Illustration: Magictorch

Life force

Antidegradants have long been a static technology, but environmental pressures may bring major scientific changes

Ian Salusbury

Antioxidants, together with antiozonants, are the most important members of the antidegradant class of additives. These chemicals are used in tires to protect against the effects of the atmosphere, ultraviolet light and fatigue, and they make up approximately 1% of a car tire's weight and around 2% of a truck tire. Although the main classes of these chemicals are well-proven and reliable, efforts are being made to develop higher performance versions to make tires last longer. The possibility that some of these substances may be found to be damaging to human health or to the environment gives added impetus to the development of alternative products.

Oxidation of rubber proceeds through the formation of free radical species, as Gary Hamed, professor of polymer science at the University of Akron, USA, explains: "The species that result from oxidation either crosslink the rubber chains, or cause chain scission – they take the network and either overcrosslink it or cut it up. It becomes brittle, because it becomes either softer or stiffer. And whether it becomes stiffer or softer depends on the specific rubber compounds. In either case, the rubber loses its extensibility." Antioxidants work by mopping up these reactive free-radicals.

Ozone attacks in a different way. Ozone is made up of three oxygen atoms

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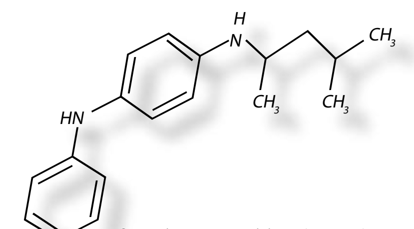
and although it is only present in very small quantities at ground level (at most, 0.5 parts per million in polluted areas), it is highly reactive. It reacts rapidly with any unsaturated double bonds in the rubber, so most of the impact is on the surface. In relaxed material the rubber surface develops a frosting effect, and in dynamically loaded rubber, cracks appear perpendicular to the direction of applied stress. There is a debate as to how antiozonants work. Some researchers have suggested they scavenge free radicals, whereas others believe that the antiozonant creates a protective film on the surface of the rubber.

Sunlight used to be directly blamed for the damage caused by ozone. It does play a part because levels of ozone are higher on sunny days. However, the direct effects of ultraviolet light are negated by carbon black filler, which absorbs the energy at these frequencies.

There is a plethora of antidegradant materials from which tire makers can choose. Some have either antioxidant or antiozonant properties, some have both, some stain the rubber, and some are non-staining. P. K. Mohamed, chief of research of technology at Apollo Tyres in India, explains that a combination of antidegradants is usually used: "It is common practice to use a mixture of two to three different types of antidegradants, as they give the best performance due to synergistic effects."

Para-phenylenediamines (PPDs) are probably the most prevalent group of antidegradants. Compounds such as N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) are thought to work by scavenging the free radicals before they can do further harm to the rubber network. Hamed confirms the importance of this class of compounds: "The PPDs are the real workhorses. They prevent the action of both oxygen and ozone, which is a good thing from the standpoint of the durability of rubber." They also provide protection against flex fatigue of tires.



6PPD's composition (above) may be outlawed in favor of EPDM

Stuart Andrews, materials applications development manager at Cooper Tire and Rubber in Europe, agrees that 6PPD is probably the most used compound, but notes, "This PPD is sometimes not good enough for certain more rigorous applications. There are better systems out there that are based on the same materials but are more aggressive." He also explains that the staining properties of 6PPD can create difficulties: "These PPDs tend to stain any white components. This causes a problem for us in making motorcycle tires with a white sidewall, but in the USA it is even more of a problem as they tend to have embossed white lettering on the side of their tires."


The popularity of white sidewalls in the US market presents problems due to PPD staining

Waxes also play an important role in protecting tires. They are soluble in rubber and migrate to the surface of the tire, creating a physical barrier on the tire surface, which is eventually worn off. Mohamed says, "Wax acts as a very good antiozonant in rubber. Paraffinic, microcrystalline wax blends are generally used for ozone protection, especially in their static condition". The flexing of tires that are in service makes the wax 'bloom' to the surface, which also helps the other antidegradant chemicals to diffuse through the rubber.

Andrews notes that the supply of wax does become exhausted: "There's usually enough wax around in the system to continue coming to the surface, but obviously you can't get enough wax in the rubber to do that forever. So eventually that wax system becomes invalid."

Although a radical overhaul of antidegradants is not imminent, some industry figures and researchers anticipate changes in the medium term. Mohamed says, "The future expectation is that antidegradants should have low volatility, limited solubility, higher chemical stability, improved processibility, and be in a solid form." Also, as these chemicals are costly, tire-makers would prefer to be able to use lower dosages.

Hamed thinks that things are currently quiet in antidegradant development and says there are no 'Eureka!' moments on the horizon. Jacques Noordermeer, professor at the University of Twente, the Netherlands, agrees. However, he does draw attention to the ambitious goals of Japanese tire makers: "Their aim is to have a passenger vehicle tire that does not change modulus (or hardness) over time to ensure the grip performance is constant upon aging. This could be done by developing long-lasting stabilizers that are slower migrating than the common ones, and take longer to migrate to the surface."

Health and the environment

Antidegradants enter the environment via two routes: through tire abrasion, or leeching out of the tire into water. The scale of this release is significant: Swedish studies suggest that in the EU up to 0.35 million tons of rubber end up in the air or on the roadside every year.

The effects of 6PPD have been studied by the OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic. Although the commission found that 'risks to marine organisms are expected to be negligible', its high production volume (over 130,000 tons/year) means that OSPAR is going to keep 6PPD and its metabolites under review.

The fact that antidegradants prolong the life of rubber does not have any effect on tire disposal. Degradation is not a significant issue as, since July 2006, EU regulations have meant that car tires (whole or shredded) cannot be disposed of in landfill, although some tires are used for engineering purposes in these sites. Similar regulations apply in a number of the US states. Those tires that cannot be retreaded are used to fuel industrial installations such as cement kilns or power generators, or are turned into 'chip' or 'crumb' for use in rubberized playground surfaces or roads. It has even been projected that the demand for waste tires in the UK will soon exceed supply.

Noordermeer also predicts that government regulation will force a change at some point: "Sooner or later, my bet is that 6PPD is going to be banned and the tire-makers will have to find another solution. One possibility is to replace some of the rubber with a saturated rubber such as ethylene propylene diene monomer (EPDM). If you have 30 parts per hundred of rubber of EPDM, you can get an ozone resistance that is directly comparable with the use of 6PPD. But it is not that simple because a tire is a complex combination of many components and they all contribute to the total performance. If you drastically change one of the components, you have to adjust the others as well. So you don't change anything until you have to."

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Mohamed predicts that new types of antidegradants may be in use in the next 5-10 years: "To meet future needs, several new antidegradants have been developed, including polymer-bound antidegradants. These may be used in the future as they can improve dispersion and reduce volatile loss, and their higher retention in rubber provides a longer protection period." Polymer-bound antidegradants involve anchoring the compounds to the rubber network to prevent them being gradually leeched. Their use during tire manufacturing also results in lower losses of these materials at that stage. Antidegradants can also be made longer-lasting by increasing their molecular weight by adding hydrocarbon chains, making them less volatile. Legislation on the lifetime for tires may help to drive this change, but environmental factors will also prove critical. ***tire***

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