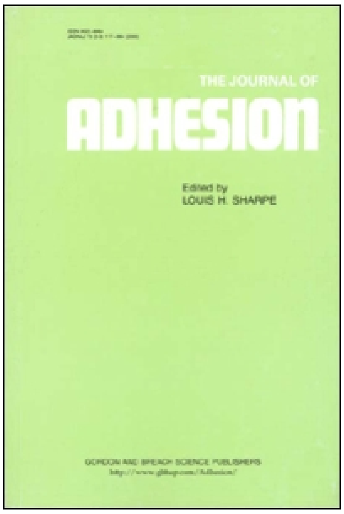

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Marshall, David W.(2000) 'Copper-based Conductive Polymers: A New Concept in Conductive Resins', The Journal of Adhesion, 74: 1, 301 — 315
To link to this Article: DOI: 10.1080/00218460008034533
URL: http://dx.doi.org/10.1080/00218460008034533

J. Adhesion, 2000, Vol. 74, pp. 301–315
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Copper-based Conductive Polymers: A New Concept in Conductive Resins*

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(Received 7 August 1999; In final form 15 February 2000)

The history of making plastic materials conductive to both electric currents and to the transfer of thermal energy has traditionally been accomplished by the addition of metallic particles into a resin matrix. Principally, such metals as aluminum, silver, gold, nickel and copper have been used. Copper has had a limited success due to its tendency to form a non-conductive oxide surface layer and currently such adhesives depend primarily on silver for high conductivity.

An intense research effort to eliminate the problems associated with copper-filled conductive polymers resulted in a treatment and preparation of copper flake that allows the stable formation of a conductive structure within a polymer matrix. Once the activated copper particles are in the resin, the formulation is stable. Most of the resins evaluated have been epoxy resins although certain thermoplastic resins have also been made conductive. Volume resistivities as low as 10^{-5} ohm-cm have been achieved.

Keywords: Electrically conductive adhesive; Copper; Epoxy; Volume resistivity; Applications

INTRODUCTION

Since most plastics are thermal and electrical insulators, it is necessary to add a conductive material to the polymer in sufficient volume that a conductive path can be found through the matrix. The inherent conductivity, the shape of the particle, and the nature of the particle surface are all important but particle-to-particle contact is a

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*Presented in part at the 22nd Annual Meeting of The Adhesion Society, Inc., Panama City Beach, Florida, USA, February 21–24, 1999.

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necessity [1]. Conductivity is usually determined by measuring volume resistivity which is given by $Vr = RA/L$ where R is the measured resistance between two points, A is the cross sectional area through which the current flows and L is the distance between the two points. Therefore, the lower the volume resistivity, the higher the conductivity. The volume resistivity of some typical metals is given in Table I.

It should be noted that the largest volume of commercially-available conductive polymers is not based on the addition of metals but on the addition of carbon particles. These materials are largely based on thermoplastic resins and are used principally for static shielding. They are relatively inexpensive but have volume resistivities only in the range of 10^1 to 10^3 ohm-cm. This class of conductive materials will not be considered further since their conductivities are low compared with the better metal-filled systems. Also, the discussion below is limited to thermosetting resins with the brief exception of the mention of a copper-filled thermoplastic polyethylene polymer.

The most common metals used include aluminum, silver, gold, nickel and copper, along with some non-conductive materials such as glass fiber or spheres, which have been coated with a conductive metal [2]. Despite the availability of these materials and the large number of powder or flake metals that could be used, virtually all the high-performance conductive resins are based on silver particles. This is primarily due to silver's inherent high conductivity and the fact that silver has an oxide coating which is conductive [3]. From the data in Table I, one would suspect that aluminum, gold and copper would also result in highly conductive polymers. This is true for gold but the cost of gold powder precludes its use in all but the most demanding cases. A layer of aluminum oxide always covers aluminum surfaces.

TABLE I Electrical conductivity of metals

	Specific gravity *gms/cm*^{3}	ρ = *Volume resistivity* *ohm-cm*
Silver	10.5	1.6×10^{-6}
Copper	8.9	1.8×10^{-6}
Gold	19.3	2.3×10^{-6}
Aluminum	2.7	2.9×10^{-6}
Nickel	8.9	10×10^{-6}
Platinum	21.5	21.5×10^{-6}
Eutectic Solders	–	$20–30 \times 10^{-6}$

This oxide is a good insulator and prevents aluminum-to-aluminum particle contact when aluminum particles are used as a filler in a resin formulation. However, aluminum particles are occasionally used to make thermally-conductive polymers because of their low cost.

Copper also forms a non-conductive oxide layer but its oxide layer is not as stable or as tightly attached as that of aluminum. If this oxide could be eliminated or changed to a conductive form and the surface kept in that state, copper-filled compounds would be very effective conductors. One way of eliminating the oxide is to add reducing agents such as certain amines to the resin. These agents partially reduce the oxide to copper metal but have been found to be ineffective in providing long-term protection against oxidation and they often adversely affect the cured properties of the resin system. The overall result of using reducing agents has been a general unreliability with progressive loss of conductivity over time. Since copper is a relatively low cost metal compared with silver or gold, there is a considerable driving force to develop a surface treatment for copper particles that would result in conductivities similar to those of the more-precious metals.

PROCEDURE

An intense research effort to eliminate the problems associated with copper conductives produced a novel treatment for the copper which results in the ability to use copper particles in a resin matrix to form an electrically-stable system. Much of the technical work was done some years ago but little has been published since the process was originally patented [4] and the techniques used were considered proprietary. The treatment consists of a four-step chemical process to activate the copper surface. These steps include using a solvent to remove any coating on the particles, then chemically removing the oxide from the surface, drying the particles under vacuum and storing them under nitrogen or vacuum until ready for use.

For example, to treat copper flake for incorporation into a typical two-component epoxy resin, the following steps were taken. A one-pound blend (454 grams) of flakes consisting of a 50–50 mixture of US Bronze Powder's USB 6500 and C-100 copper flakes was made.

These flakes have a thickness of approximately 2 microns and an average diameter of 20 microns and 60 microns, respectively. Purity of the flake was 99.99%. Lower purity could result in poor conductivity. The flake was placed in a glass vessel and covered with trichloroethylene equal in volume to 8 times the flake volume. The mixture was stirred for one-half hour and then filtered under vacuum through a Büchner funnel. The flake was rinsed in the funnel three or four times with denatured alcohol. This removed any processing aid from the flake mixture.

The flake was then removed from the funnel and mixed with one quart (0.95 l) of 1 molar citric acid and stirred overnight. The mixture was then filtered again through the Büchner funnel and rinsed with distilled water until the filtrate was clear. The flake was then rinsed with denatured alcohol. The damp flake was then placed in a vacuum oven and dried under vacuum at 100°F(38°C). One can tell when the copper is dry by the vacuum held. When it is stable around 77 mm the flake should be dry. It can be stored under vacuum or under nitrogen. The copper flake should not be removed from the oven before it cools to room temperature or it may ignite.

Depending on the particle size of the cleaned flake, it can be left in air for several minutes to several hours before incorporating into a resin. The flake can be added to any epoxy resin by simply mixing into the liquid using a low-shear mixer such as those made by Ross Machine Co. Once the particles have been added to a typical epoxy resin the uncured system is stable for a year or more. Loading of the copper flake in the resin can vary from 40% by weight to 60%. Higher loading is difficult to achieve because of the rapid build-up of viscosity. Lower loadings have insufficient copper to provide particle-to-article contact.

Mechanical, thermal and electrical properties were determined for several formulations containing copper treated in the above manner. The following ASTM methods were used: Tensile strength and modulus-ASTM D638, Lap shear-ASTM D1002, Density-ASTM D1622, and Volume resistivity-ASTM D2739. Thermal conductivity measurements were made using a calorimeter. Viscosity measurements were performed using a Brookfield viscometer with a Heliopath stand. Speed and spindle were chosen to give a reading near the middle of the viscometer's scale. Test results are discussed in the following sections.

DISCUSSION OF RESULTS

Although copper powders could have been used, copper flake is easier to treat and most formulations studied used particles of that shape. The flake nature of the copper filler enhances the electrical conductivity and its stability in the resin matrix. One reason for this is discernable under microscopic examination where a "House of Cards" structure can be seen [4]. The edges of flakes rest against the flat portion of other flakes and form a structure similar to a "House of Cards". In most cases, the interface between particles or flakes can not be differentiated since the contact is so intimate. This structure makes it difficult to screen-print formulations made with the treated copper since the "particle association" tends to clog the screen.

Unlike prior copper-filled epoxy systems, a simple amine cured bisphenol A epoxy resin with copper flake treated in the above manner to form an activated copper surface will retain its conductivity indefinitely.

Copper flake fillers with an average diameter of 30 microns and a thickness of 2 microns are the easiest to treat. Varying the ratio of the two flake sizes used can vary the viscosity of a resin to a certain extent using this blend. Viscosities tend to be high, a few million centipoise, but typical formulations are thixotropic and, if necessary, can be thinned with ethyl alcohol. An activated copper flake loading of 56% by weight in a typical bisphenol A resin cured with an aliphatic amine will have a volume resistivity of around 10^{-3} ohm-cm. In some systems, volume resistivities as low as 10^{-5} ohm-cm have been achieved. It should be noted that the "percolation theory" [5] which describes the mechanism of electrical conduction through metal particles in a polymeric matrix does not apply in the case of these flake-filled composites nor does it apply for metallic fibers such as stainless steel [6]. Metal fibers or fibrils typically are made from stainless steel and have a diameter around 8 microns with an aspect ratio of about 750. These fibers can be effective at loadings as low as 3% by weight.

Assuming the values for silver can be used for copper, since they are similar in conductivity, the percolation theory gives a critical value of 30 percent by volume [7]. The volume of copper in the above formulations is around 15%. Since photomicrographs of the filled resin exhibit the "House of Cards" structure, it is evident that the structure requires less copper for conductivity. Because of the flake alignment and the activation treatment, it is theorized that a charge is present on the flake surface with the edges being either positively or negatively charged and the flat surface oppositely charged. This would account for the structure and the relatively small amount of copper necessary for electrical conductivity.

Particles can also be treated but their stability in air is limited and much higher loadings (around 80% by weight) are required to obtain high electrical conductivity. The volume percent copper necessary for conduction, in this case, more nearly matches that predicted by the percolation theory. Such compositions tend to be more sensitive to the ingredients used in the resin formulation. The resistivity is affected principally by the cure temperature but also by the chemical composition of the resin itself. Lovinger [8] has verified that there can be an effect of chemical composition on the conductivity of metal-filled composites. Acetate and hydroxyl groups were found to be beneficial. Stearates and other processing aids were detrimental. In the case of copper-filled epoxies, amines, anhydrides, and certain diamides and imidazoles have been found by the author to be conducive to conductivity but not sufficient for long-term conductivity. High cure temperatures, particularly in the case of particle-filled resins, promoted the formation of copper oxide and reduced conductivity. Activated copper was found to be quite sensitive to this and storage life outside the resin is limited, even at room temperature [4].

Some compositions, particularly single-component epoxies, cured at elevated temperatures, exhibit a current inrush effect. This occurs when resistance is initially high but drops precipitously when a sufficiently high voltage (usually around 12 volts) is momentarily applied [9]. Once the resistance has dropped, it remains at the lower level indefinitely. It is likely that either a thin layer of epoxy, or copper oxide, formed on the surface of the particle. This necessitated a sufficiently high voltage to break through the insulating layer. Properties of a typical conductive two-component epoxy resin, consisting of a bisphenol-A resin such as Dow's DER 332 and triethylenetetramine (TETA) curing agent, in the ratio of 13 parts TETA to 100 parts DER 332, and containing 56% of the copper blend mentioned in the previous section, are given in Table II. A conductive single-component

TABLE II Typical copper-filled epoxies

Type	*2-Component rigid*	*1-Component rigid*
Copper Wt. %	56	56
Cure	24 hrs @ 75°F (24°C) or 1(1/2) hrs. @ 150°F (66°C)	1 hr @ 350°F (177°C)
Density	2.29 g/cc	2.29 g/cc
Tensile Strength	34,500 kPa	31,000 kPa
Elongation	1%	–
Lap Shear, Al–Al	8,300 kPa	8,300 kPa
Modulus	7×10^5	–
Volume Resistivities	0.001 ohm-cm	0.01 ohm-cm
Thermal Conductivity W/m/°C	∼3	∼3
Viscosity	6×10^6 cps	12×10^6 cps
Shelf Life at 70°F (21°C)	12 months	6 months
Comments	Good all around properties	Best high temperature properties

TABLE III 2-Component flexible adhesive

• Designed to bond materials with different thermal expansions	
• Tensile Strength	22,000 kPa
• Lap shear (Al–Al)	14,500 kPa
• Elongation	4%
• Modulus	1.4×10^6 kPa
• Volume Resistivity	.001 ohm-cm
• Viscosity	11×10^6 cps.

epoxy resin containing the same amount of copper in a DER 332 dicyandiamide blend cured at 350°F(177°C) is also shown in Table II.

A flexible version of the two-component system shown in Table II using a polyglycol modified epoxy is shown in Table III. For comparison purposes, typical values for other metal-filled polymers is shown in Table IV along with values using activated copper. Note that treated copper, the earlier antioxidant method for making conductive copper-filled epoxies, has poor thermal stability.

Other resin systems have been evaluated, including polyolefins, some of which have been moderately successful and provide conductivities superior to those of carbon-filled polyolefins. However, copper-filled epoxy polymers have exhibited the highest conductivities and most of the data collected have been on those systems.

TABLE IV Comparison table: conductive metal-filled resin

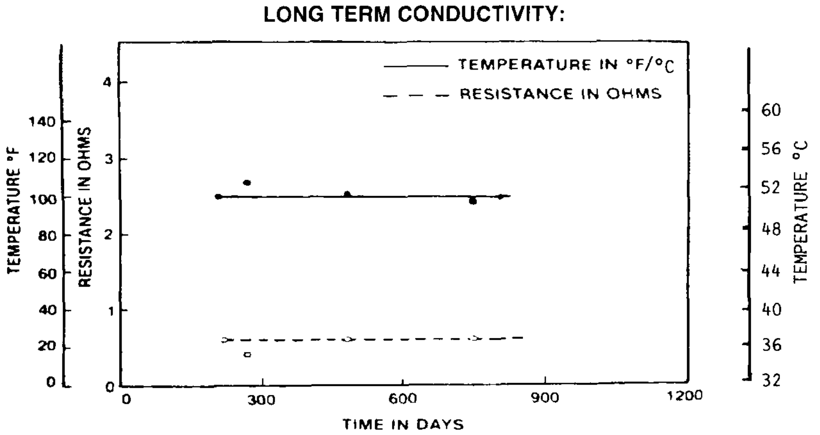
Metal filler (in epoxy resin)	*Volume resistivity range in ohm-cm (initial)*	*Cured stability at 100°C at normal atmosphere*
Aluminum	1.0×10^{10}	Good
Silver	$.1 - 1.0 \times 10^{-3}$	Good
Gold	$.1 - 1.0 \times 10^{-4}$	Good
Treated Copper	$1.0 - 5.0 \times 10^{-3}$	Poor
Activated Copper	$.5 - 1.0 \times 10^{-3}$	Good

TYPICAL MATERIAL PROPERTIES AND APPLICATIONS

Electrical

One of the early products made using a copper-filled polymer was a heating panel. This panel was made with a polyamide-cured epoxy resin. The intended application was an economical home-heating panel that could be operated at low voltage. The panel was made by spreading the resin on a strip of gypsum board 2.4 meters long and 0.6 meters wide. Copper foil strips were embedded in the resin at each end as contact points. The panel was operated at 12 volts. This resulted in a surface temperature of about 38°C. Because of the low voltage used, the panel exhibited a minimal shock hazard making it suitable for walls as well as ceilings. If a nail were driven into it or a cut made, it would continue to operate without presenting a shock hazard to the worker. Figure 1 illustrates the panel's stability. As the graph shows, there was essentially no change in either surface temperature or resistance over approximately 900 days. Because of the costs involved in stepping down normal household voltage at current electrical rates this particular application was not pursued.

Other products have shown various copper-filled adhesive formulations to have excellent long-term stability. In one case, a "Positive Temperature Coefficient" (PTC) heating device was bonded to an aluminum plate in a food-warming tray [9]. This tray consisted of two aluminum inserts set into a conventional plastic cafeteria tray. The PTCs (based on barium titanate) were bonded to the back of the inserts and connected to terminals located on the bottom of



Stability of a 50% copperflake filled epoxy resin.

FIGURE 1 Stability of the conductivity of copper-flake-filled epoxy resin.

FIGURE 2 Heated cafeteria tray.

the tray. Figure 2 shows the tray and Figure 3 the larger insert with three PTC disks bonded to the aluminum insert.

Several trays fit into a cart that contains a 12-volt battery as a power supply. A connection is made with the tray causing the PTC

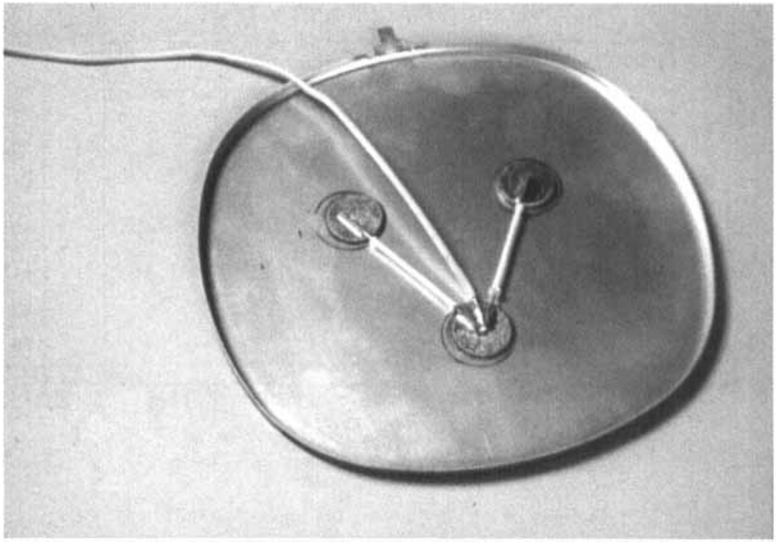


FIGURE 3 Cafeteria tray insert showing PTC heating devices.

devices to heat and keep the food placed on the inserts warm. The trays were designed for use in hospitals and similar institutions where food had to be distributed from a central kitchen. The trays originally used a silver-filled adhesive to bond the PTC devices but, during use, severe corrosion problems occurred resulting in debonding of the PTC disks. When copper was substituted for the silver and the trays run through several commercial dishwasher cycles, as well as thermal stability tests, the trays outlasted silver-filled epoxy bonded trays and did it at a lower cost. The copper-based adhesive used in this application is a single-component resin. Its properties are given in Table V. Some of the testing involved bonding a PTC device to an aluminum plate and measuring the resistance through the device over time at 177°C to determine the electrical stability of the bond. The copper adhesive performed very well as can be seen from Table VI. It should be noted that the operating temperature of the tray is only around 66°C.

Tables VII and VIII show the superiority of the copper adhesive in both cycling and drop tests. Note that after three years bond failure is rare.

TABLE V Copper based tray adhesive

Properties	
Copper wt%	56
Density	2.29 g/cc
Tensile strength	31,000 kPa
Thermal conductivity	~ 3 W/m/°C
Volume resistivity	0.01 ohm-cm
Lap shear strength	10,300 kPa
Cure	1 hour @ 177°C
Viscosity	6×10^6 cps

TABLE VI Stability of one-component copper based PTC adhesive

177°C Aging test
cure time 1 hour @ 177°C

Test time (hours)	*Resistance (ohms)*
0	5.2
150	5.2
800	5.8
1500	5.8
1600	5.3
2300	5.7

TABLE VII Cycle tests Test I

Heater heater bond	*Heater resistance (ohms)*	*Temp. °C*	*% Change*
Silver Epoxy			
Initial	4.6	96	–
40 cycles	4.8	89	4.3
100 cycles	7.1	79	54.3
Copper Epoxy			
Initial	4.1	84	–
40 cycles	4.0	82	2.4
100 cycles	4.9	82	19.5

- On/off cycle for 5000 cycles. No difference between copper and silver adhesives.
- On/off cycle in water 6 min. on -6 min. off.

A single-component, copper-filled epoxy adhesive has been used for a number of years to bond the base and provide electrical conductivity with the filaments in 6 and 12-volt T2 type lamps (see Fig. 4). These lamps were used in push-button telephones at one time but are now largely used as indicator lights in various types of equipment. These bases were originally bonded with silver-filled

TABLE VIII Completed tray Test-II

- 1000 dishwasher cycles plus
  686 cycles of 6 min. on – 6 min. off
- Drop-tested onto a concrete floor from a six foot (2 meter) height-Twice.
- Copper adhesive passed
- Silver adhesive, after approximately 400 cycles, had one of three disks unbonded and the rest so corroded test was stopped
- After 3 years of copper adhesive use, bond failure is rare.
  ≫ When failures occur it is usually a solder joint that failed.

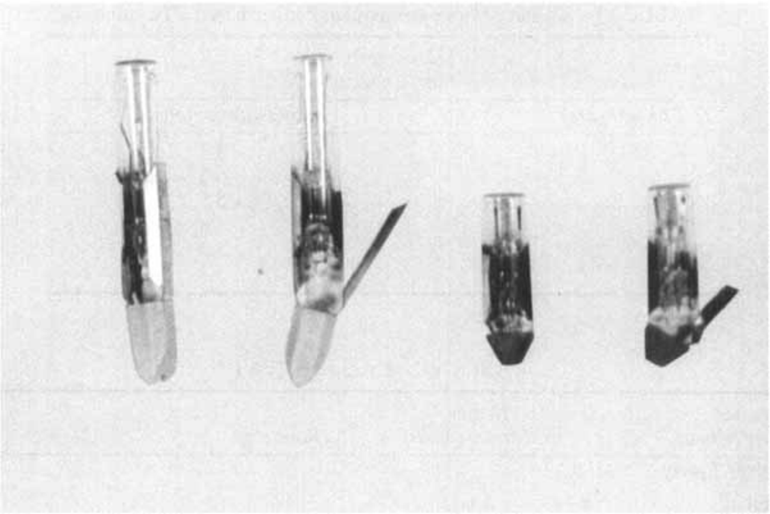


FIGURE 4 Minature lamps showing the bonding of the lamp base. (See Color Plate III).

epoxy resins. The copper system was much less expensive and a single system replaced two grades of silver epoxy with one high-conductivity copper adhesive. This application requires dispensing at a high rate of speed on a production line.

Thermal

The inherent high thermal conductivity of copper can also be utilized. Heat transfer properties of copper-filled *vs.* silver-filled resins are within the same range, with copper providing an equivalent thermal conductivity at a fraction of the cost.

Table IX illustrates thermal conductivity of various filled epoxy resins.

A room-temperature-curing, flexible, copper-filled epoxy resin has been used to replace solder in solar heating panels in the "do-it-yourself" home market. In this case, it is much easier to bond the tubing to the collector plate rather than to try and solder the large sections of tubing.

EMI Shielding

The electrical properties of the copper-filled epoxy systems also result in their providing excellent shielding against EMI radiation [10]. Again, this protection is similar to that of silver-filled resins at a fraction of the cost. The following table, Table X, shows the shielding effectiveness of the room-temperature-curing, copper-filled systems and other high conductivity shielding materials. Table XI gives the properties of a copper-based coating under both a magnetic and plane wave fields. As a result of FCC regulations, allowable electromagnetic emissions of commercial and industrial equipment are limited. Commercial or industrial equipment such as computers or high voltage connectors are designated as Class A by the FCC and require a

TABLE IX Thermal conductivity of epoxy resin system *vs.* type filler

Filler type	*Wt. % filler in resin*	*Thermal conductivity* $Wm^{-1}\ deg^{-1}$
Activated Copper	56	2.8–4.3
Silica	65	0.8–1.1
Aluminum	50	1.1–1.4
Calcium Carbonate	50	0.7–1
Silver	50	2.8–6.9
Alumina	50	0.8–1.1

TABLE X EMI shielding effectiveness

	10 *Mhz to* 1 *Ghz Attenuation* (*db*)
Silver Epoxy	59–87
Copper Epoxy	67–73
Graphite filled	27–40
Nickel filled	35–50
Zinc Metal	70–90

TABLE XI EMI shielding effectiveness of activated copper systems

	Magnetic field		*Plane wave*		
Frequency	150 KHz	200 KHz	400 MHz	1 GHz	10 GHz
Avg. Attenuation	70 db	67 db	70 db	73 db	75 db

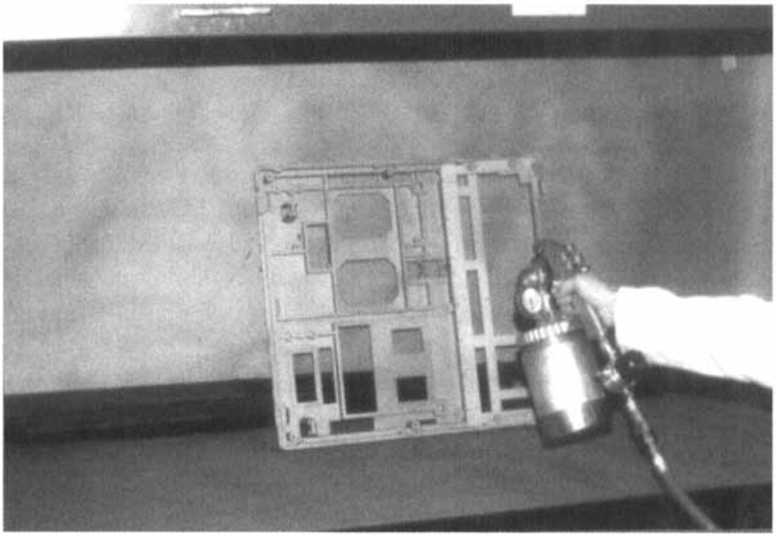


FIGURE 5 The spraying of a computer housing.

minimum attenuation of around 60 db. Most military EMI requirements are for attenuations of 70 db or higher.

Figure 5 shows a computer housing being sprayed with an activated copper coating to shield it against EMI radiation. The coating resin was made by thinning a 2-component, activated copper-filled epoxy resin with ethanol to make a sprayable solution. It can then be applied with conventional spray equipment.

CONCLUSIONS

A treatment for copper particles has been developed that, when combined with the proper resin systems, results in a stable conductive material. Although preliminary work has been successful with certain thermoplastics such as polyethylene and polycarbonate, most of the development has been concentrated on epoxy resin systems. These systems have been shown, in most cases, to be comparable with, or superior to, silver-filled epoxies at a significantly lower cost. They offer superior environmental resistance over silver epoxies where corrosive conditions exist but are not yet suitable for screen-printing or for applications where intermittent surface contact is needed, as in a membrane switch.

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