

The evolution of conductive coatings

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Overview of conductive coatings

Metallized films serve various needs

Films and papers with bright vacuum-deposited or sputtered metals have been used for eye appeal in the graphic arts field for a number of years. Top coatings with dye or pigment not only inhibit oxidation and abrasion of bright aluminum but can also transform a silver appearance to gold, bronze, or copper.

During a startup, shutdown, or mishap in the vacuum metallizing process, someone discovered that a very light deposit of aluminum was transparent. A metallized film placed on a window at 40–60% light transmission (called "solar plate") will allow one to view what is happening on the more intensely lighted side of the glass. (This is the two-way mirror effect that we have to bear in mind when standing in front of a window that looks black from the inside at night.) While retaining adequate transparency, this amount of metal will reflect heat in the summer and retain heat in the winter, reducing heating and air conditioning bills.

By overcoating the metal side of the film with a light-stable, transparent, gel-free pressure-sensitive acrylic adhesive over the metal, the metal is protected from abrasion, cleaning chemicals, and oxidation. The adhesive permits the metallized film to be applied easily on both commercial and residential windows with a simple squeegee.

Conventional release papers used for pressure-sensitive adhesives were found to impart optical "defects" to the adhesive. These defects were not readily removed with light squeegee pressure. The solution was to develop release coatings for smooth, clear, pliable films, which permitted alignment on installation (Fig. 1).

Packaging for electronic components

Antistatic pink polyethylene used for packaging electronic components consists of tertiary amines based on a fatty acid (tallow or coconut oil) in polyethylene film. These amines bloom to the surface upon cooling after extrusion. Being hygroscopic, they absorb enough water from air at a reasonable humidity to dissipate some static charges. The

fatty acid imparts lubricity to inhibit the buildup of static charge (triboelectric charging) during shipping and handling. With electronic components becoming smaller and more sophisticated at higher mounting densities, they also become more sensitive to static charge dissipation from "microlightning." This is the type of spark you experience when you touch a doorknob after walking across a rug in the winter.

Back in the late 1800s, there was an Englishman named Faraday who was crazy enough to sit in a metal cage to demonstrate that a cage would protect him from "macro-lightning." On a smaller scale, the "solar plate" deposition of metal on a clear film provides Faraday cage protection to electronic components and still allows enough transparency for visual or optical scanning of part numbers and barcodes.

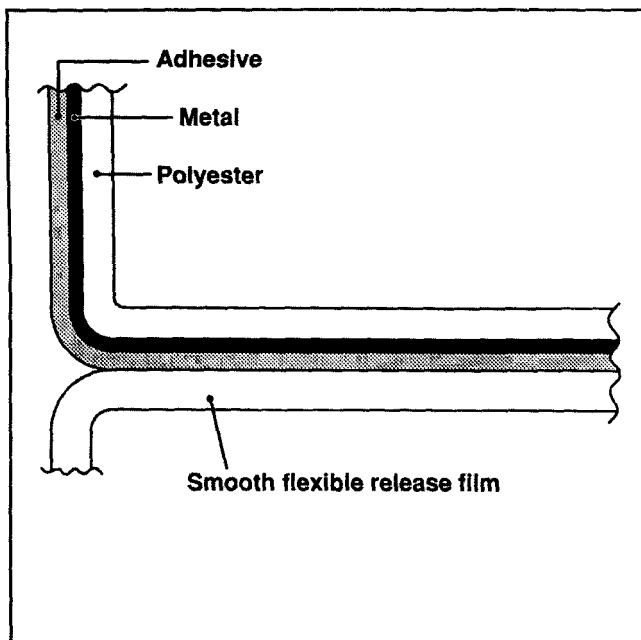
Laminating the solar plated film to the antistatic polyethylene (Fig. 2) minimized internal tribocharging while exhibiting a Faraday cage effect, but the metal exterior needed protection. One version (Fig. 3) had a light resin top coat that maintained the top end of the conductive range (surface resistivity = 10^4 ohms/square). Unfortunately, metal chunks could still be abraded off to contaminate clean rooms and short out high-density circuitry. In another approach (Fig. 4), the metal was laminated between the polyethylene and the polyester film, burying the metal. However, the bare polyester exterior acted as a capacitor to store charges that could migrate to the interior of the envelope.

By controlling the coating weight with poorly insulating resin compounds, a static dissipative top coating (10^9 ohms/square) could be imparted. This coating was found to slowly bleed off charges to a grounded workbench without shocking personnel or the electronic components. The coating also imparted resistance to abrasion, chemicals, and oxidation.

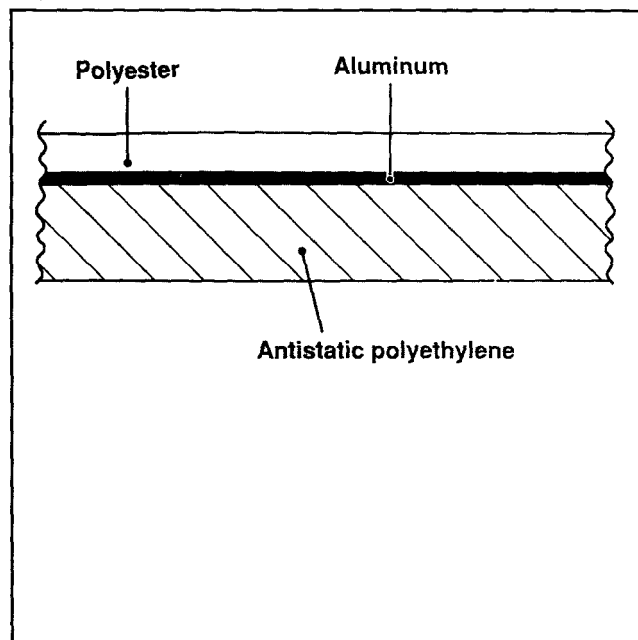
A real challenge surfaced when someone asked for the best of both worlds. If both sides of the polyester could be metallized with half of the aluminum normally used for solar plate, visibility would be retained in a package with a double Faraday cage (Fig. 5). A top coating that was a compromise between a conductive and static dissipative coating (10^6 ohms/square) was requested to protect the exterior metal layer and minimize static charges passing directly to handlers. This was provided by a semiconductive formulation consisting of conductive carbon dispersed in a dielectric binder.

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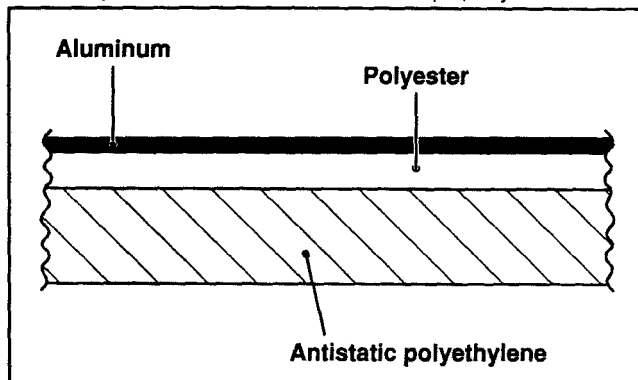
1. Pressure-sensitive solar plate film



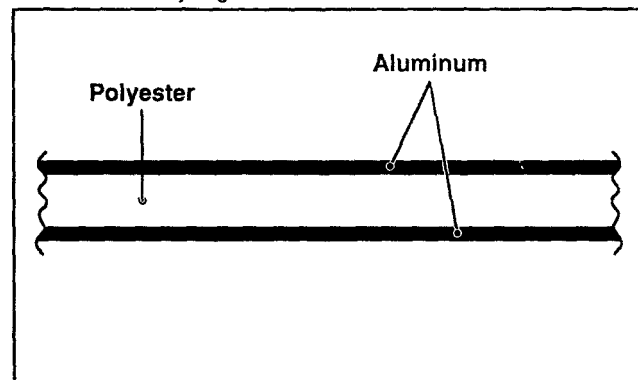
4. "Buried" metal, laminated between the polyethylene and the polyester film



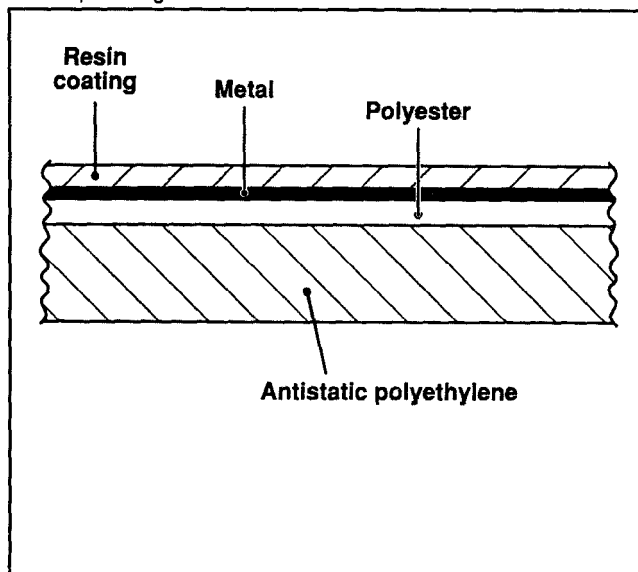
2. Solar plate film laminated to the antistatic polyethylene



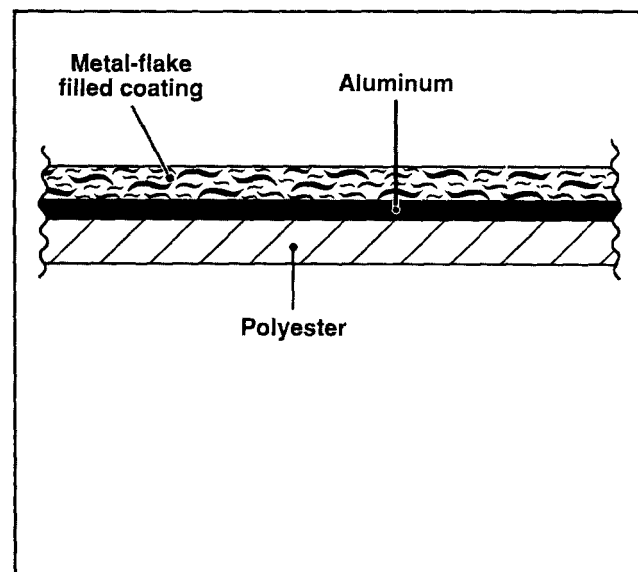
5. Double Faraday cage film



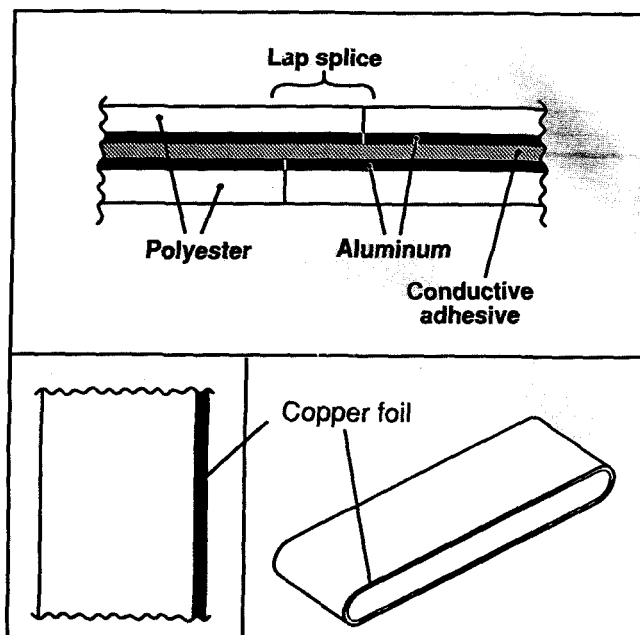
3. Solar plate film laminated to the antistatic polyethylene, with a light resin top coating



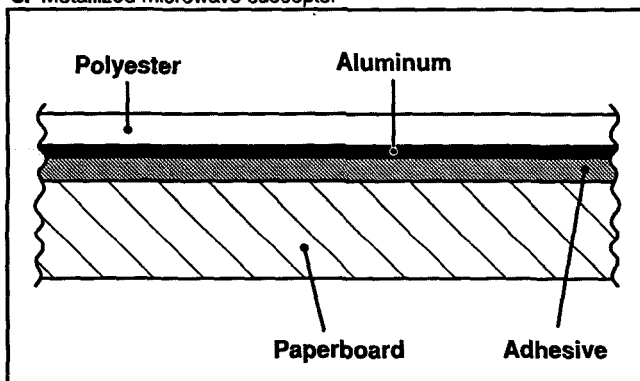
6. Section of the electrostatic printing belt



7. Construction of the electrostatic printing belt



8. Metallized microwave susceptor

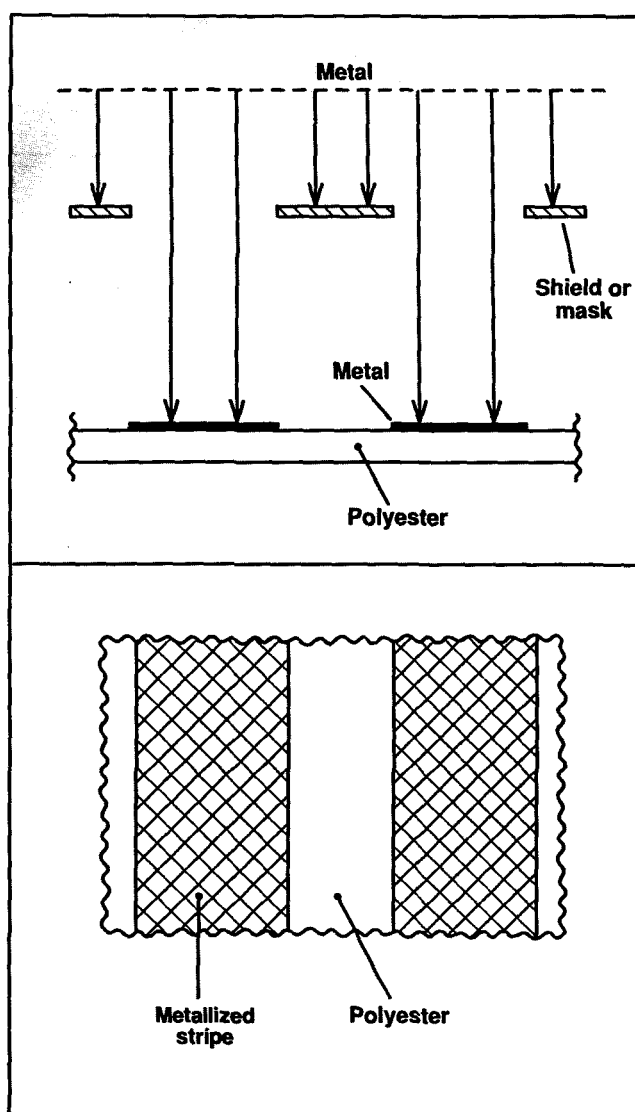


Conductive printing belt

With experience in insulative, static dissipative, and semiconducting coatings, the next test was to marry two metallized films together with a conductive heat-activated adhesive for an electrostatic printing belt. We discovered that a conductive polymeric coating composed of metal flake filler at a low loading would have the same surface conductivity as the base metal substrate. What was surprising was that the same coating applied to a naked dielectric (insulating) film had negligible conductivity. We concluded that the electrical path from surface contact to the metal and from the metal back to the surface was short enough to offer minimum resistance (Fig. 6).

The resulting seamless belt was constructed with two layers of metallized polyester, laminated metal to metal, with an offset edge. A heat or solvent soak of the adhesive permitted assembly of a lap splice. A copper foil strip was laminated with a conductive adhesive to the exposed edge to provide brush contact (Fig. 7).

9. Stripe pattern metallizing process



Microwave susceptors

Meanwhile, the field of microwave packaging was heating up. Aluminum foil would provide shielding, and more than one piece of aluminum foil in a microwave oven could result in the buildup of a charge differential with subsequent arcing (microlightning discharge). In the typical range of 10–100 nm of bright vacuum-deposited aluminum on film, the aluminum would just sit there.

Someone discovered that the “solar plate” level of deposition would heat up in a microwave oven to the point where a polyester film carrier would melt and shrivel up, and the “susceptor,” or microwave-interactive coating, was born. Lamination to a “dimensionally stable” base (such as paperboard, Fig. 8) would maintain flat contact with pizza or breaded and battered fish to make crisping and browning possible. Popcorn popping could also be accelerated to provide more complete popping or make popping possible in an oven with reduced power.

Since heating without a food load can result in scorching of the paper or paperboard, four schemes were concocted

to confine the heat to the area of the food load. Stripe pattern metallizing with shields or masks in the vacuum chamber allowed slitting and lamination in register (Fig. 9). Sheetting and letter-window-type placement lamination were also employed (Fig. 10). Printing a resist, selectively etching, and laminating in register is also done (Fig. 11). Finally, selective adhesive printing and single- or multiple-transfer lamination of "solar plate" metallization in register was proposed to provide more browning and crisping to the area of the food where it was needed most, such as the center of a pizza (Fig. 12).

Within functional and cost limitations, these approaches all have utility, but the food formulations had to be tailored to the heat output of the metallized susceptors. We then said to ourselves, "Wouldn't it be nice to be able to print a microwave susceptor coating exactly where it is needed to control the heat output in the configuration required for the specific food in the package?" The susceptor could be adjusted for the heat necessary for the optimum processing of the best recipe of the specific food.

Susceptor technology

Converting microwaves to sensible heat

Microwaves are a part of the electromagnetic spectrum with wavelengths ranging from less than 1 cm to about 30 cm. As do all forms of electromagnetic energy, they exhibit both electric and magnetic components. The electrically conductive coatings utilize both components to heat up when irradiated with microwaves. The electric current is used directly, and the magnetic component is used via induced eddy currents.

Conductive coatings reflect (r), transmit (t), and absorb (a) impinging microwaves (Fig. 13):

$$r + t + a = 100\%$$

The degree to which the coating does each depends on its conductivity. A nonconductive coating will transmit essentially all microwaves. As its conductivity is increased, the transmission drops, while absorption and reflectivity increase.

In the equation, r ranges from 0% to 100%, and t ranges from 100% to 0% as conductivity increases. Absorption increases much more rapidly than reflectivity, then it peaks and declines as conductivity increases. As absorption increases, reflectivity slowly increases; as absorption decreases, reflectivity increases more rapidly, approaching 100%.

The conductivity of a coating varies with the type and amount of conductive material used in the coating. By adjusting these two basic parameters, the r , t , and a values can be modified.

Although all three properties change with the conductivity of a coating, absorption is the primary characteristic considered when susceptor coatings are formulated. Absorbed microwaves are converted to sensible heat, which is used to augment the direct microwave cooking of a food item placed on a susceptor coating. Transmitted microwaves will bounce back and interact with anything on the incident side of the coating, but absorbed microwave energy will be transformed by the conductive coating into heat. This transformation happens via resistive heating.

The susceptor coating provides a medium for an electric current induced by microwave energy. With vacuum-metallized films, the magnetic component of the electromagnetic field induces eddy currents. Conductive pigment-and-binder coatings are filled with conductive particles that are polarized by the electromagnetic field's electric component. The dipole charges of the particles continuously and rapidly reverse as the field oscillates, causing a current to flow. In both cases, there is a current flow and an inherent resistance to that flow.

This resistance R to the electric current I causes power to be dissipated in the form of heat. The dissipated heat Q is proportional to I^2R , and the current is proportional to the number and size of conductive particles. In effect, particles touching each other form larger particles. If particle sizes are reduced, spaces in the particle chain are formed, and the current decreases much more rapidly than would be expected from just the size reduction of individual particles. Another problem with forming gaps between the particles is that arcing will occur within a certain range of gap distances.

Arcing can be controlled

Arcing, or a discharge through ionized air, occurs when the voltage differential between two particles is at some critical level. The breakdown voltage, or the minimum voltage at which this occurs, depends on the spacing between any two conductive particles.

If the conductive particles are removed from contact with the air, which can be ionized by the current, no arcing will take place. Air contact can be minimized or eliminated by good wetting out of the conductive particle with insulating binder and by covering the conductive coatings with insulating binder coating. However, when the conductive coating heats up upon exposure to microwaves, the binder expands more than the conductive particles, leaving air pockets between the conductive particles and the insulating binder. This air can become ionized, and arcing could occur.

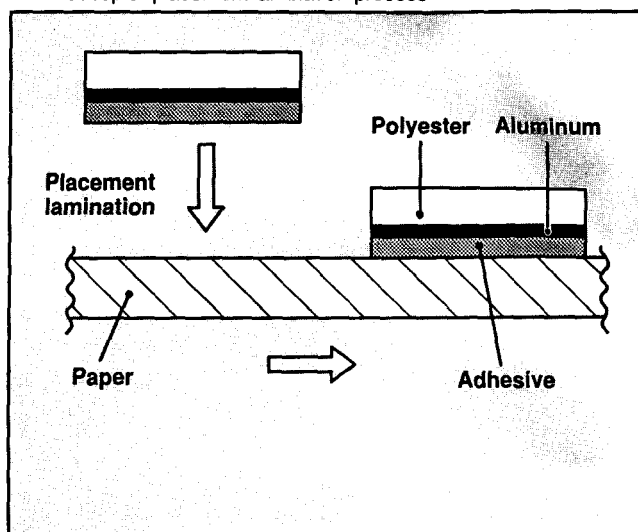
To solve this problem, semiconductive particles are added to the coating and are put in contact with all parts of the insulating binder. Air gaps that may form upon heating are then between conductive and semiconductive particles. Due to the low resistance and partial contact, the voltage differential built up is minimal.

Conventional coating techniques vs. metallization

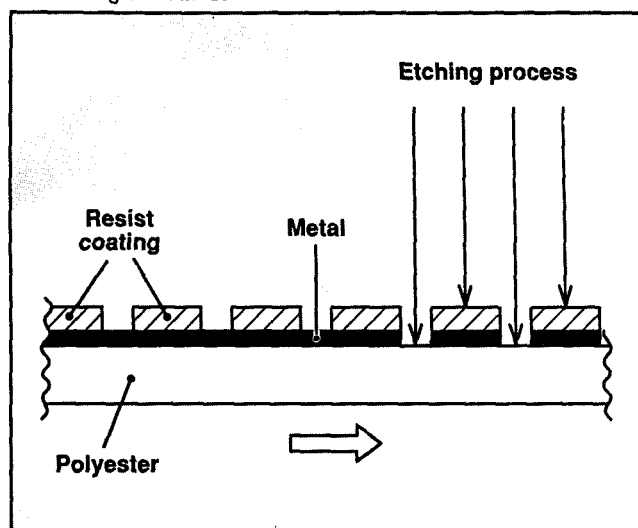
Two basic types of conductive coatings can be used for microwave susceptor packaging: thin metal films and relatively thick conductive coatings of the pigment and binder type. Thin metal films are processed by evaporative deposition, electron beam deposition, and sputtering.

Evaporative deposition film, manifested as metallized aluminum, is the mainstay of the current commercial susceptor market because the process has been around for a while and is inexpensive. However, the deposition limits have to be very tight for the film to work well as a susceptor. Aluminum is deposited on polyester film to a thickness of less than 3 nm. Deposits this thin are difficult to measure, so optical density is used as a criterion. Generally, an optical density (transmission) of 0.18–0.29 is required for metallized aluminum to work as a susceptor. Optical densities that fall below this range are insufficient to

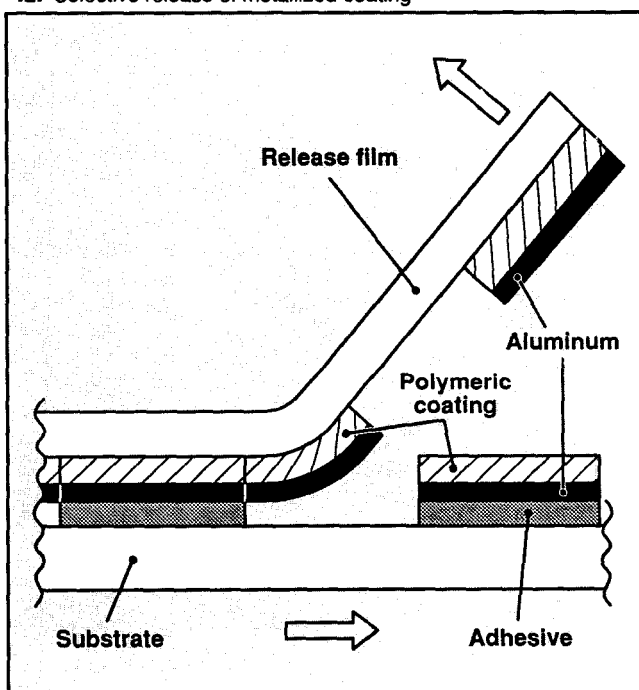
10. Susceptor placement lamination process



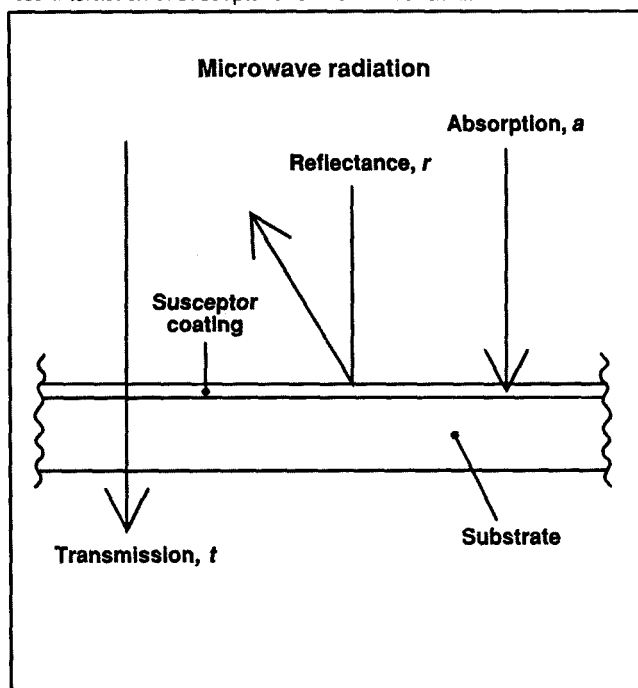
11. Etching of metallized film



12. Selective release of metallized coating



13. Interaction of susceptor and microwave radiation



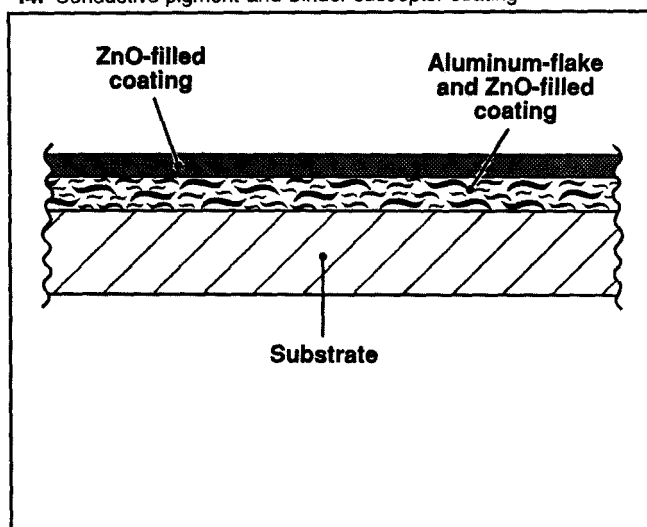
provide heating, and optical densities that are above this range reduce the particle spacing to the point where arcing and reflection occur. Due to the nature of metallizing, an insulating binder cannot be co-deposited with the aluminum to prevent arcing. Co-deposition of a semiconductor might be feasible via sputtering techniques but would probably be too expensive. The acceptable optical density range corresponds to a range of only a few nanometers in thickness, making it essentially impossible to vary the heating capability of a metallized susceptor with today's equipment.

The second type of conductive coatings—conductive coatings made from pigment and binder—is meant to contend with the shortcomings of the thin metal films. Arcing problems can be solved by adding more binder,

a different binder, wetting the pigment better with the binder, or adding semiconductive particles. There is more leeway in varying the heating capability of the conductive pigment-and-binder coating, because its particles are so much larger than those of thin metal films. Simply adding more coating (increasing the coating weight) makes it hotter, because there is more material to absorb microwaves. For the same reason, increasing the conductive particle concentration will also make it hotter, but this tactic increases the chances of arcing. However, adding semiconductor minimizes that possibility.

Conductive pigment-and-binder coatings can be made by any of the established methods by which other filled organic coatings are made. They can be made as water-based, solvent-based, high-solids, or hot-melt coatings.

14. Conductive pigment-and-binder susceptor coating



They can be coated, extruded, cast, powder-coated, or printed. Conductive particles can be incorporated in many forms such as powders, flakes, fibers, beads, and needles. Blends of different forms and particle sizes can be used to achieve various desired effects and minimize filler loading. Different conductive species such as aluminum, copper, silver, nickel, zinc, brass, bronze, and stainless steel can be used.

One embodiment of a conductive pigment-and-binder susceptor coating is aluminum flakes and zinc oxide (ZnO) dispersed in polyether sulfone (PES) resin. Aluminum was chosen for its electrical conductivity, and the flake form was selected to provide good particle-to-particle contact to further improve its electrical conductivity. The ZnO, a semiconductor, was added to eliminate arcing. PES resin was chosen for its high melting point and resistance to thermal degradation. Since the susceptor will get very hot, any thermally-induced physical changes in the binder that would adversely affect the susceptor's performance should be eliminated or delayed. PES also has a high breakdown resistance, further reducing the chances of damage from arcing. PES was used in solution form. Further protection from arcing can be achieved by overcoating the susceptor coatings with a ZnO-filled PES coating. This overcoating diminished the chance for ionized air to come in contact with the aluminum flake particles (Fig. 14).

Other semiconductors can be used to further improve the heating capability of the susceptor. The addition of carbon black accelerates microwave heating because, unlike ZnO, carbon black absorbs microwaves readily, due to its high dissipation factor. The absorbed energy is dissipated as heat. Unfortunately, this heating cannot be slowed down in the absence of a heat sink as long as microwaves are impinging on the susceptor coatings, so heating continues until the susceptor coating or the food or substrate in contact with it ignites. Such uncontrolled heating is called "thermal runaway." Carbon, as the sole susceptor coating filler, causes the most severe thermal runaway, but other susceptor coating fillers also cause this effect to a lesser degree. Because of this thermal runaway problem, susceptors embodied as conventional coatings have not replaced metallized coatings in the marketplace.

Unlike a coated susceptor, a vacuum-metallized susceptor will "shut off" or stop heating with thermally induced breakdown of the metallized film.

A typical metallized susceptor is coated on polyester film and laminated metal-side-down to the paperboard. When it is subjected to microwave radiation, the induced current initiates resistive heating. As the polyester film approaches its melting point, it starts to shrink, and small cracks appear in the film. These cracks isolate the aluminum layer into islands, reducing the rate of microwave absorption. Essentially, the susceptor goes from being conductive to insulating and therefore from absorptive to transmissive, and it is no longer capable of converting microwaves to heat.

To date, there are no commercial alternatives to metallized film for disposable film packaging. There are nonmetallized-type conductive coatings on permanent cookware, but they are reusable and are not limiting in temperature, and the cookware can withstand repeated high temperatures. To avoid burning the paperboard packaging, the susceptor must not reach 451°F, yet most foods need temperatures of over 400°F to be properly browned or crisped. Therefore, the susceptor temperature must level off between 400°F and 450°F or must simply shut off if paperboard is used.

For a susceptor to stop being absorptive or to shut off, the coating must become more conductive or more resistive, so that it becomes microwave reflective or transmissive, respectively. The former tactic is more difficult because most conductive materials are inherently more conductive at lower temperatures. Semiconductors, such as titanium (III) oxide, increase in conductivity with increasing temperatures, but they are not conductive enough in the first place to be significantly microwave absorptive. Conductive coatings that do work as susceptors, on the other hand, do lose some conductivity with increasing temperatures but not to a significant degree at 450°F. Some way must be found to break up the conductive path at specified temperatures by (a) reducing the conductivity of individual particles (i.e. oxidation) or (b) separating the conductive particles so that the current can't jump the gap.

An example of increasing conductivity is to add ferric chloride (FeCl_3) to an aluminum-filled coating. Upon microwave heating, the FeCl_3 will react with the aluminum, but toxic fumes of hydrogen chloride (HCl) are produced as a by-product. Safer reactants that react at the necessary temperatures and speed have not been found.

An example of increasing resistivity is to make a coating with aluminum flakes in polyethylene. When the susceptor heats up, the polyethylene expands, and the aluminum flakes move during the expansion process. Unfortunately, the coating doesn't flow outward in its original shape. Arms may radiate outward, or holes may form in the middle. Furthermore, the aluminum flakes do not separate evenly but tend to agglomerate, forming dense spots that heat even more, and arcing may occur between the agglomerates. If these problems can be solved, coatings could be developed that shut off at various temperatures or shut off with varying delay times.

An inherent advantage of susceptor coatings that are conventionally applied is that they can be printed into any desired shape. Vacuum-metallized susceptors have to be

stenciled, stripped off, or hot stamped to achieve even an approximation of a desired size or shape. Printing would allow the exact dimensions needed. Since no excess would be used in a package, costs could be reduced.

Printed susceptors have been developed which were tuned to specific food loads, types of heating requirements, and geometries, but they are not yet fully idiot proof. A manufacturer or supplier must remember that a seven-year-old child might punch in 50 min rather than 5 min, walk off to the television set in another room, get interested in cartoons, and be unaware when food starts burning in the microwave oven.

Conclusions

While Dennison has capabilities for vacuum metallizing, we also have a wealth of experience in converting and printing. Combining this with the growing home microwave cooking market was a logical match. Printing microwave susceptor patterns is consistent with the type of large-scale commercial printing routinely done by our Packaging Systems Division. Conductive coatings were developed for specific food products with faster heat-up rates and longer heating times than could be obtained with existing metallized film technology. When cooking instructions are followed, the printed susceptor will provide optimum cooking of a deluxe pizza with thick sauce, extra cheese, and toppings, for example, but without a soggy crust in the center. This has resulted in two patents on conductive microwave coatings. Localized microwave radiation heating: U.S. pat. 4,864,089 (Sept. 5, 1989) and U.S. pat. 4,876,423 (Oct. 24, 1989).□

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