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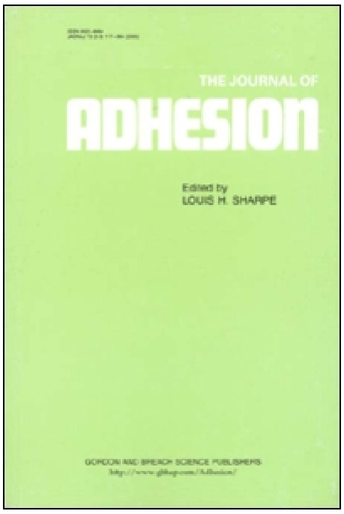

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Development of Electrical Conduction in Silver-filled Epoxy Adhesives

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Although percolation theory predicts that insulators containing *ca.* 20% or higher volume loadings of dispersed metallic particles should be electrically conductive, some commercial silver-filled epoxies fail to be so unless subjected to thermal cure. It was found that this is due to an insulating coating on the silver particles, presumably added to promote dispersibility. This coating consists of a mixture of fatty acid salts of copper, and is removed under the action of heat, primarily through decarboxylation. When the silver powder is heated alone or as a dispersion in an inert matrix (silicone oil), this occurs above 200°C, rendering the specimens conductive. The onset of electrical conduction can be brought down to much lower temperatures by addition of small amounts of solubilizers, such as long chain organic compounds containing numerous ether linkages. Such materials, when added to commercial conductive epoxies at very low concentrations, increased the conductivity by a factor of two to three. Shrinkage of the matrix during heating did not have any significant effect on ultimate resistance or on the initiation of electrical conduction.

INTRODUCTION

Metal-filled thermoset polymers were first patented as electrically conductive adhesives in the 1950s.[1-3] In the ensuing years, extensive use of such materials, particularly in adhesion of miniature devices (e.g. light emitting diodes and integrated circuits), has resulted in partial replacement of the traditional eutectic bonding and thermal compression techniques. However, fundamental understanding of the scientific principles and physico-chemical processes governing the onset of electrical conduction in these materials has lagged far behind their commercial utilization.

It has been generally recognized that percolation theory,[4] first introduced by Broadbent and Hammersley,[5] can be used to describe the mechanism of electrical conduction by metallic particles within an insulating polymeric matrix. Percolation is a theory that complements diffusion; while in fact they both describe the random passage of a "fluid" through a "medium," diffusion concentrates on the properties of the former, whereas percolation does so for the properties of the latter. As regards electrical conduction, percolation theory predicts a critical volume fraction, ε_c, of the conducting substance randomly distributed within the insulating medium, below which the overall conductivity will be zero. For $\varepsilon < \varepsilon_c$, i.e. for volume loadings smaller than the "percolation threshold,"[6] the probability is zero that a conductive passage will span the length of the sample. Establishment of such conductive veins requires uninterrupted particle-to-particle contacts of the metallic filler. Aharoni[7] has shown theoretically that initiation of conductivity will take place when the average number, M, of contacts per particle becomes greater than one. At this point, for every particle with zero contacts there exists another one with two contacts, so that the probability of conductive chain initiation becomes non-zero and the resistance of the composite begins to decrease. This will continue until $M = 2$, at which stage all particles have a sufficient statistical probability of participating in infinite chains. Further increase in M beyond 2 will not cause any appreciable decrease in resistance, since two contacts per particle suffice to assure full conductivity.

It is clear in the above theories that the actual mechanism of conduction is assumed to be metallic, i.e. that electrons will travel along continuous chains formed by metallic particles in contact rather than by hopping across insulating gaps. Experimental support for such an ohmic mechanism has been provided by volt-ampere measurements,[8,9] as well as by optical [10] and electron[11] microscopy. One author[12] mentions that at lower loadings band conduction, electron hopping, and possibly ion diffusion may also play a role.

The volume fraction of conducting particles that is required for M to be between 1 and 2 has been experimentally determined for a variety of materials and configurations. For silver in Bakelite, Gurland[10] found $\varepsilon_c = 0.30$. Aharoni[7] observed conduction of iron-filled poly(imide-amide) polymers at 20% loading. Gul's group[13] obtained electrical conductivity in carbon black-loaded rubber at $\varepsilon_c = 0.18$, while a *ca.* 30% loading was needed in nickel-filled epoxies.[14]

The onset of conductivity is also a strong function of the particle size of the conductive powder. Malliaris and Turner[15] showed that the smaller the size of nickel particles dispersed in a polyethylene or PVC matrix, the smaller is the loading needed to assure conduction. While Gul' *et al.*[14] observed the same effect in nickel-filled epoxies, they also showed that this tendency is reversed upon application of a magnetic field during cure, since the larger particles can be more effectively oriented by the action of the field.[16] Furthermore, it was shown that the total surface area of the contacting particles is also of importance: equal loadings of carbon black powders of different shapes produced higher conductivities at increased surface areas.[13] This has also been reported by Miller[17] who found that silver flakes and powders of irregular shapes give rise to conduction at a lower loading than do spherical particles.

Miller's work[17] also reported on the kinetics of cure of silver-filled epoxies. Conductivity was seen to be initiated faster at higher cure temperatures and to reach better ultimate values for the same volume loading of silver (27%). Partial cure at low temperatures, followed by increased heating, gave a less conductive material than that obtained by a one-step cure at the higher temperature. This is in agreement with the results of Waller,[18] who showed that the faster the rate of heating of a silver-filled epoxy adhesive to its ultimate cure temperature, the lower the resistivity produced.

These last results appear puzzling at first, because the temperature history was not found to be a controlling parameter in any of the other conductivity studies,[7-16] nor is it apparent that it would influence particle-to-particle contacts in a manner so significant to the ultimate electrical properties of the mixture. At the same time, it is known that individual silver particles of commercial conductive powders may be coated with an organic layer in order to maximize dispersion, which—as is clear from the above—is essential for high ultimate conductivity. It was thus decided to investigate the mechanism of removal of this organic layer during heating, aiming at an explanation of the conditions that initiate electrical conduction, as well as at consequent ways whereby lower final resistances or more efficient curing conditions might be made possible.

EXPERIMENTAL

Materials

The conductive powder investigated (DuPont V–9) is composed of silver particles which in the optical microscope appear to be flakes having a narrow size distribution around 1–2 μm. As has been mentioned in previous reports,[17] such conductive powders are commonly coated with a thin layer of stearic acid compounds in order to improve their dispersibility. The V–9 silver powder was used as received or as a dispersion within the following materials:

a) Silicone oil, 20,000 cp in viscosity (Dow Corning 200 fluid).

b) Diethylene glycol monobutyl ether ($C_4H_9(OCH_2CH_2)_2OH$), b.p. 231°C (Union Carbide "butyl carbitol").

c) Diethylene glycol monoethyl ether acetate

$$(CH_3COO(CH_2CH_2O)_2C_2H_5),$$

b.p. 218°C (Union Carbide "carbitol acetate").

The powder was manually mixed with each of these at room temperature to volume loadings ranging between 20 and 30%, until smooth and uniform pastes were obtained. For comparison purposes, a one-part commercial conductive epoxy compound containing the same silver powder at an approximate volume loading of 20% was also used.

Apparatus and procedure

The samples were spread as thin films on the strip specimen holder depicted in Figure 1. This holder consists of a precleaned glass slide onto which are epoxy-bonded two copper strips (0.013 cm thickness) whose free ends extend beyond the same side of the glass surface. A pressure-sensitive tape was applied onto the slide, and a 0.35 cm wide strip was removed from the tape in the lengthwise direction. The sample was then spread within this space by means of a second glass slide, and the remaining adhesive tape was finally removed. Thus, the length of the specimen is determined by the distance between the copper pads (2.54 cm); its thickness is that of the adhesive tape (0.007 cm); and its width is that of the initial gap in the tape (0.35 cm).

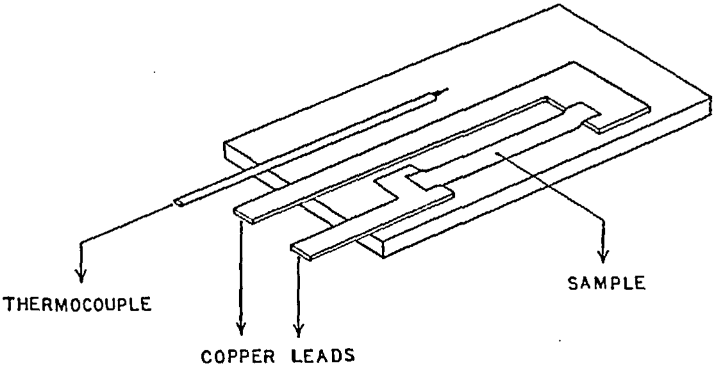

FIGURE 1 Strip specimen holder used for measurements of resistance as a function of temperature and time.

For electrical measurements during thermal treatment, a thermocouple was attached onto the glass slide, and the complete specimen holder was then inserted into a constant temperature oven (Mettler FP 52) capable of being placed within the optical path of a microscope. A Keithley 160 B digital multimeter, having a range of measurable resistances from 10^{-3} ohms to 10^{9} ohms, was connected to the ends of the copper strips which were protruding out of the oven. The outputs from the multimeter and from the thermocouple were plotted as functions of time on a Hewlett-Packard 7046-A two-pen recorder. Visual changes during heat treatment were observed under a Reichert Zetopan microscope.

RESULTS AND DISCUSSION

a) Coating analysis

As has also been previously reported,[17] conductive epoxy compounds are insulators in the uncured state, and become conductors only after cure (ordinarily involving heat treatment). The first question to be answered in this respect concerns the reasons for this pre-cure insulation and post-cure conduction. Does the barrier to the development of electrical conductivity lie within the epoxy matrix *per se*, or rather within the dispersed particles? As the individual silver particles may be coated with a dispersion-promoting organic layer, it was decided to investigate *its* role in the onset of conductivity.

To this end, a comprehensive series of analyses was conducted independently to determine the chemical composition of this coating. The organic layer was extracted by means of a ternary azeotrope (30% acetone, 47% chloroform, 23% methanol; b.p. 57.5°C), yielding 22 mg of extract per 100 gr of original conductive powder. Infrared spectroscopy showed it to be a fatty acid salt, possibly of copper. To determine the anion, part of the residue was acidified and extracted with ethyl acetate. Gas chromatography-mass spectrometry of the extract revealed about equal amounts of stearic, palmitic, and myristic acids, as well as of a lower member of this homologous series—possibly lauric acid. Emission spectroscopy and x-ray fluorescence spectroscopy indicated the major metals to be copper, calcium, and magnesium, with weaker signals from silver and iron. Atomic absorption spectroscopy performed on a sample extracted by a 33.5% ethanol–66.5% ethylene dichloride azeotrope (b.p. 70.5°C; yield 0.025%) gave the following amounts for the metal cations as parts of the total weight of the conductive powder: 20.0 p.p.m. Cu, 3.8 p.p.m. Ca, 1.5 p.p.m. Mg, and 0.5 p.p.m. Ag.

From the above, it appears that the coating is primarily a mixture of copper stearate, palmitate, myristate, and possibly laurate. While its function is clear, its origin is less so. Evidently, the commercial scarcity or even unavailability of some of these copper salts, coupled with their high prices, would make them extremely unlikely candidates for coating materials—especially when contrasted with the inexpensiveness of their respective free acids. It is therefore possible that the copper salts are produced *in situ* during the manufacture of the conductive particles. Powder formation in metals is most commonly accomplished by grinding and ball milling. If the pulverization equipment contains copper (e.g. in the form of brass rollers or balls), and if a fatty acid mixture is added to the silver powder in this apparatus, it is very likely that the heat generated by the frictional forces on each particle will on the one hand melt the organic acids, and on the other cause them to react with the copper. Thus, a thin layer of fatty acid salts of copper will be deposited on the surface of the silver particles. Such commercial fatty acid mixtures are readily available and very cheap; their melting points lie between 44 and 70°C, so that friction during pulverization would readily provide the local heat needed to melt them; and, because of the high reactivity of copper metal, their reaction with it proceeds quite easily above the melting point. Silver is, of course, much less reactive than copper, a fact which would explain the minute quantity of silver fatty acid salts extracted from the organic coating. The small amounts of calcium and magnesium compounds are not uncommon in technical grades of these organic acid mixtures. While the above scenario cannot be better than conjectural, it nevertheless suggests a totally plausible and experimentally consistent explanation for the origin of the organic layer.

A second point of interest in the description of the insulating coating is its thickness. An approximate value may be estimated by assuming that each silver particle is a sphere covered by a surface shell of uniform thickness. Then, on the basis of the extraction results (0.025% of the conductive powder) and of an assumed density of 1 gr/cm^3 for the organics, an average layer thickness of *ca.* 5 Å is obtained for the 1 μm particles. This value is obviously much too low to be realistic, since it only barely exceeds atomic dimensions and is just a small fraction of a monolayer. In order to approximate monolayer dimensions, the thickness of the coating would have to be around 50 Å; this would require the diameter of the silver particles to be *ca.* 10 μm. To clarify this point, the conductive powder was examined by transmission and scanning electron microscopy. The majority of the particles were observed to be of irregular shape with dimensions not exceeding 2 μm. At the same time, however, a significant percentage of them were clumped together in aggregates whose dimensions were commonly 5–10 μm or even higher.

Furthermore, there is no need for *all* of the particles to be uniformly coated, or even to be coated at all for that matter. On the basis of percolation theory, [4,5] electrical conduction of a composite containing less than *ca.* 18% by volume of metal powder is impossible, because the average number of contacts is insufficient to ensure continuous conducting paths throughout the insulating matrix. Consequently, if we assume that while some of the silver particles are not coated, many others are to be found within aggregates having an outer coating, a thickness of at least one or two monolayers would certainly be consistent with the extraction results.

b) Electrical measurements

Once the physical and chemical nature of the insulating coating has been determined, the next step must clearly concern its removal from the surface of the silver particles, which is a necessary prerequisite for electrical conduction. The effect of temperature on the electrical properties of the conductive powder was studied by spreading the particles onto the strip specimen holder of Figure 1. The 100% conductive powder strips gave resistances at room temperature that were beyond the range of the electrometer used (i.e. greater than 10^9 ohms), indicating that the initial resistivity was at least 10^6 ohm-cm. Insertion of the sample into an oven maintained at temperatures above 200°C caused a precipitous drop in the resistance of the sample, as is seen in Figure 2. At temperatures higher than *ca.* 220°C the initial slope of the resistance *vs.* time curve is practically infinite, i.e. once a certain temperature-dependent induction time has been exceeded, development of electrical conduction is almost instantaneous. Below 220°C the drop in resistance is slightly more gradual, especially at 200°C, where an initial region of slow decrease precedes the main drop in resistance. At temperatures less than 200°C no changes in electrical behavior were observed for samples even after 3 hours.

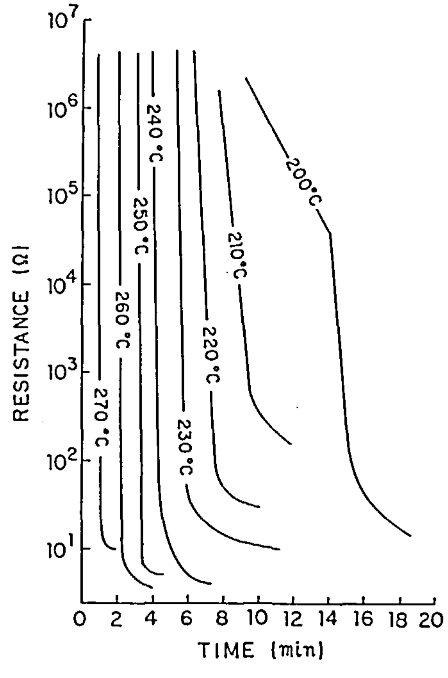

FIGURE 2 Changes in resistance of 100% conductive powder specimens at various temperatures.

The fact that conductivity develops only at 200°C or above is in direct contradiction to the results from epoxies filled with the same silver powder,[18] for which conduction was obtained at 120°C. In the latter case, it was suggested[18] that this is due to initiation of cure occurring at that temperature and resulting in substantial shrinkage of the matrix, which then forces the particles into mutual contact. This, however, is neither a necessary nor a sufficient condition for conduction. It is not necessary because both in the epoxy mixtures and in the silver powder the number of particles exceeds the minimum required for conduction on the basis of percolation theory[4,5]; nor is it sufficient, because simple shrinkage of the composite without simultaneous removal of the organic layer from the silver particles would not render the mixture conductive. This has been experimentally confirmed by use of room temperature curing epoxies, into which V-9 conductive powder had been blended to a 30% volume loading. Not only was there no conduction after cure at room temperature, but even subsequent heating of the cross-linked sample to 280°C produced no decrease in resistance. It can therefore be inferred *a posteriori* that high temperature establishes conductive paths not by bringing about a contraction of the matrix, but rather by removal of the insulating organic layer from the surface of the silver particles. The mechanism whereby this removal is accomplished, as well as the reasons for its occurrence at lower temperatures in the epoxy mixtures, will be discussed in the following section of this report.

TABLE I

Melting points of the constituents of the silver powder coating (°C)

Anion		Cu^{2+}	Ca^{2+}	Mg^{2+}	Ag^{+}
Stearic	$(CH_3(CH_2)_{16}COO)^-$	125	180	88	205
Palmitic	$(CH_3(CH_2)_{14}COO)^-$	120	dec. 150	121	209
Myristic	$(CH_3(CH_2)_{12}COO)^-$	—	—	132	211
Lauric	$(CH_3(CH_2)_{10}COO)^-$	113	182	150	212

In almost all cases, the stripping of the organic layer is completed at such a rapid rate that the ultimate resistance is reached within 2 minutes after the initial drop. The reasons for the slower stripping at 210°C and—especially—at 200°C, together with the fact that no conduction is obtained below that temperature, tend to point to a chemical mechanism. In the absence of a surrounding medium, the organic coating could undergo only two drastic physical changes that might lead to electrical conduction: melting and vaporization. The first of these phenomena takes place between 113 and 125°C for the copper compounds present (Table I), resulting in no discernible effect on the resistance; apparently, the fatty acid salts do not coalesce away from the silver particles, but continue to coat them even in the molten state. Vaporization to any significant extent does not take place for these compounds, because they decompose before reaching their boiling point. This leaves as the most likely primary mechanism a chemical one—possibly decomposition. The absence of conduction below 200°C could then be attributed to the energy of activation for such a chemical reaction, while the prolonged slow decrease in resistance around 200–210°C could be due to a low reaction rate at these temperatures. Carboxylic acids and their salts are known to undergo decarboxylation reactions quite easily at elevated temperatures. In fact, gas chromatography-mass spectrometry on a sample of V–9 conductive powder heated to 200°C detected evolution of CO_2 gas. More details on the nature of the chemical changes during heating are presented in connection with the thermal studies later on in this paper.

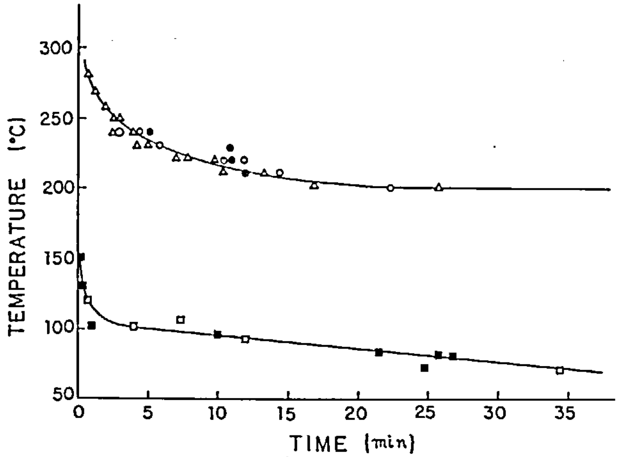

FIGURE 3 Time required for the resistivity to drop to less than 0.1 ohm–cm. △: 100% V–9 conductive powder; ○: 30/70 vol. % V–9 in silicone oil; ●: 20/80 vol. %V–9 in silicone oil; ■: 30/70 vol. %V–9 in "butyl carbitol"; □: 30/70 vol. % V–9 in "carbitol acetate".

The final resistances obtained in the strip specimens of the conductive powder varied quite significantly, as can be inferred from Figure 2. This should not be very surprising, taking into account the fact that the sample is not one continuous phase, but rather a collection of individual particles. A similar, but less pronounced, tendency was observed in the induction time for conductivity development. As is seen in Figure 2, the higher the temperature of the sample, the shorter the time needed to assure electrical conduction. This is better illustrated in Figure 3, which depicts as a function of temperature the time needed by a variety of samples to reach an arbitrary conductivity of 0.1 ohm-cm, i.e. for their resistance to drop below *ca.* 100 ohms. It is interesting to note in this figure that the same behavior is followed exactly by samples consisting of 20 and 30 vol. % of the conductive powder in silicone oil. This carrier for the silver particles was selected in order to duplicate as well as possible the physical characteristics of uncured epoxies, without the complications arising through cross-linking or through the influence of the very reactive chemical groups present in these mixtures.

In accordance with percolation theory,[4,5] the 20% volume loading is adequate to assure full conductivity, and no improvement either in the induction time or in the final resistance is observed by increasing the loading to 30%. The fact that the particles are now embedded in a continuous matrix does not appear to affect the development and extent of conductivity. Expansion of the silicone oil as it was heated up to 250°C did not delay the onset of electrical conduction, because the increase in volume was too small to reduce the volume loading below ε_c. Similarly, the shrinkage that occurred upon cooling to room temperature did not reduce the ultimate resistance by more than about 50%—which is what would be expected from the temperature coefficient of resistance alone. A similar reduction was also observed in the 100% silver powder, for which cooling should have caused the particle surfaces to move away from each other rather than to come together.

This parallelism in behavior between the 100% conductive powder and the silicone oil mixtures is somewhat puzzling. First of all, decomposition should yield different products in each case. When the particles are heated in air, strong reactions with oxygen are expected to occur; these should be absent in the anaerobic conditions characterizing heat treatment of the silicone-embedded particles. Furthermore, the gaseous reaction products escape to the atmosphere in the first case, whereas in the second they are trapped within a very viscous matrix, in which they are insoluble. Also, the solid products of the decomposition would include a significant percentage of copper in the anaerobic case, while atmospheric heating would primarily yield copper oxide, which is only a semi-conductor. It is most probable that the similarity in electrical behavior of the two types of samples is simply due to the thinness of the organic layer. Once it decomposes, conduction will ensue in any case, as its quantity is minute in comparison with the overwhelming preponderance of the now liberated silver particles.

Precisely because high viscosity silicone oil—a material physically but not chemically similar to uncured epoxies—produces the same electrical behavior as the isolated V–9 particles, we must now concentrate on the chemical species of epoxy compounds in order to explain conduction at lower temperatures. Clearly, heating above *ca.* 100°C causes some component in the epoxy matrix to initiate removal of the organic layer. It might then be asked why this component does not do so at room temperature. While this may imply a critically temperature-dependent rate of removal, it might also be due to the very major chemical transformations that occur in the epoxy matrix *per se*. Curing, usually accomplished by incorporation of amine compounds, involves nucleophilic attack on the epoxy end-groups, ring scission, and subsequent hydroxylation prior to cross-linking.

It was thought that perhaps this abundance of hydroxyl groups, and the consequent association through hydrogen bonding that they might provide with the organic coating, could aid in its removal. Furthermore, presence of compounds containing ether linkages—as is the case in epoxies—could provide a solubilization effect which might enhance removal of the coating at lower temperatures. This hypothesis was tested using two close analogues of the basic epoxy resin structure—diethylene glycol monoethyl ether acetate ("carbitol acetate"), $CH_3COO(CH_2CH_2O)_2C_2H_5$, and diethylene glycol monobutyl ether ("butyl carbitol"), $C_4H_9(OCH_2CH_2)_2OH$. Both are viscous liquids, boiling above 210°C and having very low vapor pressures (less than 0.05 mmHg at 20°C); both possess two ether linkages to alkyl groups of a length similar to that found in epoxies. It was found that copper stearate is readily soluble in these two compounds.

Electrical behavior of the conductive powder dispersed in each of these organic carriers to a 30% loading is seen in Figure 3. As expected, conduction is initiated at much lower temperatures, and this time the curve does not become asymptotic at a given temperature, but appears instead to be monotonically decreasing. It was found that samples left at room temperature had become conductive overnight. Both solvents seem to be equally efficient in initiating conduction, and no difference is observed on account of their characteristic groups (hydroxyl *vs.* ester) or of the length of their terminal n-alkyl group (C_4 *vs.* C_2).

As a consequence of their solubilization effect, these compounds could become very useful additives in silver-filled epoxy mixtures. This was illustrated by incorporation of 2.5% by weight of these solvents into a one-part commercial conductive epoxy having a *ca.* 20% silver loading. Ultimate resistances of the order of 0.04 ohms were commonly obtained, corresponding to a resistivity of 6×10^{-5} ohm-cm; this is about two to three times lower than the average value for this conductive epoxy batch. Of course, the lower viscosity of these mixtures might play a role in the higher ultimate conductivity. Incorporation of these solvents into the cured matrix is also expected to have some effect on their mechanical or thermal stability. These minor problems could, however, be easily circumvented by adopting other solvents of similar chemical composition that would eventually become part of the three-dimensional matrix. Low molecular weight homologues of poly(ethylene oxide) would be very suitable in this respect, as they are bifunctionally hydroxy-terminated. Secondary or tertiary alcoholic chain ends or pendant hydroxyl groups would reinforce cross-linking of these solvents and incorporation into the cured epoxy structure.

This is in agreement with results by Sharpe *et al.*,[19] who introduced small amounts of a poly(ethylene oxide) of molecular weight around 200 into an epoxy mixture containing approximately the same concentration of V–9 conductive powder as used in this study. Incorporation of this material at concentrations of *ca.* 1.5–6% (based on the resin mix alone) was shown[19] to exert a strong effect on the resistivity, lowering it by 40–60%, while depressing T_g by not more than 5–10°C.

The actual conditions that aid in the removal of the coating in a commercial epoxy system are undoubtedly more complicated. The fatty acid layer is now in the midst of strong chemical species participating in drastic transformations of the immediate chemical environment. Reactions between the original or transient species in the epoxy mixture, on the one hand, and the paraffinic or metallic groups in the coating, on the other, could be expected to take place during cure, thus further promoting the breakdown of the insulating layer around the silver particles.

c) Thermal characterization

To gain a better understanding of the chemical and physical changes that take place in the organic layer during heating, a number of thermal characterization procedures were employed. The first of these involved controlled heating of the conductive powder extract in the microscope stage of the Mettler FP–5 melting point apparatus. The initial optical appearance of the extract can be seen in the photomicrograph of Figure 4a, taken at room temperature. Heating the material at 10°C/min gave an optical melting point between 124 and 126°C; the molten extract is seen in Figure 4b. Above *ca.* 160°C, gas evolution could be inferred from the ripples in the visual image of the sample; this continued through about 220°C. Around 195°C, small dark spots appeared in the material, producing an overall image such as is seen in Figure 4c. Their number and intensity increased with temperature, and the sample became markedly darker up to about 240°C. Continued heating to 300°C showed no further changes. The gas evolution observed marks the beginning of decarboxylation, and is followed by the subsequent vaporization of the hydrocarbons constituting the alkyl chain of the fatty acid salts. The dark spots that are formed must be primarily copper oxide with small amounts of copper metal and organic degradation products.

A second series of thermal investigations was carried out by differential thermal analysis on a DuPont DSC Model 900. The differential traces obtained are seen in Figure 5. Curve 1 shows the thermal behavior of the conductive powder extract under anaerobic conditions similar to those existing in an epoxy mixture. The first endotherm around 120°C corresponds to the melting of the copper fatty acid salts. As a result of the number of species present, the melting endotherm is rather broad, especially in curve 2, which was obtained from a similar sample heated in air. At higher temperatures, curve 1 shows two additional endotherms. Both are broad and result from the decomposition of the fatty acid salts that is caused by heating. The first one peaks around 225°C and is probably due to the decarboxylation reaction and the consequent evolution of CO_2, which had also been observed in the optical microscope. Once decarboxylation has begun, the parent

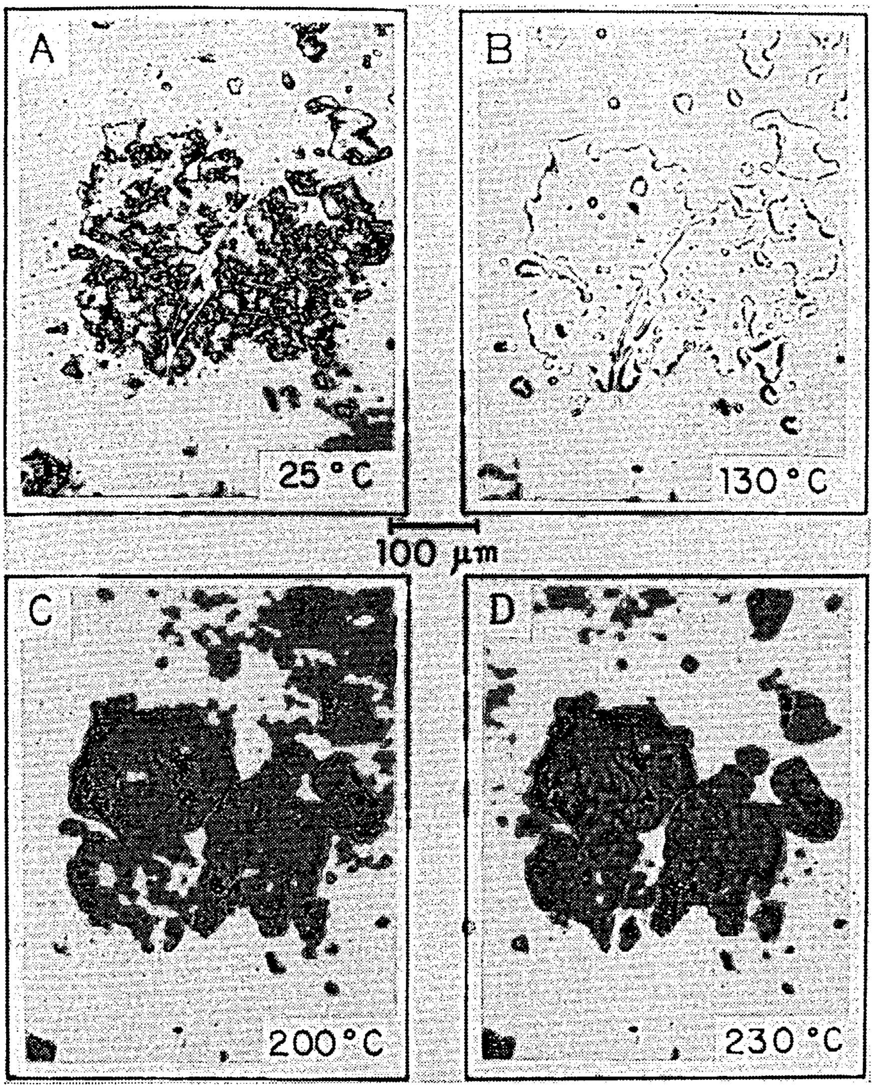

FIGURE 4 Optical micrographs of the conductive powder coating at different temperatures: (a) 25°C; (b) 130°C; (c) 200°C; (d) 230°C.

hydrocarbons will be continuously produced together with CO_2; their boiling points ($C_{13}H_{28}$: 234°C; $C_{15}H_{32}$: 271°C; $C_{17}H_{36}$: 303°C) are slightly above the decarboxylation temperatures, so that they will vaporize, causing a second endotherm to appear.

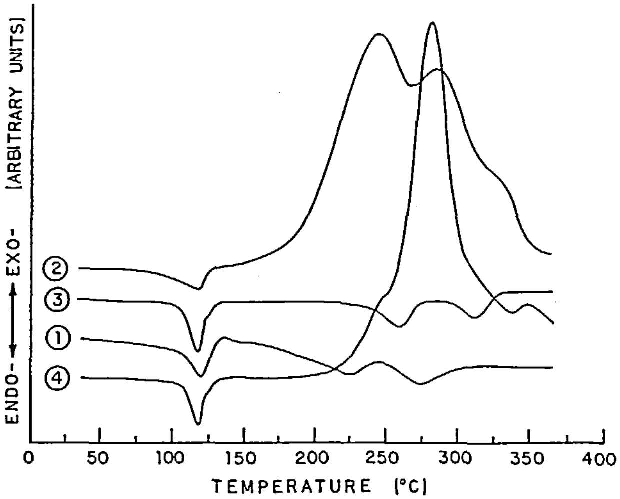

FIGURE 5 Differential scanning thermograms of the conductive powder extract (curves 1 and 2) and of copper stearate (curves 3 and 4); 1 and 3 in nitrogen, 2 and 4 in air. 1 gr samples, $\Delta T = 0.1°C$, heating rate = 20°C/min.

This mechanism is supported by the DSC trace of technical grade copper stearate heated in nitrogen, as seen in curve 3. Here, the decarboxylation endotherm is found at higher temperatures because of absence of the lower fatty acid salts. The final endotherm peaks very closely to the boiling point of heptadecane, and both endotherms are much sharper than in curve 1.

Heating of the silver powder extract in an atmosphere of air (curve 2) yields an exceptionally strong combination of exotherms in the expected temperature range, corresponding to the oxidation reactions that take place after decarboxylation. This behavior is also followed by the copper stearate (curve 4), with the sole difference that—as a result of the relative purity in comparison to the extract—the oxidation exotherm is now much stronger and sharper.

CONCLUSIONS

Although the volume loading of silver in certain commercial conductive epoxies is adequate to produce electrical conduction at room temperature, such is not obtained because the silver particles are coated with an insulating organic layer. This is added to promote dispersibility, and is composed primarily of a mixture of fatty acid salts of copper. The onset of electrical conduction during cure is the result of removal of this coating by decarboxylation, followed by vaporization of the parent hydrocarbons. Shrinkage of the epoxy matrix does not play a significant role either in the development or in the final value of conductivity. The silver powder becomes conductive above 200°C when heated alone or as a dispersion in an inert matrix (e.g. silicone oil). This temperature may be greatly reduced by incorporation of solubilizing agents such as long chain organic compounds containing numerous ether linkages. Addition of small amounts of these compounds to commercial conductive epoxies has been found to result in ultimate resistances that are two to three times lower.

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