Hart Coating Technology

Nickel-Coated Graphite

– an answer to electronic shielding problems

What is electronic shielding ?

During the past 20-30 years the electronics industry has been expanding at a rate that can only be described as phenomenal. There is now an immense variety of electronic devices widely available - for both industrial and consumer applications - that were simply only bright ideas in the minds of far-sighted engineers and designers in the 1970s and 80s. The quantities in which these devices are produced are, quite literally, astronomical; for example the world-wide production of mobile telephone sets is probably well in excess of 500,000,000 units per year.

Electronic devices have become a seemingly irreplaceable part of our business and personal lives over the last three decades. During this time they have catalysed tremendous changes in the way in which we conduct our affairs. They have conferred on our society a very wide range of social advantages that benefit not only advanced industrialized countries but also developing nations.

However - as with so many other technological innovations in our sophisticated, industrialized society - electronic devices do exhibit a number of disadvantages. One of the major ones is they are able to receive and also transmit extraneous radiation. This phenomenon, known as radiofrequency or electromagnetic interference (RFI/EMI), can cause the device to malfunction with potentially catastrophic consequences. In response to this situation all of the major industrialized countries have enacted legislation to ensure that these products are properly shielded from unwanted out-going and in-coming radiation. As a consequence, all categories of electronics equipment must now comply with shielding standards that have been devised to ensure their reliable operation. North America, for example, is covered by appropriate FCC Regulations while EU Directive 89/336/EEC sets the standards in Europe.

Shielding technology

As a result of these technical and legislative requirements a large, sophisticated industry has grown up over the last 25 years to ensure that electromagnetic compatibility (EMC) is achieved between the many different types and huge numbers of electronic devices. A variety of highly effective methods have been devised for shielding from in-coming radiation and, at the same time, preventing out-going radiation. These have been developed and refined to meet all types of specifications from the relatively simple ones required for domestic devices to the highly complex systems required for military and aerospace uses.

The other factor that has increased the impact of this problem is that the vast majority of electronics devices are enclosed in plastics housings. This is due to the relative ease, compared to metals, with which plastics materials can be fabricated into complex shapes, combined with the lightness and excellent corrosion resistance of the product. Unfortunately, plastics enclosures – since they are non-conductors of electricity – do not provide shielding from radiation in the way that metal ones do. It has therefore become necessary to incorporate shielding technology into the plastics housings in which the working electronics circuits are enclosed. One well proven method of achieving this is to coat the interior surfaces of this enclosure with a thin, electrically conductive layer – such as nickel-containing paint.

There is, however, an additional problem. Electronics enclosures, such as mobile telephones, are normally assembled from a number of component parts that inevitably have joints between them. In order to provide complete electromagnetic compatibility for the overall device it is therefore necessary to shield these joints, as well as the surfaces of the moldings themselves. This is generally achieved by the use of a purpose designed electrically conductive shielding gasket.

The design and manufacture of shielding gaskets for electromagnetic compatibility applications has become a highly specialized segment of the shielding technology industry. These gaskets must obviously satisfy the demanding specifications needed to achieve the required shielding performance. They must, however, also meet the other physical and mechanical requirements of any type of gasket to ensure effective and durable mechanical sealing in terms of hardness, compression set and tensile strength.

There are a number of techniques used to manufacture shielding gaskets. These include the use of simple metal foils or pressings and metal meshes over a foam core. One of the most important, however, is the use of elastomeric resins, mostly silicone-based, that are loaded with a suitable, electrically-conductive filler selected to achieve the required degree of interference attenuation.

Conductive Fillers used in Shielding Gaskets

Six basic types of particulate filler can be used to provide the necessary electrical conductivity required of elastomeric gaskets employed in shielding applications.

- Pure Silver
- Silver-Coated Materials
- Nickel-Coated Graphite
- Spherical Nickel Powders
- Copper Particulate Fillers
- Carbon-based Materials

The silver and silver-coated fillers obviously exhibit the greatest electrical conductivity and can therefore be expected to provide the best shielding performance, but obviously at a higher cost. So, in applications where performance is the overriding factor – for example space satellites – then one of the silver-based products would almost always be specified. At the other extreme there are applications, typically in the domestic sector, where less expensive carbon-based fillers can provide an adequate level of shielding.

There are also a number of metallic-based materials used in this application that provide shielding performance intermediate between silver and carbon-based products. One of the most important of these is Nickel-Coated Graphite. (It is worth noting that particulate aluminium fillers are not regarded as suitable for this application, despite the inherently high conductivity of the metal. This is due to the highly insulating oxide film that spontaneously forms on the surface of aluminium metal when exposed to oxygen, thus preventing the formation of a conductive particle network.)

Nickel-Coated Graphite Particles

Nickel-Coated Graphite particles have become widely accepted in shielding technology applications over the past decade since they provide an excellent solution to performance requirements. They consistently deliver a very high level of shielding attenuation - in some instances approaching that of silver and silver-coated products. However, the cost is much less than that of silver-based products and therefore more commensurate with large scale commercial applications, rather than with smaller scale military and aerospace ones.

The manufacture of coated particles of this type involves highly specialized technology since the process of coating the surface of a mass of small graphite particles with a uniform nickel coating is not an easy task. Although there are a number of techniques for achieving this, one of the most effective employs a chemical vapour phase deposition technique known as the 'carbonyl process'. This elegant process, which was invented towards the end of the 19th century by Dr. Ludwig Mond, is based on the ability of nickel to react with carbon monoxide to form a gaseous tetracarbonyl compound.

$$Ni + 4CO \longrightarrow Ni(CO)_4$$

Since this type of reaction is specific to the three Group VIII elements - Iron, Nickel and Cobalt - it provides a highly effective method of refining these metals from a mixed ore body. In addition, the volatile carbonyl compounds of these three metals have significantly different boiling points; this enables extremely pure nickel tetracarbonyl gas to be isolated from the mixed gas stream. The commercial usefulness of the process, however, relies on the fact that the chemical reaction between nickel metal and carbon monoxide is reversible.

$$Ni(CO)_4 \longrightarrow Ni + 4CO$$

Under the correct reaction conditions, the gaseous tetracarbonyl will decompose to yield very pure nickel metal plus carbon monoxide, which can be recycled around the process stream. By skilful chemical engineering this simple reaction is employed on an industrial scale to produce massive forms of nickel, such as pellet and powders, and also to coat small particles, of a substrate material such as graphite, with nickel metal.

In practice, graphite particles – having been pre-treated to give the required particle size distribution – are suspended as a fluidized bed in a gas steam consisting of carbon monoxide containing a carefully controlled quantity of nickel tetracarbonyl. When the particles are heated using infra-red radiation the resulting increase in surface temperature causes the nickel tetracarbonyl gas to decompose. This produces a highly uniform coating of pure nickel on the surface of the graphite.

The quality and characteristics of the basic graphite particles used as substrate material influence both the final particle size distribution and apparent density of the nickel-coated composite. They therefore have a critical effect upon the electrical and shielding properties of the final product.

Following the coating stage the composite particulates subsequently require further screening together with closely controlled blending to achieve consistency of particle size distribution and apparent density. Control of these properties is essential to produce consistently a material capable of providing the properties demanded in the electrically conductive composite product.

Three basic types of Nickel-Coated Graphite particle are available commercially with nickel contents of 25%, 60% and 75% respectively. With the 25% nickel grade, the surface coverage of the graphite core by nickel metal is only partial; consequently conductivity properties are not particularly good and this grade is not used in electronic shielding applications With both the 60% and 75% nickel grades, however, the graphite core can be considered to be completely encapsulated by the metallic outer skin and consequently these materials exhibit excellent characteristics in shielding applications.

Of the two grades used for the manufacture of shielding products the 75% nickel material is generally produced from a basic graphite stock of a finer particle size. This yields composite particles typically within the 45 – 100 microns range. The 60% nickel product, on the other hand, is controlled to give a larger finished particle size range, generally between 60 – 140 microns.

Screen Size (US Mesh)	75%Nickel-Coated Graphite	60%Nickel-Coated Graphite
+ 100	0.0 %	0.4 %
- 100 + 150	1.3 %	16.6 %
- 150 + 200	8.3 %	62.3 %
- 200 + 250	26.4 %	12.9 %
- 250 + 325	57.8 %	6.0 %
- 325 + 400	4.5%	0.9%
- 400	1.7 %	0.9 %

Typical Nickel-Coated Graphite Screen Analyses

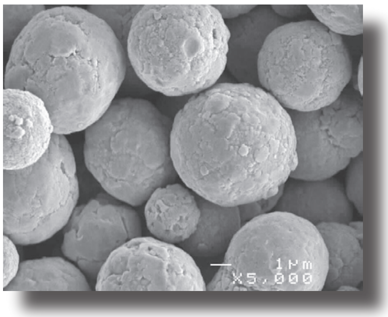
Conductive composite production

A significant range of conductive products, including paints and printing inks as well as gaskets can be made using a non-conductive resin base filled with an electrically conductive particle. The type of particle that provides optimum performance varies according to the nature of the product.

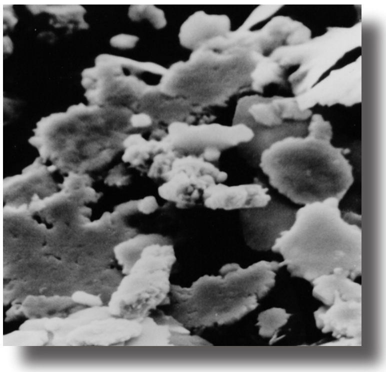
For example, three distinct shapes of nickel particles - spherical, flake or filamentary – can be used to produce conductive paint coatings or inks.

For the manufacture of electrically conductive shielding gaskets nickel flakes and filamentary nickel are considered unsuitable although pure nickel spheres and silver-coated nickel spheres have been used extensively for this type of application.

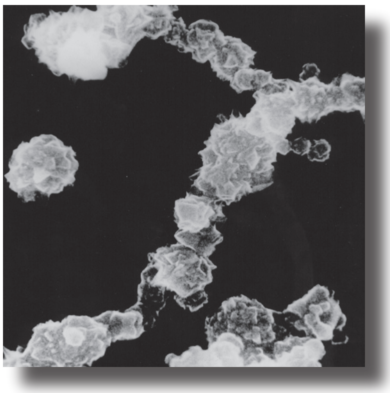
Nickel-Coated Graphite particles are radically different to these other types of product in that they have a random three dimensional shape.



Spherical Conductive Nickel Powder



Conductive Nickel Flake



Filamentary Conductive Nickel Powder

Nickel-Coated Graphite Particles

The conductivity that can be achieved with this type of particle is considerably higher than might be expected. These materials, for example, always out-perform pure spherical nickel particles. At first glance its seems somewhat strange that a particle in which the core consists of less conductive material - i.e. carbon - would give a higher conductivity than one which consists of 100% of a more conductive material, nickel. This is a clear indication that the inherent conductivity of the constituent elements of the composites is not the only factor governing their electrical performance. The other properties such as morphology, particle size distribution and surface chemistry critically influence the conductivity that can
be achieved in practice and the level of shielding effectiveness that can be attained. It is generally considered that the type of packing that can be obtained with this unique particle morphology is the critical factor in the unexpectedly good performance of these products.

It has been found, as a result of years of practical experience, that the particle size distribution must be closely controlled during the production process if maximum electrical performance is to be achieved when it is incorporated into the resin base. The type of distribution profile demonstrated above has been found to give the optimum results. The particle size distribution is also one of the factors controlling the apparent density of the product which is a key quality control parameter for this type of material.

Nickel-Coated Graphite composites

Electrical and Shielding performance

Composite products that consist of an electrically conductive filler suspended in a non-conductive resin matrix conduct electricity by the simple mechanism of 'particle-to-particle' contact. Therefore, until a sufficient quantity of filler has been added to create a connecting network of conductive particles there is little or no conductivity. However, when the point is reached where particle-to-particle contact has been created then a whole network of electrical circuits will be set up, thus creating a fully conductive composite. As a first approximation there is no significant conductivity until the filler content reaches about 45% by weight. Increasing the quantity of filler above this level produces a gradually increasing level of conductivity. Ultimately the limiting value is achieved when the filler content reaches 70% by weight. An increase in filler content above this level not only has little beneficial effect on conductivity but may also render the composite difficult to work (by adversely affecting the viscosity of the product) as well as making the ultimate mechanical properties unacceptable.

The property normally used to quantify the conducting capability of these composite materials is the volume resistivity - expressed in ohm-cm. It is an easy property to measure and also gives a good correlation with the shielding effectiveness of the material. A volume resistivity of less than 0.1 ohm-cm is generally considered to be adequate to provide effective shielding for most commercial applications.

This level of volume resistivity can be achieved with Nickel-Coated Graphite at loadings of 50 – 55% and considerably lower values can frequently be obtained as the filler content approaches the limiting value of 70%.

Filler material	**Silver-Coated Glass**	**Silver-Coated Copper**	**Silver-Coated Aluminium**	**Carbon**	**Nickel-Coated Graphite**
Volume resistivity ohm-cm	0.01	0.004	0.02	8	0.1
Shielding effectiveness (dB)					
100 MHz (E-Field)	100	120	100	80	100
500 MHz (E-Field)	100	120	100	80	100
2 GHz (Plane wave)	90	120	90	60	100
10 GHz (Plane wave)	80	120	80	50	100

Attenuation of conductive fillers in silicone-based composites

Typical resistivity and attenuation values for silicone-based composite materials containing a number of different types of conductive filler demonstrate that the shielding effectiveness that can be achieved with Nickel-Coated Graphite filled composites is comparable, at lower frequencies, to that obtained with silver-coated fillers. At higher frequencies, Nickel-Coated Graphite appears to give superior shielding performance even though the basic resistivity of the composite is apparently higher.

Another factor that frequently affects the ultimate resistivity of the filled composite is the type of curing agent used in the silicone resin. Many of these are strong oxidizing compounds – typically peroxides – which may react with the conductive filler and, in time, increase resistivity. However, with Nickel-Coated Graphite composites post-cure heat treatment processes can effectively be used to remove residual curing agents.

Processing considerations

There are a number of processes that are regularly used for manufacturing electrically conductive gaskets:

i) Cutting from pre-formed sheet
ii) Compression molding – for example of 'O' and 'D' rings
iii) Extrusion of solid or hollow profiles in configurations such as 'D' channel.
iv) Screen Printing – for gaskets with low profile and/or intricate shape
v) Co-extrusion of an outer layer of non-conductive elastomeric material over the top of a conductive elastomer as an improved environmental seal
vi) Mould-in-place (form-in-place) – a rapid technique suitable for very high volume production, such as for mobile phone sets, where the conductive elastomer is dispensed direct onto the component

Nickel-Coated Graphite filled materials are suitable for use in all of these manufacturing techniques. However, the compounds must be formulated so as to optimize their properties for the specific forming process to be used. For example, 60% Nickel-Coated Graphite particles tend to be preferred for extruded, molded and sheet gaskets. On the other hand, the 75% Nickel-Coated Graphite particles, since they are generally of a finer overall size, are preferred for printing processes and for extrusion of fine section profiles.

Apparent density (defined as the actual physical volume occupied by a given mass of filler) is the property of Nickel-Coated Graphite that is most commonly used as a quality control parameter to regulate the electrical and other properties of the composite material. The apparent density tends to decrease with decreasing particle size and also with particle roughness whereas it increases as the particles approach more closely to a regular spherical morphology.

All coated conductive fillers show batch to batch differences in the measured values of apparent density due to differences in particle size distribution and coating thickness. This affects not only the resulting electrical conductivity of the composite product but also the viscosity in the uncured state and other mechanical properties – such as hardness – in the cured state. In the manufacturing process it may be necessary to make adjustments for the apparent densities of different lots of the filler in order to achieve consistent properties of the final product. Filler batches with higher values of apparent density will require a greater loading than those with lower apparent density values.

Resin matrix suitability

Silicone resins are by far the most widely used in this particular branch of shielding technology. However, other elastomeric resins can be successfully employed and will, in appropriate circumstances, actually show advantages compared to silicone. Fluorosilicone resins, for example, are used in two part formulations for form-in-place operations since they cure relatively rapidly at ambient temperatures. Fluorocarbon/ptfe resin is used in high volume applications where a fast cure time is critical if the required production volumes are to be achieved.

Nickel-Coated Graphite particles can also be successfully incorporated into thermoplastic resins. At the moment, however, this type of conducting composite is not as widely produced as those based on elastomeric materials. However, since thermoplastic resins are generally less expensive than silicones volumes may increase in the future.

What does the future hold for Nickel-Coated Graphite?

There is no doubt that, during the last decade, Nickel-Coated Graphite fillers have proved to be a valuable part of the shielding technology market. During this period there have been enormous improvements in all types of electronics devices such as miniaturization, much faster operational speeds, greater memory capacity and increased versatility. Nickel-Coated Graphite products have proved capable of coping with all of the radical changes in design and construction that these improvements have required.

The electronics industry is almost certainly the most innovative and rapidly changing branch of manufacturing technology in the modern world, and promises to remain so. So far Nickel-Coated Graphite fillers have met – and, indeed, positively contributed to - all of the challenges that this industry has faced. They are well placed to become an integral part of shielding systems designed to ensure reliable operation of new, advanced products in the future.

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