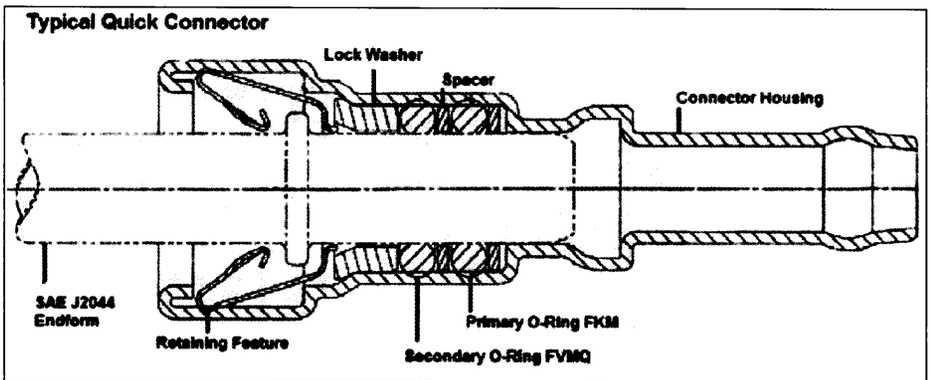

Figure 1. Cross-section of a typical metal quick-connect for automotive fuel lines.

Additive	100% Fuel C: volume change, %	85% Fuel C / 15% methanol: volume change, %
Nanotubes	+2.7%	+11.3%
Carbon black	+8.6%	+17.7%

Table 2. Swell after exposure to fuel for 70 hours at room temperature.

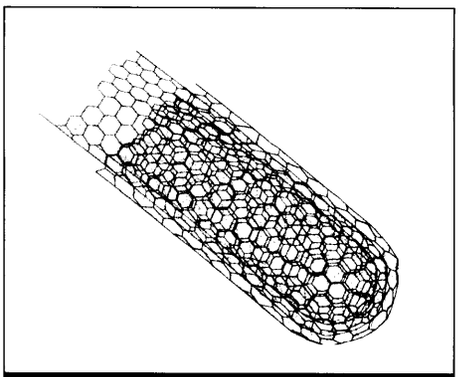

Figure 2. The graphitic multiwall structure of the nanotubes.

Additive	Average permeation rate, g mm/m²/day
Nanotubes	3.6
Carbon black	15.7
Mineral filler	9.6

Table 3. Average permeation rate of 85% Fuel C/ 15% methanol after 28 days at 23°C.

by diameter) of 1000 means that a very low loading is needed to form a percolating mixture in a polymer compared to materials with lower aspect ratios, such as carbon black, chopped carbon fiber, or stainless steel fiber.

The effect of nanotubes on FKM formulations

Precix has introduced new formulations for fuel system seals in conjunction with technology partner Hyperion Catalysis Inc. High-fluorine FKM formulations containing carbon nanotubes provide electrostatic dissipation without the shortcomings of conductive carbon black.

Most notable is the much lower loading of carbon nanotubes required for comparable volume resistivity. The lower proportion translates into a softer material, providing easier assembly and better sealing. **Table 1** compares the hardness for typical nanotube-based, high-fluorine FKM formulations with conductive carbon black fillers. Stress/strain profiles follow the durometer hardness trend.

The nanotube compound with a higher proportion of FKM polymer provides better resistance to fuels compared to current technology. **Table 2** compares the volume swell for two high-fluorine FKM compounds immersed in standard fuel tests.

Of particular interest is the improved resistance of the O-ring to gasoline permeation. Automobiles sold in the US have been mandated to not only lower emissions from the exhaust, but also to lower total evaporative losses of fuel. An O-ring with improved sealing characteristics and better barrier properties is critical to meeting these increased performance targets.

In **Table 3**, we compare high-fluorine FKM materials intended for quick-connect O-ring fuel seals. Permeation resistance in flex-fuel is inferior for both conductive carbon black and mineral-filled, non-black formulations, when compared to the nanotube compound.

A particular benefit of nanotubes as the conductive additive is the change in resistivity with applied stress, or strain. Typically, as a conductive O-ring made with carbon black is deformed, the resistivity increases. This is a result of the breakage of the carbon black structure. The effect can be seen in both tension and compression.

A standard rubber dumbbell specimen can be used to highlight this effect in high-fluorine FKM. In **Table 4**, volume resistivity is measured before and after a 25% strain. The increase in resistance, *i.e.* decreased conductivity, is dramatic with conductive carbon black, but actually decreases slightly with nanotubes.

Table 5 shows a similar effect when compressing O-ring samples. It is thought that the nanotubes are compressed closer together, which increases conductivity, but because of their strength, they do not break.

O-ring fuel seals must exhibit minimal compression stress relaxation (CSR). This is a measure of sealing stress decay over time. In **Figure 5**, CSR is shown for two high-fluorine FKM materials – one containing nanotubes (F98), and the other a mineral filler (F86). The nanotube material is comparable to the mineral-filled compound. The mineral-filled FKM has a successful history of use for fuel seals.

A last consideration is ease of manufacturing for the rubber fabricator. FKM that contains nanotubes is not sensitive to processing technique, over mixing, so good incorporation and optimum conductivity can both be achieved. Higher capability can be achieved. **Table 6** is a property summary of an 80 durometer nanotube loaded high-fluorine FKM.

The future

Additional testing of the nano-filled fluorocarbon is under way to validate many of the initial results. One such test is a diurnal permeation test. While many of the tests are pending, there have been some positive trends thus far. One trend is

Additive	Original volume resistivity, Ω cm	Volume resistivity after 25% stretch, Ω cm
Nanotubes	125	120
Carbon black	32	525

Table 4. Effect of tension on resistivity.

Additive	Change in resistivity with 4.5 kg compression stress, %
Nanotubes	–292%
Carbon black	+224%

Table 5. Effect of compression on resistivity.