New Developments in Metallized Products

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INTRODUCTION

The current trend toward the use of smaller and smaller circuits operating at lower voltages and amperages results in increasing susceptibility to stray radiation. While metallized products offer solutions in some applications, each material's effectiveness is limited by its specific combination of electrical and physical properties. A new family of metallized materials has been developed to offer versatile solutions to EMI problems. These materials consist of thin, continuous layers of various metals strongly bonded to a variety of substrates (fibers, fabrics, films, etc.) of almost any chemical composition. An additional feature of these metallized materials is that plating can be limited to specific portions of the surface. A unique combination of patented and proprietary technologies produces metallized materials which combine the electrical properties (conductivity, EMI shielding, reflectivity, etc.) characteristic of metals without sacrificing the original mechanical properties (strength, flexibility, etc.) of the substrate.

A new family of metallized products has been developed to offer versatile solutions to shielding, reflectivity and other EMI applications.

The key to retaining the substrate's properties after metallization lies in the ability to achieve a continuous conductive layer with metal layers. Since the continuous metal layers in these new materials can be as thin as 0.2 microns, the topography of the original substrate is maintained after metallization. As an example, a yarn composed of 1000 filaments is uniform in color and retains its flexibility after metallization with copper. This indicates that the metallization followed the topography of the substrate yarn since each filament was plated and little or no bridging has occurred between filaments. (The topography of the yarn is all of the surface area of the component filaments.) A second example of topographic retention after metallization is that a holographic pattern on a transparent film retains its holographic image after metallization, even though the film takes on the characteristic color of metal. The absence of a surface etching step in the process used to prepare these materials also promotes precise retention of ultrafine details in the substrate's original topography.

CONCEPTUAL UNIVERSE OF THESE NEW METALLIZED MATERIALS

A great variety of products can be prepared through combinations of substrate form, substrate chemistry, specific metals used, thickness of each metal layer, and the portions of the substrate's surface that are selected for plating. This versatility allows these metallized materials to be optimized for many uses. Applications include EMI shielding, plated plastics, plated holograms, tuned resonant dipoles, infrared reflectors, printed circuits, antistatic garments, and lightning strike protection materials.

The substrate used to produce the metallized material may be of virtually any geometry and surface chemistry. Substrate geometries that have been metallized include fabrics (woven, nonwoven, and knitted), multifilament yarns (continuous and staple fibers), chopped yarns, films, and three-dimensional articles. Chemical compositions that have been plated successfully include aramid, polyimide, polyphenylene oxide, glass, quartz, silicon carbide, aluminum nitride, graphite, polyamide (nylon), acrylic, polyester and cellulosics. Since no chemical swelling or acid etching treatments are used in preparing these materials, even substrates of delicate chemical composition and/or extremely fine geometry (e.g., ultrafine diameter organic fibers) can be metallized. Chemistries which have not been plated satisfactorily are those whose low surface energies inhibit adhesion (e.g., fluorocarbons, polyethylene, polypropylene, etc.).

In principle, substrates can be plated with any metal that can be deposited by an electroless process. Some of the metals that have been deposited are copper, nickel, tin, iron, cobalt, gold, silver, palladium, and platinum. While the intrinsic properties of a specific metal layer generally are those one would expect from a typical electroless deposition on an insulative substrate, two exceptions should be noted. The first exception worth noting is that copper layers in these new metallized materials are much higher in ductility and oxidation resistance than one would expect of thin layers of copper deposited by an electroless process on an insulative substrate. This copper has a ductility of about 10%, which is significantly better than the ductility of about 3.5% cited in the literature for thin layers of electroless copper deposited on a nonconductive substrate.[1] In addition, substrates plated with copper still retain their shiny appearance after two years of storage under ambient laboratory conditions. (Thin layers of copper plated by a conventional electroless plating process on insulative substrates lose their shiny appearance through oxidation in a matter of a few days.) The second exception evolves from the fact that the composition of electroless nickel varies widely with the specific chemistry of the plating solutions used. The solutions currently used to deposit nickel in these metallized materials produce nickel compositions which contain about 10% of phosphorus. Relative to pure nickel, this alloy has improved hardness and corrosion resistance along with reduced conductivity.

One of the valuable aspects of this new technology is that selected portions of the substrate's surface can be activated so that only those areas are metallized. This feature has been used to produce articles as complex as photographs of individuals and circuit diagrams plated in copper on plastic film substrates, or as simple as a multifilament glass yarn that has been nickel-plated in segments that are 1-inch long and are separated by 11 inches of unplated yarn.

CURRENTLY AVAILABLE METALLIZED MATERIALS

While all of the cited substrate forms and chemistries have been plated with various metals as part of an ongoing R&D effort, the initial commercial product development has focused on the production of rolls of nylon, polyester, acrylic, graphite or aramid woven and nonwoven fabrics [up to 72 inches (1.83 m) in width and 500 yard (457 m) in length] plated with copper, and silver over copper. (The fabric must, of course, have a reasonable wet strength - e.g., a nonwoven fabric bonded with a water soluble adhesive is not a suitable substrate for metallization since it would fall apart in the aqueous plating solutions.)

One of the key properties of these new metallized materials is that the uniformity of the metal layer produces products with low resistivities even when the amount of metal is only a fraction of an ounce per square yard. Table 1 illustrates this point with surface resistivity data on metallized nylon, acrylic, and graphite nonwoven fabrics plus a nylon ripstop woven fabric. The metal content of each of the fabrics in Table 1 is in the range of 0.4-0.7 oz/yd^2 (14-24 g/m^2). Since the relative resistivities of copper: silver:tin:nickel (with 10% phosphorus) are 1:1.6:52, it is not surprising that the fabrics with the lowest surface resistivities are the nylon woven and nonwoven fabrics (which are composed of continuous filaments) in which copper or copper plus silver are the only metals present, and that the next lowest resistance is found in fabric in which copper was overplated with tin. As would be expected, the fabrics overplated with nickel have the highest resistivities except in the case of the graphite fabric where the higher level of copper (and/or the conductivity of the substrate fiber) lowers the fabric resistivity. The only fabric in the table composed of nonconductive discontinuous filaments is the acrylic nonwoven, and it is not surprising that this fabric plated with nickel over copper has the highest resistivity.

Table 2 illustrates the change in resistivity of some metallized fabrics after exposure in a hot, wet environment. The testing was done in a Weather-O-Me-

SUBSTRATE FABRIC TYPE	BASIS WT. (oz/yd^2)	METAL(S) ** oz/yd^2	SURFACE RESISTIVITY ohms/sq
Nylon nonwoven	1.0	Cu(0.45)	0.04
Nylon nonwoven	1.0	Sn(0.04)/Cu(0.39)	0.10
Nylon nonwoven	1.0	Ni(0.16)/Cu(0.29)	0.23
Acrylic nonwoven	1.05	Ni(0.35)/Cu(0.35)	0.43
Graphite nonwoven	0.75	Ni(0.10)/Cu(0.67)	0.09
Nylon Ripstop	1.0	Cu(0.30)	0.04
Nylon Ripstop	1.0	Ni(0.15)/Cu(0.32)	0.13
Nylon Ripstop	1.0	Ag(0.19)/Cu(0.22)	0.07

* Measured according to ASTM 4496-85
** Outer metal layer/inner metal layer

TABLE 1. Surface Resistivity of Selected Fabrics.*

SUBSTRATE FABRIC	METAL(S)*	RESISTIVITY (OHMS/SQ) INITIAL	FINAL	WEATHERING TIME (HOURS)
Nylon nonwoven	Cu	0.04	0.29	433
Modacrylic Woven	Ni/Cu	0.3	0.70	450
Modacrylic Woven	Sn/Cu	0.3	3.1	450
Modacrylic Woven	Ni	1.3	15	450
Nylon Ripstop	Cu	0.10	0.43	322
Nylon Ripstop	Ag/Cu	0.11	0.41	322

* Outer metal layer/inner metal layer

TABLE 2. *Weather-O-Meter Test Results.*

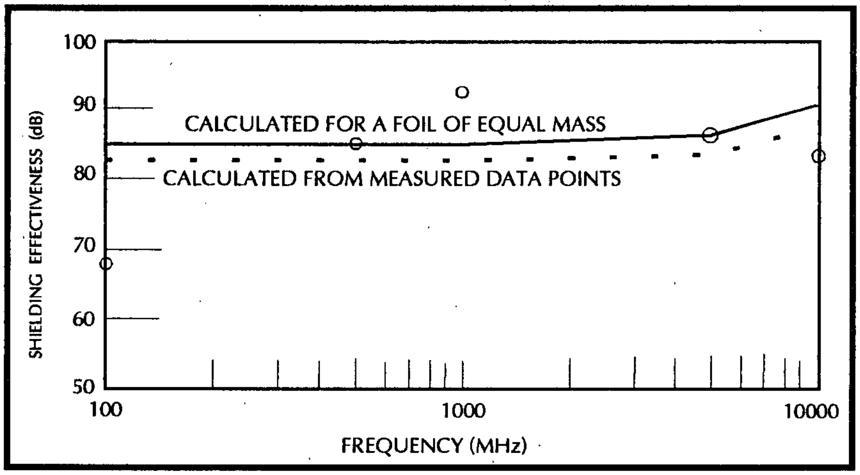

FIGURE 1. *Far-field Shielding: Cu/Nylon Nonwoven.*

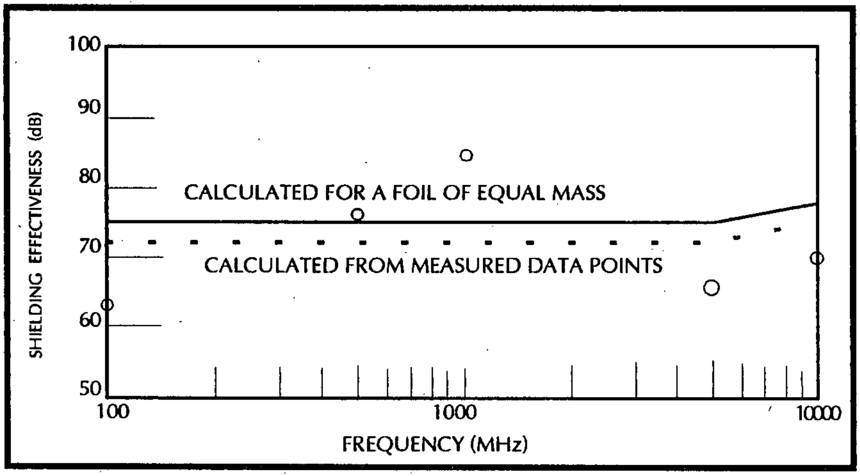

FIGURE 2. *Far-field Shielding: Sn/Cu/Nylon Nonwoven.*

ter according to ASTM G-26. Essentially, the metallized fabric samples were held in a chamber heated by xenon lamps to a black body temperature of 63°C and sprayed with water for 18 minutes every two hours. As one can see from the data in Table 2, the changes in resistivity are relatively small. The small increases in resistivity are particularly unusual for copper deposited in thin layers on an insulative substrate. This provides additional evidence of the unusually good oxidative stability of copper deposited in these metallized materials.

A number of applications for metallized materials requires electromagnetic shielding properties. Figures 1 through 3 show far-field test results for the three metallized nylon nonwoven fabrics identified in Table 1. These tests were conducted by an independent laboratory in accordance with MIL-STD-285 using a 24-by-24 inch port. The samples tested were each prepared from three strips of metallized fabric and contained two "seams" formed by overlapping the strips 1.5 inches and gluing the strips together with conventional wallpaper paste. In these figures, the circles are the actual data points. The data supports three conclusions:

1. A high level of shielding is achieved with a small amount of metal. Shielding levels ranging from 56 to 90 dB were measured on fabrics plated with 0.43-0.45 oz/yd^2 (15 g/m^2) of metal.
2. As would be expected, the level of shielding decreases as the fabric resistivity increases.
3. A simple curve connecting the data points in these figures has no theoretical basis and does not represent the best interpretation of the data.

One way to interpret the nuances in the data in Figures 1 through 3 is to assume that the "true" shape of the shielding curve is the same as that of a metal foil containing the same amount of metal per unit area. In Figure 1, the calculated "foil curve" represents the expected shielding, based on accepted equations and figures,[2] for a copper foil that is 1.7 microns thick. (A foil of this thickness contains the same weight of copper per unit area as the metallized fabric.) The same kind of "foil curves" (Figures 2 and 3) were calculated for the tin on copper and the nickel on copper nylon nonwoven fabrics described in Table 1. In these

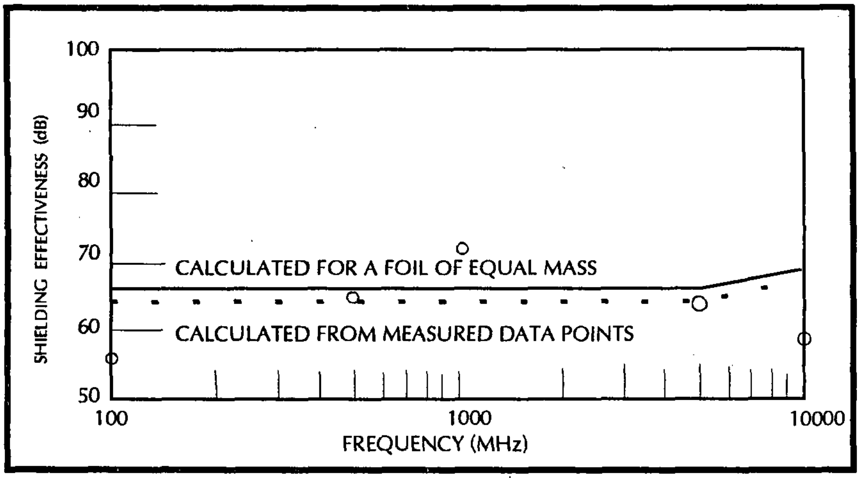

FIGURE 3. *Far-field Shielding: Ni/Cu/Nylon Nonwoven.*

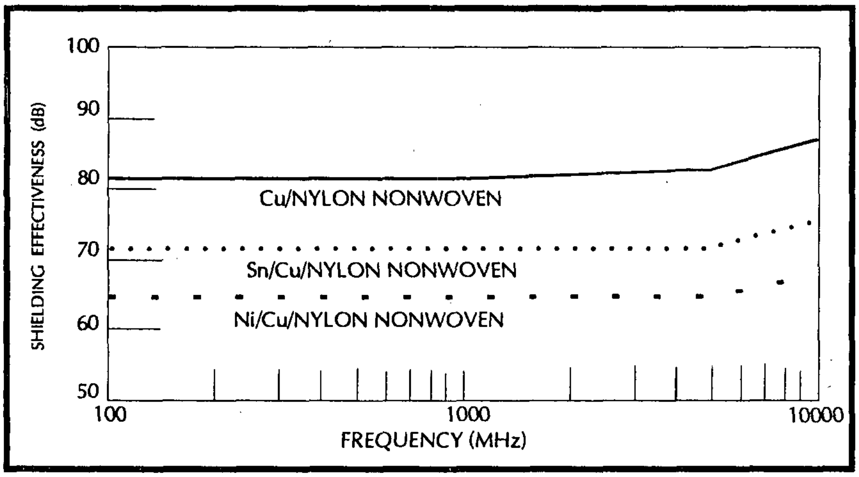

FIGURE 4. *Far-field Shielding: Various Nylon Nonwoven.*

figures, the foil curves were calculated from the sum of the reflection and absorption equations[2] using the assumptions that 1) all reflection was due to the outer layer of metal and 2) absorption could be approximated as the sum of the absorptions of the individual metal layers. Figures 1 through 3 also show curves that were calculated from the measured shielding data by a least squares fit of the experimentally measured data points to the shape of the calculated foil curves. In view of the potential sources of error in any single data point (resonance effects in the test stand, effects of the seams in the samples, the precision of the measuring equipment, etc.) the fit of the experimental data to the least squares curve is quite reasonable. The comparison of the foil curves and the curves generated from the measured shielding data for each of the metallized fabrics indicates that these metallized fabrics provide 95-97% of the decibels of shielding that would be provided by an equivalent mass of metal in foil form. The curves calculated from the measured shielding data for the three fabrics are combined in Figure 4 to again demonstrate the expected inverse correlation between resistivities of the copper, tin over copper, and nickel over copper-plated fabrics (0.04:0.10:0.23 ohm/sq) and their shielding effectiveness.

Two final points should be made with respect to the shielding properties of these new metallized fabrics. The first is that one should not assume that these metallized fabrics will exhibit the increased shielding levels at higher frequencies that are normal for solid sheets of metal. Plating individual filaments means that there are unplated spaces between filaments which will act as significant holes at some frequency above 10 GHz. The second point is that the data in Figures 1 through 4 should not be taken as indicative of the highest shielding levels obtainable, but rather that respectable shielding levels can be obtained with fabrics containing low weights of metal and that higher shielding levels can be obtained by increasing the amount of metal deposited.

Qualitatively, the abrasion resistance of metallized fabrics is good to excellent based on fabric appearance after a Taber Abraser or modified Atlas Crockmeter test or the removal of metal from a metallized fabric by the common scotch tape test. However, the adequacy of abrasion resistance depends on a number of factors, of which the most important is what is required in a specific application. Therefore, applications involving unusually severe abrasion conditions should be evaluated on a case-by-case basis.

Some applications, such as architectural shielding, may require meeting flame retardance specifications. These metallized fabrics can meet this need. As an example, a 4.5 oz/yd^2 (153 g/m^2) modacrylic woven fabric, plated with 1.2 oz/yd^2 (41 g/m^2) of copper, was tested for flame retardance with and without the addition of 0.8 oz/yd^2 (27 g/m^2) of a proprietary flame retardant plastisol. The results of these tests are shown in Table 3. The values shown for the flame-retarded sample meet the specifications of FED-STD-191, Method 5903 and MVSS-302.

SAMPLE	AFTER GLOW, sec	CHAR LENGTH, inches
Untreated	15.2	6.5
Treated	1.7	5.0

TABLE 3. *Flame Retardance Tests.*

PROPERTY	UNPLATED	Cu	Sn/Cu	Ni/Cu
MD Stress, lb/in	14.0	14.9	15.9	16.1
TD Stress, lb/in	5.72	7.46*	8.98*	7.28*
MD Strain, %	36.4	34.8	30.9	31.2
TD Strain, %	25.8	33.6	31.3	23.5
MD Energy, lb/in	431	429	412	438
TD Energy, lb/in	145	218	236*	156

NOTE:
1) Each data point is based on 5 samples.
2) Sample dimensions were 0.27" wide and 1.66" long.
3) Strain rate was 100%/minute.
4) Results with * are statistically different from the unplated fabric at the 90% confidence level.

TABLE 4. *Tensile Testing to Failure of Nylon Nonwoven Fabric.*

In general, these new metallized materials retain the physical properties of their precursor substrates, and no major changes in these properties have been observed upon the metallization of fabrics. Tensile test results for nylon nonwoven fabrics metallized with copper, tin over copper, and nickel over copper are shown in Table 4 along with the test results for the unmetallized fabric. (The fabrics tested were from the same rolls of metallized fabric used to generate the resistivity data in Table 1 and the shielding data in Figures 1 through 4.) Testing was done in accordance with ASTM 1682. A characteristic of this particular nonwoven fabric is that a greater fraction of fiber is aligned in the long axis (machine direction) of the fabric than is aligned in the transverse direction. Because of this asymmetry, the test results on stress, strain, and energy to rupture are reported separately for the machine and transverse tests. The only statistically significant changes that appear to result from the metallization process are the beneficial increases in the transverse direction breaking strengths (TD stress) of all of the metallized fabrics and the TD energy (to break) of the fabric metallized with Sn/Cu. It is felt, however, that these apparent beneficial changes are better viewed as being the result of minor nonuniformities in the substrate fabric (aggravated by the small size of the specimens actually ruptured) or as being due to the nylon fibers annealing slightly at the temperatures used in a production process drying step, rather than as a direct result of the metallization process.

SUMMARY

In principle, these new metallized materials may be prepared from almost any substrate (of virtually any chemistry) and any metal that can be plated by a electroless deposition process. Useful features of these materials include: 1) layers of metal that are well adhered to the substrate, 2) metal layers that are continuous even when the metal layer is quite thin and 3) the option of plating all or part of the substrate's surface. Woven and nonwoven fabrics plated with nickel, copper or copper overcoated with a layer of tin, nickel, or silver are currently available. These materials possess the physical characteristics of the original substrate fabrics plus the electrical properties of the metal layer(s). A nonwoven fabric plated with only 0.45 oz/yd^2 (15 g/m^2) of copper provided over 80 dB of shielding. Metallized fabrics have been prepared that combine 95-97% of the shielding (in decibels) expected of a foil containing the same amount of metal with the desirable properties of the substrate fabric (e.g., flexibility, strength, the ability to be easily glued to a surface, air permeability, etc.). Among the applications envisioned are EMI shielding, and surge protection materials.

REFERENCES

1. J. Wynschenk, *Insulation/Circuits*, March 1977, p. 41.

2. D.R.J. White and M. Mardiguian, Electromagnetic Shielding, 1988, p. 1.22-1.25, p. B.5.

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