The use of carbon nanotubes to improve conductive elastomers

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There is a growing requirement for the seals in automotive fuel system connections to have electrostatic dissipation properties. Fluorocarbon (FKM) elastomeric O-ring seals are a significant component in the conductive pathway. Providing this conductivity through the incorporation of carbon nanotubes considerably improves properties over the use of carbon blacks. This results in a seal which is softer with improved processing, stable electrical properties and better permeation resistance.

Electrostatic dissipation needs in a fuel system

Flowing fuel can build a static charge, and so it is necessary for the fuel system components to be electrostatically dissipative. Components from the fuel rail, to the fuel lines, the sender unit at the tank, and especially the fuel filter are thus made from metal or conductive thermoplastics. Fuel systems are earthed, or grounded, at a number of points along the path from tank to engine, to prevent a build-up of the static charge.

The fuel quick-connect is an important component in connecting the fuel tank to the engine via the fuel lines. Replacing torque-sensitive tube nuts, the quick-connect provides ease of assembly to standard SAE J2044 endforms and a durable, leak-tight joint. Quick-connects are manufactured in various size and shape combinations to meet the environmental routing needed for fuel feed, fuel vapor and fresh air applications.

Available in either deep-drawn steel or in fuel-resistant plastic form, the connector typically contains a two-seal system: a primary seal providing excellent fluid resistance made of high fluorine content fluorocarbon elastomer (FKM), and a secondary seal made from fluorosilicone elastomer (FVMQ), providing excellent low-temperature resistance. Quick-connects in metal form are crimped to nylon over-braided PTFE tubing, while the electrostatic dissipative thermoplastic type is inserted into dissipative multilayer nylon tubing. A cross-section of a typical metal quick-connect is shown in **Figure 1**.

Fluorocarbon elastomers

Thermosetting fluorocarbon rubber (FKM) formulations have been a mainstay for automotive fuel system sealing for many years. The higher fluorine versions of these polymers provide the most versatile fuel resistance, especially with flex-fuel blends. This is especially true for the O-rings in fuel line quick-connects. FKM materials are frequently referred to by the raw material tradename, with DuPont Viton and Solvay Tecnoflon being typical examples.

Conductive carbon black

Conductive carbon blacks have been the conventional filler technology used in electrostatic discharge elastomeric formulations. Their use has been well established over many years, especially in the wire and cable industry. Current versions of FKM formulations for fuel systems employ this technology.

However, the relatively high filler loading necessary for stable conductivity presents engineering challenges. A major concern is the high hardness and modulus resulting from this conventional approach. Seal performance can be affected as the formulation becomes less 'rubbery'. In addition, the high loading reduces the proportion of the elastomeric polymer in the material formulation, which can increase fuel permeability, particularly with flex-fuels, which are a mixture of gasoline and ethanol.

One reason for using high-fluorine fluorocarbons is to optimize permeation resistance, and hence conductive carbon blacks can be counterproductive. This effect is also seen in non-conductive FKM formulations.

Furthermore, any stress applied to an elastomeric FKM formulation filled with a high proportion of conductive carbon black can break the conductive bridge, resulting in increased resistivity.

Other issues related to the conductive black filled FKM are invisible to the end-user, but a significant hurdle for the rubber product fabricator. The formulations can be difficult to process, as good conductivity and good dispersion are opposing goals.

In the light of the above facts, an improved technology is required.

Carbon nanotubes

Multiwall nanotubes (MWNTs) have been in commercial use as a conductive additive for engineering resins, such as polycarbonate and nylon, since the early 1990s. Recently, they have been used in thermosetting fluoroelastomers used to make O-rings for automotive fuel line connectors.

Multiwall nanotube characterization

Carbon multiwall nanotubes were first synthesized in 1983 by scientists at Hyperion Catalysis International.

These nanotubes are approximately 10 nm in diameter and 10 μm long. They are made by a continuous, catalyzed, high-temperature gas phase reaction. **Figure 2** is a representation of the graphitic multiwall structure.

Figure 3 is a transmission electron microscope image of a portion of a nanotube, showing the multiwall structure surrounding the hollow core. **Figure 4** is a scanning electron microscope image showing the curvilinear structure of multiwall nanotubes.

Carbon nanotubes have proved to be an excellent additive to impart electrical conductivity in plastics. Their high aspect ratio (length divided

Additive	Typical Shore A durometer
Nanotubes	76–80
Carbon black	86–92

Table 1. Comparison of the hardness of nanotube- and carbon-filled materials.