduction in workability of the paint.

By using a silver volume fraction of 0.01861, a carbon black volume fraction of 0.0108 and a total solid weight fraction of 0.7163 (i.e., carbon black amounting to 0.0549 of the total filler volume, or 0.0099 of the total filler weight), a paint that gives a film with resistivity (1.88 ± 0.25) × 10^{-3} Ω·cm and thickness 47 μm ± 3 μm has been attained. This film is more scratch resistant than films made from two commercial silver paints.

The vehicle in the paint compositions is a solution of silane and 1-methoxy-2-propanol (1:1 weight ratio). The use of silane without the propanol greatly increases the resistivity, in addition to degrading the scratch resistance. The propanol helps because it causes the formation of a siloxane backbone.

The addition of carbon black (up to 0.008 volume fraction) to a commercial silver paint of low resistivity and poor scratch resistance increases the resistivity slightly, but improves the scratch resistance. This is because carbon black enhances the connectivity between silver particles, though it decreases the workability.

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