

Conductive Fillers for EMI/RFI Shielding Coatings

by Anthony C. Hart, Hart Coating Technology, Brierly Hill, West Midlands, UK, and Frank W. Heck Novamet Specialty Products Corp., Wyckoff, NJ

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INTRODUCTION

Electronic equipment of all types is subject to interference caused by extraneous electrical and magnetic signals which can seriously affect its operation. This interference can be caused by natural phenomena, such as lightning, or by emission from other electronic or electrical equipment, since such equipment can both emit and receive these signals. These effects are known as radio frequency and electromagnetic interference (RFI and EMI respectively). The majority of interference problems are, in fact, experienced in the radio frequency range between 10 Kilohertz and 100 Gigahertz.

To ensure reliable operation of electronic equipment it has become necessary to see that it is shielded from this type of interference. This has become an increasingly important requirement as the number of electronic devices has proliferated both in traditional user areas, such as aerospace, military and communications, and in newer applications in commercial and domestic equipment. Also, the reliable operation of electronic equipment has become vital in many applications. Failure resulting in disastrous consequences rather than mere inconvenience. Such is the case with the "fly-by-wire" control systems used in modern aircraft where malfunctioning of the control computers could result in loss of the aircraft.

Another technological change taking place at the same time as the growth in the market for electronic equipment has made the problems caused by RFI and EMI even more severe. This is the replacement of metals, formerly used to construct the housing for this type of equipment, by a variety of plastics. These are used since they offer a number of advantages such as weight saving, economy, easy of construction for complex shapes and superior design capabilities.

Metallic housings, however, being electrically conducting, provide a reasonable and sometimes completely acceptable degree of shielding from interference. Plastic housings, on the other hand, being nonconductive, provide no worthwhile shielding whatsoever.

It has, therefore, become necessary to devise methods by which plastic housings can be made to provide effective shielding from RFI and EMI and a new branch of the surface coatings industry has grown up in the last few years to fulfill this need. The industry uses many surface finishing techniques originally developed for other applications, including:

1. Metal spraying techniques.
2. Vapor phase deposition techniques.
3. Aqueous based coating systems, including electroplating and autocatalytic plating.
4. Conductive organic systems, such as paints.

The system chosen is determined by the technical requirement, availability of suitable equipment and cost. Each of the systems are finding applications where the particular process shows advantage in one or more of these areas.

Organic based coatings have become widely used in this industry since the overall process offers many advantages. It provides very good shielding performance at a competitive cost and uses relatively inexpensive equipment which is readily available in many locations and is flexible enough to cope with a variety of component shapes and designs. In addition, it is compatible with other necessary finishing operations, such as providing an attractive exterior finish to the component housing.

Paints, like the plastics onto which they are coated, are inherently nonconducting and, therefore, provide no shielding effect. To produce a paint

which is conductive, and which can function as an effective shield to interface, it is necessary to incorporate conductive pigments into the paint system. A range of conductive pigments is available for this application and considerable effort has gone into the development of pigments which maximize the shielding effectiveness while retaining the other vital characteristics of the coating such as acceptable appearance and applicability. Conductive pigments are generally produced from pure metals, although graphite is used in less demanding applications. Metallic pigments are, of course, widely used in organic coatings and their application has been reviewed earlier.¹ In addition to the pure metallic pigments a number of coated particles have been specially developed for this application which employ a highly conductive coating over a core which can be either conductive or nonconductive.

In this paper the properties of these conductive pigments are examined and the way in which they behave and affect the shielding effectiveness and other properties of the coating systems into which they are incorporated are discussed.

PROPERTIES OF CONDUCTIVE PIGMENTS

No single property of the conductive pigment assumes over-riding importance and the materials used are normally chosen because they exhibit a combination of properties which fit the requirements of the specific application. The cost of the pigment is also very important, except in some defense and aerospace work where performance is of prime importance and relatively expensive systems can be used.

ELECTRICAL PROPERTIES:

It is accepted that the shielding effectiveness of any coating system is closely related to the electrical conductivity

of the coating. The type of pigments used must, therefore, show good inherent electrical conductivity if this property is to be conveyed to the coating system. The metals which are generally used for this purpose and their relative conductivities (compared to copper taken as 1.00) are given in Table I.²

Table I. Relative Electrical Conductivities:

Silver	1.05
Copper	1.00
Gold	0.70
Aluminum	0.61
Nickel	0.20

The actual situation existing in an organic film containing small metallic particles is, however, more complex from the point of electrical conductivity since the metal does not form a coherent film within the organic vehicle. Rather, it consists of a series of discrete particles suspended in the coating and the electrical conductivity is greatly influenced by the way in which the individual particles make contact with each other. The properties which govern this mode of contact, such as shape, size and surface condition may, therefore, play a more important part in determining the coating conductivity than the inherent electrical properties of the particle.

CHEMICAL PROPERTIES:

The chemical properties of the pigment material are of crucial importance since they determine the surface condition of the particle. Materials which are resistant to corrosion and oxidation and are, therefore, capable of presenting a clean metallic surface generate least resistance at the point of contact. Materials which form a conductive surface oxide will similarly give low contact resistance whereas those, such as aluminum, which form insulating oxide films give high particle to particle contact resistance.

Silver, in addition to its high inherent electrical conductivity, shows good chemical properties. It does not form insulating oxide films on its surface and so gives low contact resistance. Also it is generally unreactive in the organic vehicles into which it is incorporated and so shows good storage stability. It is also highly stable in the applied conductive film, ensuring that the initial properties of the coating are maintained during service.

Table II. Environmental Testing for Conductive Coatings

a) Conditioning for 40 hours at 23°C and 50% relative humidity
b) Thermal Cycling 1 hour 85°C, followed by 1 hour 23°C, at 50% humidity, followed by 1 hour 29°C, followed by 1 hour 23°C
c) Heat Testing 56 days at 85°C
d) Humidity Testing 56 days at 35°C and 90% relative humidity

Copper particles also show excellent conductivity when suspended in suitable organic vehicles. Unfortunately, however, the chemical stability of untreated copper is poor and it can react with organic media on storage. Similarly, it does not show good stability in the applied coating film and the excellent initial conductivity deteriorates on exposure to aggressive environments due to oxidation and corrosion.

Specially developed copper pigments have, however, been produced which are stabilized using proprietary surface treatments to render them less susceptible to degradation both in storage and also in the applied coating film. Such pigments have now been developed to the stage where they give satisfactory results after environmental testing such as used by the Underwriters Laboratories in the U.S. A typical test cycle is given in Table II.

Samples are subjected to this type of exposure and then tested to ensure that the electrical conductivity is maintained and also to assess the other characteristics of the coating such as avoidance of wrinkling, blistering, pitting, corrosion, cracking and peeling. As a result of these developments, copper pigments are now available which can be successfully employed in shielding coatings; however, at present commercial acceptance is somewhat limited.

Gold obviously has excellent chemical characteristics both in terms of low particle to particle contact resistance and stability in the vehicle and applied film. Its use is, however, limited to a few critical applications due to its high cost.

Aluminum might seem, in terms of its inherent electrical conductivity, to be an excellent material for this application; however, it readily forms highly insulating oxide films on the surface of the individual particles so that in an organic vehicle little or no conductivity is achieved.

Conversely, from the values of inherent conductivity, nickel would not

seem to be a particularly good material to choose for this application. It is, however, by far the most widely used metal in conductive coatings for shielding and this is due largely to its excellent chemical properties. Nickel pigment particles, when suspended in an organic medium, exhibit low particle to particle contact resistance and hence give rise to good coating conductivity. Also nickel, being extremely resistant to oxidation and corrosion even in aggressive environments and at elevated temperatures, remains stable in the organic vehicle on storage and the applied coating retains its electrical and shielding properties even in difficult operating conditions.

The use of graphite is limited to lower performance applications due to its relatively poor electrical conductivity. Its chemical properties are, however, quite good since it does not form solid surface oxides in the way that metallic pigments do, nor does it readily deteriorate due to corrosive attack.

PARTICLE MORPHOLOGY

Since this type of conductive coating system consists of metallic particles suspended in a nonconductive matrix, the conductivity achieved depends very much upon the mode of contact between the individual particles and, therefore, upon the particle shape. There is a limit to which the shape of small particles can be controlled, however, and this is generally determined by the manufacturing process. Most metals are available in the form of roughly spherical particles and some can be obtained as flakes. Nickel, however, enjoys a considerable advantage in this respect in that it can be manufactured by a number of routes, one in particular, the nickel carbonyl process, which enables a wider range of particle morphology to be achieved. In view of this greater variation of particle shape, this section deals primarily with nickel.

The nickel carbonyl process for the refining of nickel metal was developed at the turn of this century. The principle

is quite simple. Impure nickel metal is reacted with carbon monoxide, under controlled conditions of temperature and pressure, to form gaseous nickel tetracarbonyl. If the conditions are then changed, the nickel tetracarbonyl decomposes to deposit, from the vapor phase, high purity nickel metal and releases carbon monoxide. The process has been described in more detail by Antonsen³ and Hayes and Antonsen.⁴ By subtle changes in the conditions under which the decomposition of the nickel tetracarbonyl is carried out, it is possible to obtain controlled variation in the morphology of the nickel particles.

Typical particles produced by this process are discrete "spikey" spheres of the type described by Hayes and Antonsen⁴ which are not particularly suited to the production of conductive coatings. An alternative morphology with a distinctly filamentary and dendritic shape gives much better results, due to the filamentary structure increasing the area of particle to particle contact within the matrix.

The properties of nickel powder of this type can be further improved to make them more suited to use in conductive coatings in two ways. First, by removing the large and agglomerated particles a more uniform size distribution can be achieved. This leads to better conductivity and improvements in other important properties of the coatings such as appearance and smoothness. Properties of a typical powder type pigment are given in Table III and its structure shown in Fig. 1. Secondly,



Fig. 1. Dendritic nickel pigment.

these particles can be heat treated in a controlled atmosphere producing a cleaner surface which will result in a further enhancement of conductivity.

Nickel particles produced by the carbonyl process also show, as a result of their extremely high purity, good ductility. This has been used to advantage in producing improved pigments for

Table III. Properties of Dendritic Nickel Pigment

Apparent Density:		1.1 g/cc			
Size Analysis:		Microtrac			
Screen (U.S. mesh sizes)					
+ 325 Mesh	0.5%	- 31	Microns	100.0%	
- 325 + 400 Mesh	0.1%	- 22	Microns	72.3%	
- 400 Mesh	98.5%	- 16	Microns	55.3%	
		- 11	Microns	41.8%	
		- 7.8	Microns	32.8%	
		- 5.5	Microns	15.7%	
		- 3.9	Microns	0.0%	

Table IV. Properties of Conductive Nickel Flake

Specific gravity	7.93 g/cm ³	
Apparent density	1.1 g/cm ³	
Thickness	1.0 micron	
Specular reflectance	25.7%	
Screen analysis		Trace
	+ 325	
	- 325 + 400	1%
	- 400	99%

RFI/EMI shielding in the form of nickel flakes. These are manufactured by a ball milling process as described by Antonsen.³ Flakes for conductive applications are produced with a thickness of around one micron and an aspect ratio of between 20:1 and 30:1. The proper-



Fig. 2. Flake nickel pigment.

ties of one such material which was specifically developed with a morphology designed to maximize electrical conductivity, are given in Table IV and the structure shown in Fig. 2. These flake particles are also heat treated, in a controlled atmosphere to give a cleaner surface, thereby further enhancing the conductivity.

Nickel spheres are another morphological form of the metal which can be used in conductive coatings. Particles which are very regular in shape (Fig. 3) can readily be produced and because of this regularity they can be graded to size with considerable accuracy. It is

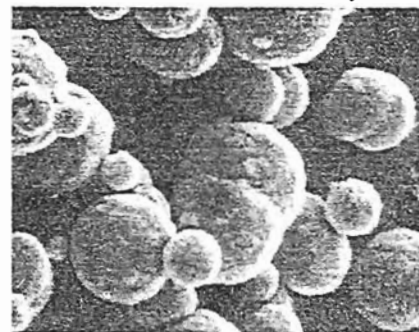


Fig. 3. Spherical nickel pigment.

possible to produce material where a very high proportion of the particles are below a given micron size. For example, the size distribution of nominally - 10 micron material is given in Table V.

This type of regular sphere is not normally used in paint coatings since the conductivity achieved is generally lower than that obtainable with the dendritic and flake nickels as described below. They are, however, used for other coating techniques, such as screen painting, where close control of the particle size is critical and where particles above a certain size cannot be tolerated. This type of technology is used in the production of conductive electrical circuits.

Table V. Typical Particle Size Distribution of 10 Micron Nickel Spheres

Screen Analysis			Microtrac		
+ 20	Microns	Trace	- 22	Microns	100.0%
- 20 + 10	Microns	1.9%	- 16	Microns	97.4%
- 10	Microns	98.1%	- 11	Microns	90.2%
			- 7.8	Microns	72.1%
			- 5.5	Microns	35.7%
			- 3.9	Microns	10.2%
			- 2.8	Microns	6.8%
			- 1.9	Microns	2.7%

Table VI. Effect of Pigment Type and Loading on Resistivity of Coatings

Pigment Loading (Wt%)	Dendritic Nickel		Flake Nickel		Spherical Nickel	
	Dry Coating Thickness (mm)	Resistivity (ohms/sq)	Dry Coating Thickness (mm)	Resistivity (ohms/sq)	Dry Coating Thickness (mm)	Resistivity (ohms/sq)
10	—	—	0.065	Over 20	—	—
20	—	—	0.070	6.3	—	—
25	0.090	1.4	—	—	—	—
30	0.080	0.75	0.065	1.4	0.085	Over 2,000
35	—	—	0.070	0.58	—	—
40	0.110	0.30	0.080	0.25	0.080	150
45	0.135	0.29	0.080	0.22	0.075	24
50	0.160	0.23	0.095	0.18	0.095	17
55	0.190	0.22	0.115	0.13	—	—
60	—	—	0.150	0.12	0.090	4.3
65	—	—	0.175	0.11	0.105	1.8
70	—	—	—	—	0.140	1.4
75	—	—	—	—	0.150	2.5

The other metallic particles used to produce conductive organic coatings are normally only available in one morphological form. Silver is usually employed as flake with a very small particle size and as such is suitable for a very wide range of applications. Copper is generally produced in the form of spheres, with a size not dissimilar to those of the nickel spheres; however, the copper spheres are generally not as regular in shape as the nickel ones.

BEHAVIOR OF METALLIC PARTICLES IN ORGANIC MEDIA

The level of coating conductivity achieved is affected by both the pigment loading and the particle morphology. When the particle loading is too low a coating is produced with relatively poor particle to particle contact. At the same time the presence of greater amounts of the organic binder acts as

a barrier to conductivity.

It would be expected that a flat particle, such as a flake with a high aspect ratio, would present a greater amount of particle area contact than the type of point to point contact expected with spheres. To demonstrate this hypothesis, various nickel pigments were mixed in an organic binder and deposited on glass plates using a doctor blade designed to apply a uniform wet film thickness of 0.380 mm. This relatively thick film was used to make it possible to examine the heavier pigment loadings without damaging the coating integrity due to scoring or other interruptions. Similar trends to those discussed below have been observed in experiments using thinner wet film thicknesses.

Table VI shows that as the pigment loading is increased, so the dry film thickness also increases. Also, it is clear that at equivalent pigment load-

ings the dry film thickness is greatly influenced by particle morphology. The results are summarized in Fig. 4 and show that the flake and dendritic pigments give very similar conductivities at equivalent loadings; however, the flake pigment results in a much lower dry film thickness in achieving the same conductivity. Also, the flake material shows a small advantage at pigment loadings in excess of about 40%. The spherical pigment requires a much higher loading to exhibit any real degree of conductivity and even then does not reach the same levels as the other two materials. This is presumably because only point to point contact is achieved, even under ideal conditions.

Using similar application techniques the effect of wet film thickness on conductivity was examined. The pigment loadings used were selected, from the previous results, at the point where conductivities leveled off (Table VII).

Table VII. Effect of Wet Film Thickness and Pigment Type on Resistivity of Coatings

Applied Wet Coating Thickness	Dendritic Nickel		Flake Nickel		Spherical Nickel	
	Dry Coating Thickness (mm)	Resistivity (ohms/sq)	Dry Coating Thickness (mm)	Resistivity (ohms/sq)	Dry Coating Thickness (mm)	Resistivity (ohms/sq)
0.100	0.055	1.1	0.035	0.48	0.045	8.9
0.125	0.065	0.72	0.040	0.40	0.060	5.5
0.150	0.085	0.55	0.050	0.30	0.075	3.0
0.250	0.110	0.40	0.065	0.22	0.085	1.9
0.300	0.130	0.32	0.080	0.20	0.110	1.8
0.375	0.160	0.23	0.095	0.14	0.125	1.3

Pigment loadings used were. Filamentary Nickel 37 Wt. %
 Flake Nickel 43 Wt. %
 Spherical Nickel 70 Wt. %

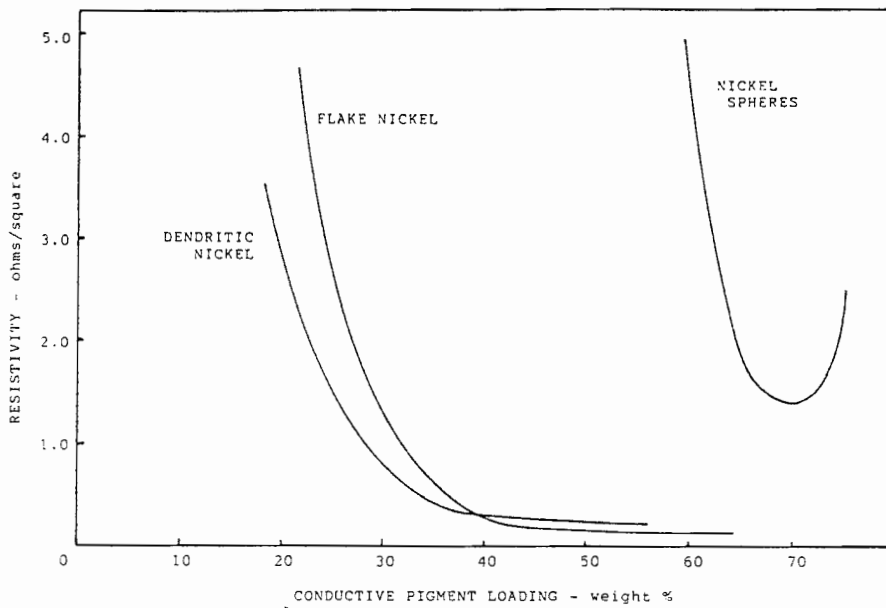


Fig. 4. Effect of pigment loading on the resistivity of conductive nickel coatings.

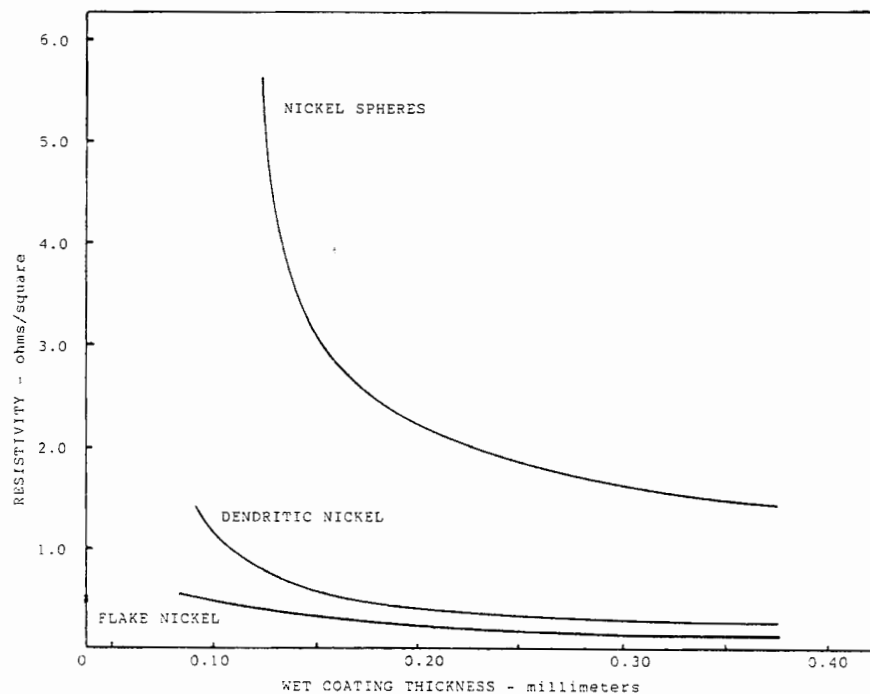


Fig. 5. Effect of wet coating thickness on the resistivity of conductive nickel coatings.

The effect of wet film thickness on conductivity is summarized in Fig. 5 and that of dry film thickness on conductivity in Fig. 6. The superiority of the flake structure is clearly demonstrated in both cases, although the dendritic material also shows conductivity approaching that of the flake. The performance of the flake is undoubtedly due to its morphology which allows much closer packing of the metallic particles and which accounts for the dry coating thickness being lower for a given level of conductivity.

The spherical nickel again shows markedly less conductivity even when the film thickness is increased. The results demonstrate quite clearly the dramatic effect of morphology on conductivity. It would be expected that other metals would behave similarly to nickel if they were available in the full range of particle shapes for testing.

USE OF COATED COMPOSITE PARTICLES

Coating technology in addition to producing effective RFI/EMI shielding

systems also has a secondary function which is assuming increasing importance. This is in the production of coated particles in which material of superior properties is deposited onto the surface of a particle of inferior shielding performance. These composite particles show properties which approach those of the coating material; however, they are usually much cheaper since the core material is normally less expensive than the higher performance coating.

SILVER COATED NICKEL:

This is available, usually as a 15% silver composite which has been found to be adequate in terms of giving full coverage of the nickel substrate. It is also available in two morphological forms, spheres and flakes. The latter is generally favored for coating systems, while the former is generally preferred for use in the production of conductive elastomeric systems, usually based on silicone rubbers.

The performance of silver coated nickel systems approaches that achieved with pure silver but at a reduced cost. The particles show excellent chemical stability in a variety of organics into which they are incorporated and the conductivity remains stable at elevated temperatures, which may be experienced in service or during the curing of the organic system.

SILVER COATED COPPER:

This is available, again generally as a 15% silver composite, but only in spherical form, and is capable of producing conductive systems which give similar performance to those using pure silver; however, this material is less stable than silver coated nickel at elevated temperatures. Copper is very soluble in silver due to the chemical similarity of the two metals, and tends to diffuse into the silver layer. This can cause problems at temperatures as low as 200°C, at which some silicone resins are treated during manufacture. The problem usually manifests itself as a darkening color of the coating system accompanied by a reduction in conductivity.

SILVER COATED ALUMINUM:

It is more difficult to coat aluminum particles with silver than it is nickel or copper due to the readiness with which aluminum oxidizes in air. Similar difficulties exist with the coating of mas-

sive aluminum. Nevertheless, it is possible to produce this type of particle reliably, although the silver content needs to be higher, around 20%, to ensure complete coverage of the substrate and, therefore, reliable performance. The greatest advantage of the aluminum based particles is their lower density which enables higher volume concentrations to be achieved at lower weight loadings. This makes the use of the material more economical and also reduces the overall weight of the system, which is an important consideration in aerospace applications.

SILVER COATED GLASS:

Silver coated glass particles are also

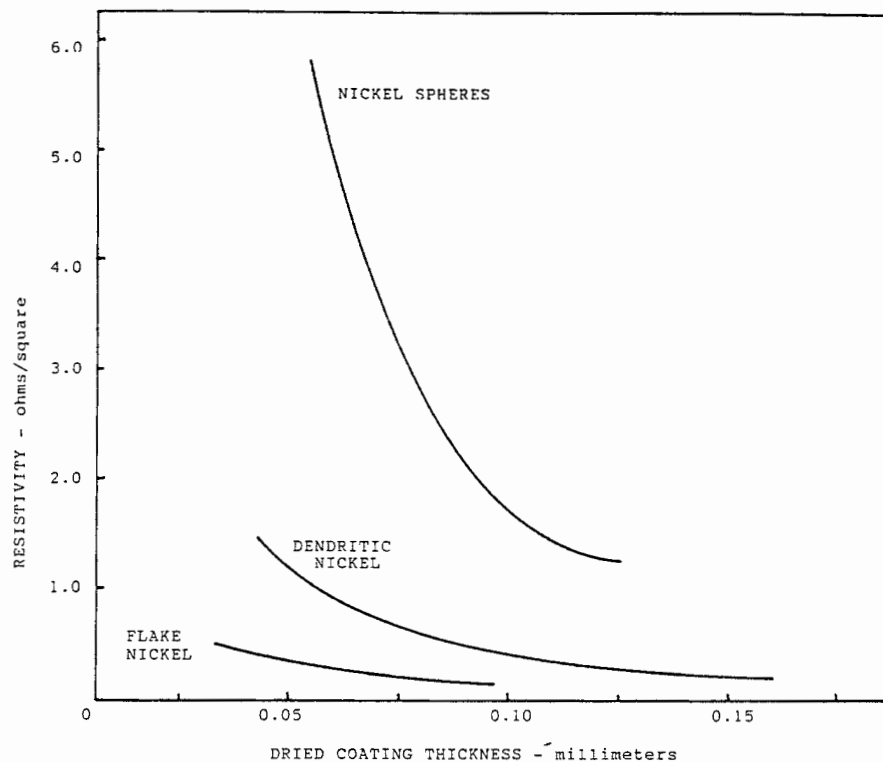


Fig. 6. Effect of dried coating thickness on the resistivity of conductive nickel coatings.

available for this application. Like aluminum they have a low density, particularly if the glass comes in the form of hollow spheres. This gives the same advantages of economy and weight saving; however, glass is obviously a very fragile substrate and it can fracture during the manufacture of the organic system or on its application which can result in inferior properties in the organic composite. It is difficult to get good adhesion of the silver onto the glass and, also, the conductivity of the silver glass composites is not usually as good as that of particles where the silver is coated onto a conductive substrate.

NICKEL COATED GRAPHITE:

Recently the philosophy behind the silver coated particles of using a higher performance coating on a lower performance substrate, has been extended to the application of nickel onto graphite. Very pure nickel can be deposited onto the surface of graphite particles using both aqueous techniques and the vapor phase carbonyl process discussed earlier. The carbonyl nickel coating of graphite is described by Rees, et al.⁵

Nickel coated graphite gives better electrical performance than the uncoated material but enjoys the lower density and, therefore, lower effective cost of graphite. At present the mate-

rials are, however, a relatively new introduction to the shielding market.

SUMMARY

An increasingly wide range of conductive particles is now available for use in organic-based systems for use in RFI/EMI shielding applications. The most suitable particle for any application is determined by a combination of the various properties of the particles.

The inherent electrical conductivity, while being of basic importance, may not be the overriding factor since the chemical properties of the particle and its morphology also play a critical part in determining its behavior in a composite organic based system. Cost is also an important factor which has led to the development of a range of composite, coated particles which combine the high performance properties of the surface layer with the lower expense of a substrate material with inferior electrical properties. MF

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