# New developments in antistatic and conductive additives

**Antistatic, electrostatic dissipative (ESD) and conductive additives are in demand for plastics compounds used in many applications, from packaging to automotive. Additive suppliers have introduced new migrating antistats, permanent antistats, and nanomaterials for this market. Jennifer Markarian reports for *Plastics Additives & Compounding*.**

## *Migrating antistats*

Migrating antistats diffuse to the polymer surface over time, creating a thin layer that attracts water molecules. The water molecules provide a conductive pathway that prevents build-up of static electricity. Antistatic additives reduce a polymer's surface resistivity to the range of $10^{10}$ to $10^{12}$ ohms/sq., providing a slow static decay rate that prevents charge accumulation (see Figure 1). Antistats are used widely in packaging such as film, thermoformed containers, and PET bottles, in which they help surfaces separate during production and reduce dust attraction for short-term cosmetic improvement. Traditional migrating antistats include long-chain alkyl phenols, ethoxylated amines, and glycerol esters like glycerol monostearate (GMS). European Union (EU) regulations for food-contact packages limit antistats to very low levels, comments Dr. Alexander Lichtblau at Clariant, which produces Hostat antistats. In the EU, regulations prohibit phenolics in food packaging, and users prefer to avoid amines, adds Paul Pitman, technical manager for polymer additives at PCC Chemax., which introduced several amine- and phenol-free antistats at K2007. Another new product, PCC Chemax's Maxomer AS-1018/75 DC, offers longer-term performance of up to a year in polyolefins, including thin films. "We can obtain a more constant performance by fine-tuning load levels and migration rates specific to the polymer formulation and application," says Mr. Pitman. Migrating antistats are also being considered for static charge protection in plastic and wood-plastic composite decking, where thick sections can hold a large reservoir of antistat to provide longer term protection, says Mr. Pitman.

While migrating antistats offer cost-effective protection for short-term applications, other applications need longer-term protection or the lower resistivity required to prevent sparks and protect electronics from electrostatic dissipation. These applications can use permanent antistats or conductive additives such as carbon black, conductive fibres and nanomaterials.

## *Permanent antistats*

Inherently dissipative polymers (IDPs) form a conductive polymer matrix or interpenetrating network within the base polymer, offering non-leaching, permanent static dissipation at a faster static decay rate than migrating antistats,

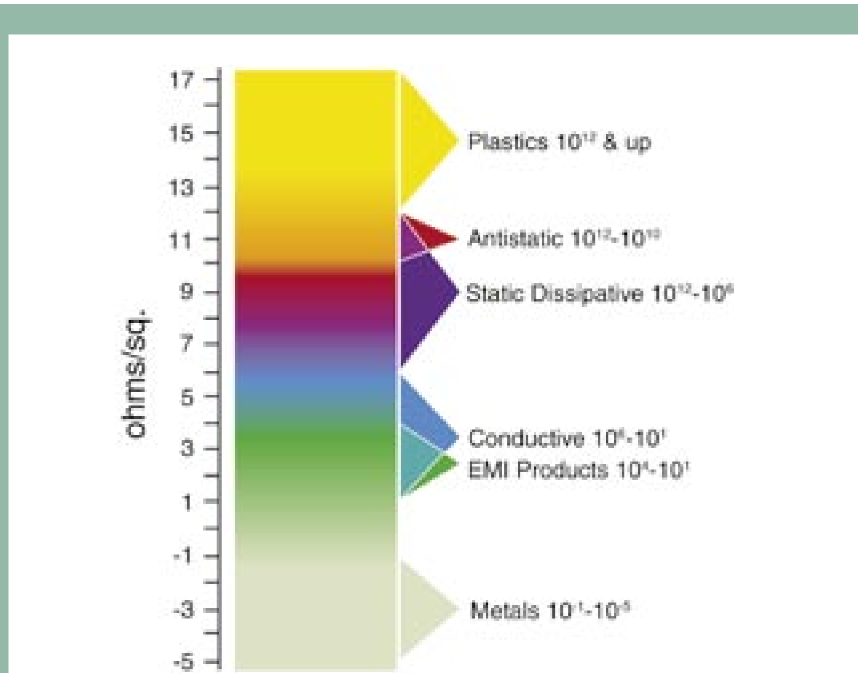



*Figure 1: Resistivity chart - the conductivity, and inversely the resistivity, of a material are described by its surface resistivity (ohms/square). Source: RTP Company.*

typically $10^8$ to $10^{12}$ ohms/sq. surface resistivity, depending on amount and dispersion of the additive in the polymer. Unlike migrating antistats, most IDPs operate nearly independent of relative humidity, although surface resistivity will be slightly higher (less conductive) at low moisture levels (see Figure 2). IDPs are colourable and non-sloughing, giving them an advantage over carbon blacks.

Suppliers say that IDPs are taking some market share from migratory antistats, but that most growth applications are in different market segments requiring long-term, reliable ESD protection. For example, the growing use of electronics in many markets is driving increased demand for ESD protection during electronics production, packaging, shipment and use. Because of miniaturization, electronics are increasingly sensitive to particulate contamination and must be protected from lower levels of static charge. IDPs in trays, conveyor belts, and cases for electronic circuit production prevent static discharge that could destroy sensitive circuits. Even in packaging of electronics, more reliable ESD protection offered by permanent antistats is desired to protect the relatively expensive packaged product during shipping and handling, say suppliers. Other key applications include copiers and printers, where IDPs prevent charge build-up that might cause paper jams or mis-feeding.

Industrial packaging is a new growth market for ESD additives, as traditional packaging like paper and metal continues to be replaced with plastic, notes Dr. Wolfgang Diegritz, European marketing manager for electrical and electronics at Ciba Corporation. Flexible intermediate bulk containers (IBC) must be protected from static discharge, because a spark could lead to fire or dust explosion. IBCs for packaging powdered pharmaceuticals are a large application area for IDPs in Europe, where stringent regulations require users to guarantee no interaction with the package contents, adds Tatiana Damian, European marketing manager for Entira Antistatic at DuPont Packaging & Industrial Polymers.

Besides these primary applications, preventing charge build-up in artificial turf is a growing business for permanent antistats, particularly in Europe, notes Basker Lalgudi, market development manager for Pebax at Arkema. In artificial turf, the non-leaching property of polymeric antistats is important.

Cost-performance of IDPs as a class has improved over the last few years as capacity expansions worldwide drove costs down and product optimization led to improved performance, explains Dr. Diegritz. He comments that with improved cost-performance, IDPs can even move into aesthetic antistatic uses, eliminating dust attraction in cosmetic packaging, automotive interiors in new cars, appliance housings and window blinds, for example.

Commercial polymeric IDPs include Arkema's Pebax®, Ciba® Irgastat® P, DuPont's new Entira™ Antistat, and Sanyo Chemical's Pelestat (distributed in the U.S. by Toyota Tsusho America). Commercial, non-polymeric permanent antistats include Kenrich Petrochemicals' Ken-Stat® organometallic KS N100 and KS MZ100. These transparent and non-blooming additives form bipolar layers that allow electron transfer through their metallic centres.

Arkema's standard Pebax antistat grades are polyether block amides based on either PA6 or PA12 chemistry. Recently, Arkema developed two new technologies that use a different chemistry to gain improved ESD performance while maintaining processability. While standard Pebax (used at 10-15 per cent) typically show resistivity of $10^9$ to $10^{13}$, the new grades achieve $10^8$ to $10^{12}$. Speciality compounders have been able to bring this down to $10^6$ to $10^8$ with their own proprietary technology, says Mr. Lalgudi. He adds: "Lower resistivity levels allow users to meet the increasingly stringent requirements from electronics producers or the strict requirements of explosives packaging. In applications that don't require lower resistivity, the new products could allow lower use levels." While currently available in pilot-scale quantities, the new grades are expected to be produced in a commercial trial this summer.

DuPont's Entira™ Antistat IDP is based on an ethylene ionomer, which makes it compatible with polyolefins as well as other polymers like ABS and polystyrene (see the May/June 2007 issue of *Plastics Additives & Compounding*). This compatibility results in transparency and a smooth surface for polyolefin packaging and blow moulded cosmetic containers, explains Dr. Karlheinz Hausmann, global technology manager for DuPont Cosmetics Packaging Solutions. Because it does not migrate, Entira™ AS does not interfere with film sealing properties. Entira™ Antistat can also be used in rigid bulk ABS containers for flammable liquids, where it meets long shelf life and translucency requirements. Entira™ Antistat MK400 has food contact approvals and maintains performance down to 35-40 per cent relative humidity. Entira™ Antistat 500 functions at 25-30 per cent relative humidity but does not have food contact approvals. MK400 and AS500 are not process temperature limited and can be used in all resins. Typical resistivity levels are $10^8$ to $10^{12}$. Entira™ Antistat SD 100 has food contact approvals and maintains resistivity of $10^7$ to $10^{12}$ at low relative humidity levels (down to 12-15 per cent), but is limited to lower processing temperatures.

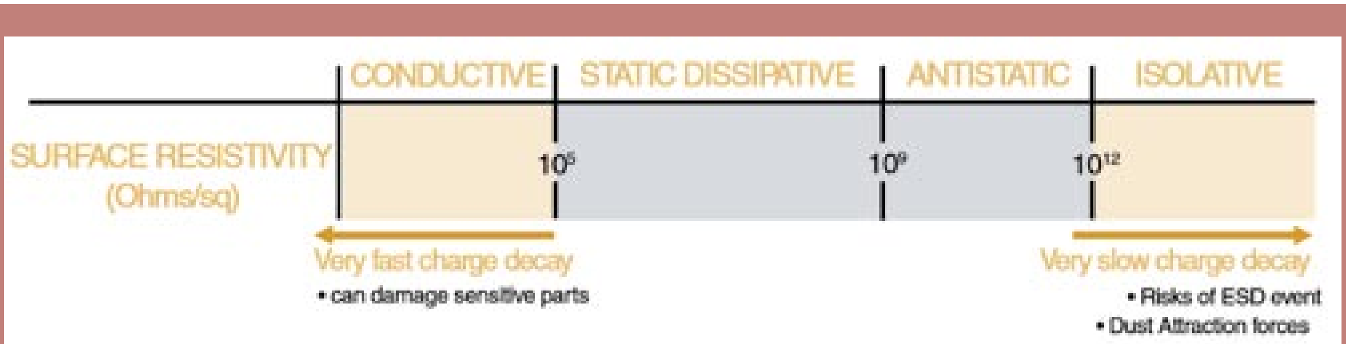
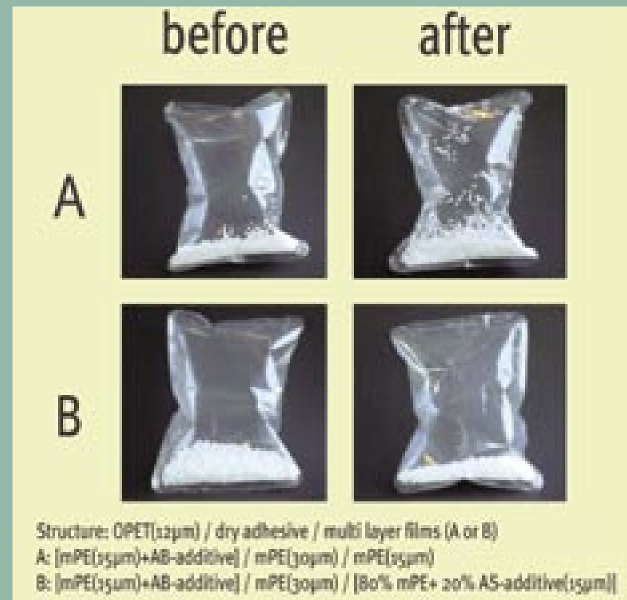



*Figure 2: Surface resistivity versus relative humidity in the air. Source: Arkema.*

Entira™ AS MK400 from DuPont combines good antistatic properties with strong ultrasonic welding performance and high moisture permeability. Potential applications include packaging for pharmaceutical and cosmetic products, electrical components, food and drink as well as pallet packaging.




Effect of the new permanent antistatic agent DuPont Entira™ AS MK400 on the development of static charge after rubbing with a cloth.

Inherently conductive polymers (ICPs), primarily used in printed electronics and coating applications, saw some use as conductive additives, but their use has dwindled. Panipol Oy stopped production of Panipol CX (its polyaniline polymer additive) in 2008, choosing to focus on inks and printed electronics. Panipol is looking for companies interested in licensing the CX technology.

### Conductive particles and fibres

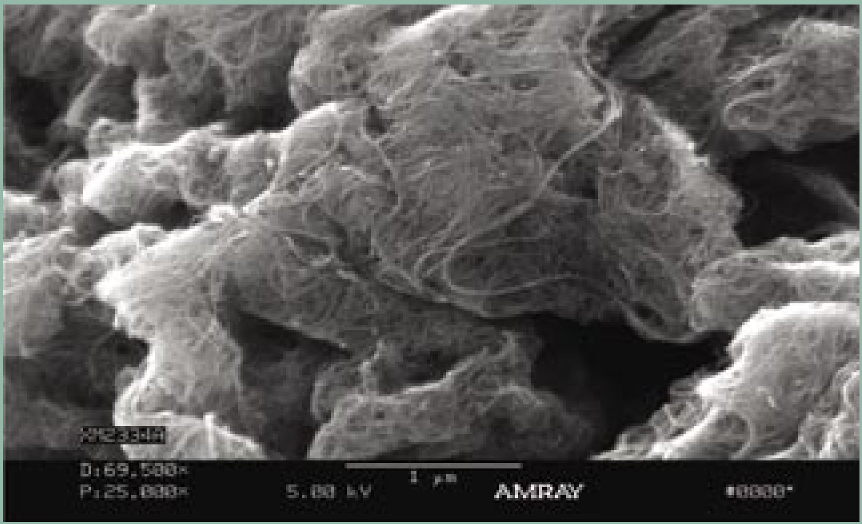
Carbon blacks and conductive fibres, including graphite and metals, can be compounded into polymers to make them conductive, with resistivities in the range of about $10^1$ to $10^6$ ohms/sq. (see Figure 1). Graphit Kropfmuehl's graphite particles, which have been optimized for high conductivity, have a high surface area that facilitates connection of the conductive particles. "At the percolation threshold, graphite particles have resistivities around $10^5$ to $10^6$, which decrease rapidly with increasing graphite levels to almost metal-like conductivity ($10^1$)," says Dr. Robert Feher, R&D director at Graphit Kropfmuehl. Graphite particles are used mainly in applications that require both thermal conductivity and electrical conductivity. Graphit Kropfmuehl is developing products optimized to perform at lower fill levels, which should allow them to compete better with work-horse carbon black in electrically conductive applications, says Dr. Feher.

### Nanomaterials as conductive additives

Carbon nanotubes (CNTs) continue to grow in use as non-sloughing, conductive additives that also maintain or enhance physical properties. CNTs are used at very low loadings that reduce weight and do not interfere with polymer properties. "Costs are coming down as more players enter the market and as larger volume application demand comes in," says Max Lake, president of Applied Sciences Inc. (ASI). He says that CNTs are used in small volumes in space and sporting goods applications, but the largest volume use is automotive applications such as electrically conductive polyamide fuel lines. "Automotive is the real future for CNTs, as the amount of plastics used in cars continues to grow. Emerging applications include under-the-hood (bonnet) electronics and electrostatically-painted body panels," says Mr. Lake. "Nanotubes still represent the pinnacle of price/performance compared to other ESD additives, but we find that the applications needing higher performance continue to grow," adds Patrick Collins, marketing director at Hyperion Catalysis. For example, in automotive fuel systems, CNTs do not affect barrier or swell characteristics. CNTs are replacing carbon black or carbon fibre in electronics applications that have increasing requirements for minimal contamination and high, uniform ESD protection in complex moulded parts. "These requirements are particularly important in the hard disk drive and computer chip manufacturing markets, where greater storage density and smaller feature diameter make devices smaller and more sensitive to ESD and contamination," explains Mr. Collins.

Multi-wall carbon nanotubes (MWCNTs) have been used commercially as conductive additives for plastics since the early 1990s and are produced by several companies, including Hyperion Catalysis, Arkema and Bayer. MWCNTs are concentric graphitic rings about 10 nanometers in diameter. Because CNTs are difficult to disperse, Hyperion Catalysis sells FIBRIL MWCNTs as a pre-dispersed masterbatch to minimize variability and dispersion problems in the subsequent custom compounding step. "Poorly dispersed nanotube-based compounds perform no better than using carbon black or carbon fibre. Dispersion is critical to seeing the nanotubes' benefits in use," cautions Mr. Collins.

Carbon nanofibres (CNF) have a larger

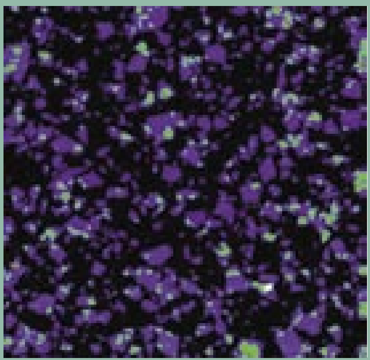



*Scanning Electron Microscope (SEM) picture of the tertiary structure of Unidym's XM conductive polymer grade of carbon nanotubes.*

diameter (10 to 100 nm) than MWCNTs. Pyrograf Products Inc., the manufacturing affiliate of ASI, produces Pyrograf-III carbon nanofibres. The graphitic structure can be manipulated to meet performance requirements for a specific application, says Mr. Lake. ASI's newest CNF, PR-25, is twice as electrically conductive as other CNFs and is also highly thermally conductive. PR-25 is currently available for commercial trials. ASI plans to transition PR-25 to the Pyrograf Products lines in September 2008 for full commercial production.

Fullerene nanotubes (or tubular fullerenes), including single wall carbon nanotubes (SWCNT), are still very new materials, says Greg Rose, vice-president of marketing at Unidym, which merged with SWCNT producer Carbon Nanotechnologies last year. He notes that fullerene nanotubes have been available in significant commercial quantities for two years now, and have high growth potential in the transparent, conductive films market for electronics applications like touch panels and displays, as well as in high performance composites.

Graphene sheets, which are essentially 'unrolled' carbon nanotubes, are one of the most conductive materials available, says John Crain, vice-president of strategy and business development at Vorbeck Materials Corp. He notes that graphene has a very high surface area (700 to 1000 $m^2/g$) even compared to CNTs (300 to 500 $m^2/g$) and expanded graphite (20 to 100 $m^2/g$). Graphene's overlapping layers and high surface area allow high electron transfer at low loading levels. Vorbeck, started up in 2006, manufactures Vor-x™ graphene nanomaterials, a unique form of graphene with an inherently functionalized surface that can be tuned to bond with a range of polar and non-polar polymers. Because graphene has such a large surface in contact with the polymer, it improves mechanical properties even under extreme high or low temperatures. "The expansion of polymers at very high temperatures causes traditional filled systems to lose conductivity because the percolation network is separated. Vor-x reduces the coefficient of thermal expansion (CTE) up to 40 per cent at less than 1 per cent loading, maintaining conductivity even at high temperatures," reports Mr. Crain. In under-the-hood (bonnet) parts, graphene offers high-temperature conductivity and inhibits solvent swelling. Vor-x is also easy to disperse. Compared to CNTs that have a tendency to tangle, Vor-x graphene sheets disperse with minimal shear in twin-screw extruders or internal batch mixers, says Mr. Crain. Vor-x is sold as a masterbatch or direct blend with loading levels of 0.1 to 20 per cent for direct addition during plastics processing. The company hopes to see commercial products containing Vor-x launched later this year.



*AFM image of Vor-x functionalized graphene showing individual sheets of graphite oxide in blue. Source: H C Schniepp and Ilhan Aksay, Princeton University; courtesy of Vorbeck Materials Corp.*

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