

Recently seen on European roads, too: diesel cars featuring SCR technology, such as the Mercedes-Benz E300 Bluetec (photo: Daimler AG)



# EPDM and HNBR versus Summer Smog

**Elastomer Hoses for AdBlue.** Nitrogen oxides in exhaust gases of diesel engines can be neutralized by adding ammonia to selectively convert them to nitrogen and water. So-called SCR systems use aqueous urea solutions (AdBlue) as the  $\text{NH}_3$  source for this. To transport the solutions from the tank to the catalyst, the technology relies on chemically resistant hoses made from specialty chemicals, such as EPDM.

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When technologically innovative solutions to problems are being developed, the devil is often found to be in the detail – the same is true of selective catalytic nitrogen oxide reduction (SCR; see box on page XX). The reason is that the urea ( $\text{NH}_3$ ) in AdBlue fuel can adversely affect technical materials. The choice of elastomer for making tubes that come into contact with the urea solution (Fig. 1) therefore poses a not inconsiderable challenge. While the trend toward high-performance rubbers for other applications in automobiles is driven more by demands on operating temperatures and service life, the chemical



peculiarities of this source of ammonia (urea) rule out the use of many “conventional” rubbers and rubber grades in AdBlue systems.

### Urea Can Damage Rubber

First, as a secondary amine, urea forms weak alkaline aqueous solutions that can enter into thoroughly undesirable chemical reactions with certain substrates. This can prove problematic, for example, with chlorinated rubber materials, such as chloroprene (CR), chlorinated polyethyl-

Fig. 1. EPDM hoses made from peroxide-cured EPDM survive contact with urea without hardening. The plasticizer-free formulation also prevents contamination of the catalyst (picture: ContiTech)

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ene (CM) and chlorosulfonated polyethylene (CSM). Added to which there is the problem of ammonium hydroxide, into which urea gradually decomposes even when properly stored at room temperature. Ammonia imparts a pungent odor to urea solutions at moderate temperatures of around 90°C and is known to be even more aggressive. For this reason, the rubber used for hoses has to be particularly resistant to chemicals. Fluorinated rubbers rule themselves out due to their sensitivity to alkaline media or the high price of their alkali-resistant variants.

Another limitation stems from the sensitivity of sulfur-vulcanized rubber to basic nitrogen compounds. Amines can activate dormant vulcanization, i.e. rupture the sulfide linkages between rubber molecules: the effect is a rearrangement of long bridges in favor of several short ones, which means essentially that the crosslinking density in the elastomer increases. As a result of this “post-curing”, the rubber hardens over time, and in extreme cases becomes brittle. Not only that, but the elastic properties of such impaired parts, as measured by compression set, start to degrade and that can adversely affect sealing properties.

### Peroxide instead of Sulfur

Hoses that carry AdBlue must therefore not be cross-linked by the widespread sulfur cure systems. One alternative is to use peroxide vulcanization reagents that link the elastomer molecules via free-radical reactions and, as experience shows, yield extremely durable, cross-links. Peroxide vulcanization simultaneously eliminates the need for double bonds in the rubber molecule that are required for sulfur vulcanization and are also responsible for the chemical and thermal sensitivity of conventional rubber. To be sure, peroxides require a more advanced vulcanization technology; however, major synthetic rubber suppliers, such as Lanxess AG, Leverkusen, Germany, help users to develop suitable methods and compounds.

Other constraints are imposed by the sensitivity of the catalyst, which ultimately decomposes the urea into the actual ammonia “building block” and converts the nitrogen oxides in the exhaust stream into nitrogen and water. Selective catalytic reduction utilizes both transition metal oxides and zeolites. In each case, it is essential when a rubber compound for AdBlue hoses

is being developed that only truly indispensable additives be employed. The content of processing aids that might be extracted from the rubber and thus come into contact with the catalyst must be kept at an absolute minimum.

Plasticizers, especially, are to be avoided. The base elastomers used should possess the necessary processing and end properties, in other words good miscibility, low viscosity and the desired end hardness, without the need for plasticizers. What is more, they must offer these properties over a very wide tem-

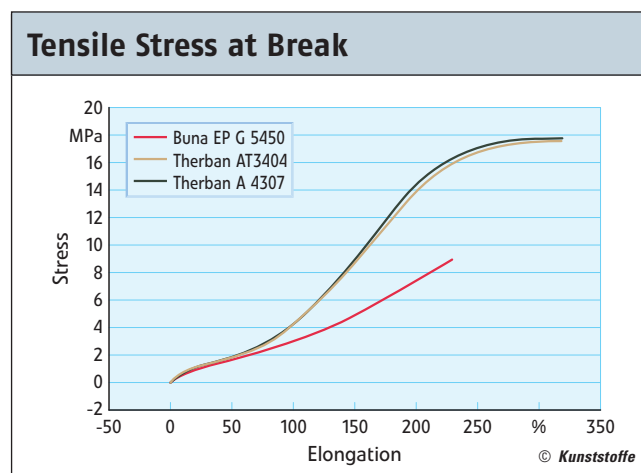


Fig. 2. Tensile stress at break tests on unconditioned samples (EPDM and HNBR variants) (source: Lanxess)

perature range, because the plasticizer-free hoses must naturally not embrittle at low temperatures either.

### Low Viscosity without Plasticizers

As detailed studies at Lanxess have shown, both peroxide cross-linked vulcanizates of Buna EP, an EPDM rubber, and of Therban, a hydrogenated nitrile rubber (HNBR), possess the necessary properties. Both are already widely used in the automotive sector: due to its weatherability, aging-resistance and good low-temperature flexibility, EPDM finds application particularly in door, window and body seals.

Therban is primarily used in toothed belts and similar demanding applications. This aging-resistant development of NBR, an oil-resistant nitrile rubber, is characterized by a long service life in hot, ozone containing air and potentially oil-containing environments and a combination of excellent dynamic properties.

Samples of Buna EP G 5450 and Therban AT 3404 and Therban 4307 A were studied in detail (Table 1). Buna EP G 5450 is an amorphous grade of EPDM that is highly flexible over a wide temperature range. By virtue of its low Mooney viscosity (50 MU), it can be readily processed and extruded even without added plasticizer. The two fully hydrogenated Therban grades studied differ mainly in their acrylonitrile content and Mooney viscosity. Therban AT 3404 has an extremely low viscosity. The AT grade is a variant of HNBR that offers a new,

Ingredients	Manufacturer	Buna EP [pbw]	Therban AT [pbw]	Therban A [pbw]
Buna EP G 5450	Lanxess	100	–	–
Therban AT 3404	Lanxess	–	100	–
Therban A 4307	Lanxess	–	–	100
Zinc oxide active	Lanxess	5	3	3
Thermax N 990	Lehmann & Voss & Co	63	80	75
Polyglycol 4000 S	Ter-Hell	3	–	–
Vulkanox HS/LG	Lanxess	1.5	–	–
Rhenofit TRIM/S	Rhein Chemie	1	–	–
Perkadox 14-40 B-PD	Akzo Nobel Chemicals GmbH	5	7	7
TAIC	Kettlitz Chemie GmbH & Co.KG	–	1.5	1.5
Maglite DE	Lehmann & Voss & Co	–	3	3
Luvomaxx CDPA	Lehmann & Voss & Co	–	1.5	1.5
Vulkanox ZMB2/C5	Lanxess	–	0.4	0.4

Table 1. Composition of the rubber compounds used to prepare test specimens for tensile stress at break tests: The content of additives was kept to a minimum. No plasticizer was required due to the low viscosity of the base elastomer (source: Lanxess)

## Nitrogen Oxides and Summer Smog

Nitrogen oxides – oxygen compounds of nitrogen such as NO and NO<sub>2</sub>, grouped together under the name NO<sub>x</sub> – have long been identified as “environmental toxins.” Their impact goes far beyond their contribution to the formation of acid rain. They play a key role in the formation of summer smog: by this is meant the formation of large amounts of ground-level ozone, which is a respiratory irritant that can harm sensitive people.

Photolysis converts nitrogen dioxide into nitrogen monoxide and atomic oxygen, which reacts with atmospheric oxygen to produce ozone. Hydrocarbons, such as those emitted when vehicles are refueled, promote this reaction by oxidizing nitric oxide in the presence of UV radiation back to NO<sub>2</sub> via a cascade of free-radical reactions. Road traffic is a major source of NO<sub>x</sub> in our cities. It could serve as a point of attack in the effort to prevent high ozone concentrations from forming in the air that we breathe.

Although attempts are being made to curtail hydrocarbon emissions through using suction systems and educating gas-station customers, nitrogen oxide emissions need to be reduced at source. According to the Association of the Automotive Industry (Verband der Automobilindustrie, VDA), the new Euro 5 pollutant limits, which are mandatory from 2009 on, call for an 86–98 % reduction compared to 1990 (Euro 0). These values represent a considerable challenge and are unlikely to be met solely via more effective engine control.

optimized manufacturing process with a very narrow molecular weight distribution and thus – while retaining the typical Therban properties – has a very low Mooney viscosity (40 MU and less; standard Therban: 60 to 70 MU).

These three elastomers can also easily take up large amounts of filler (in this case, inactive carbon black), and thus, even under high operating temperatures, ensure good values for long-term compression set, without impairing ease of processing. The expected higher end hardness of the more polar HNBR rubber has been cushioned by a slightly reduced filler content during development of the blend.

### Not Affected by Urea

The ingredients were blended in the normal way in a kneader and cured at 175°C with the aid of a peroxide crosslinker. Necessary additions of processing aids that could interact with the urea or deactivate the catalyst were kept to a minimum in the recipes.

After curing, the specimens were initially aged for 30 days in an AdBlue so-

lution that was maintained at 95°C and renewed once a week. Their tensile stress at break was then tested as per DIN EN 53504 or ISO 37 (Fig. 3), and the results were compared with those of unaged test specimens (Fig. 2). The changes wrought by ageing in AdBlue are minimal, and the resulting tensile stress at break curves are virtually identical, within the limits of measuring accuracy. It appears that not only the nonpolar chain molecules of the EPDM, but also the polar nitrile groups of the hydrogenated nitrile rubber are insensitive to attack by urea or ammonia.

The stress at 100 % elongation for unconditioned Buna EP samples was 2.9 MPa (Therban AT 3403: 4.3 MPa, Therban A 4307: 4.2 MPa; at 200 % elongation: Buna EP: 7.4 MPa, Therban AT 3403: 13.8 MPa, Therban A 4307: 14.3 MPa). The sample of Buna EP conditioned in AdBlue returned a stress value of 3.0 MPa at 100 % elongation (Therban AT 3403: 4.4 MPa, Therban A 4307: 4.3 MPa; at 200 % elongation: Buna EP: 7.5 MPa, Therban AT 3403: 13.9 MPa, Therban A 4307: 15.6 MPa). The tensile strength and the elongation at break of the conditioned samples was 7.8 MPa (EPDM, 204 %) and 18.3 MPa (309 %)/19.2 MPa (301 %, Therban grades) and therefore at the level of the reference values (8.9 MPa/228 %, 17.6 MPa/316 % and 17.8 MPa/318 %).

As expected, the volume increase due to swelling in the aqueous solution of AdBlue was slightly greater in the more polar Therban samples than in the more olefinic EPDM polymer but, at around 2.5 %, still within a technically acceptable range (Buna EP: 1.4 %).

## Summary and Outlook

In summary, it was demonstrated that both low-viscosity EPDM and HNBR rubbers are suited to the manufacture of hose and gasket material for AdBlue catalyst systems. The mechanical properties of peroxide-cured vulcanizates of these elastomers, even after contact with urea solutions, are comparable to those of unconditioned samples. Although the Therban HNBR elas-

## Nitrogen Oxide Reduction Using SCR

One promising approach to defusing the summer smog problem is to employ selective catalytic nitrogen oxide reduction (SCR) in the exhaust stream. SCR systems for commercial vehicles have been on the market since early 2005. The technology is being pioneered by Daimler AG: this OEM has recently started offering the SCR exhaust-gas-cleaning method under the name of Bluetec, not only for its truck series, but also for diesel passenger cars (title picture). At the Detroit Motor Show in January 2008, the manufacturer announced its intention to expand its range of Bluetec vehicles.

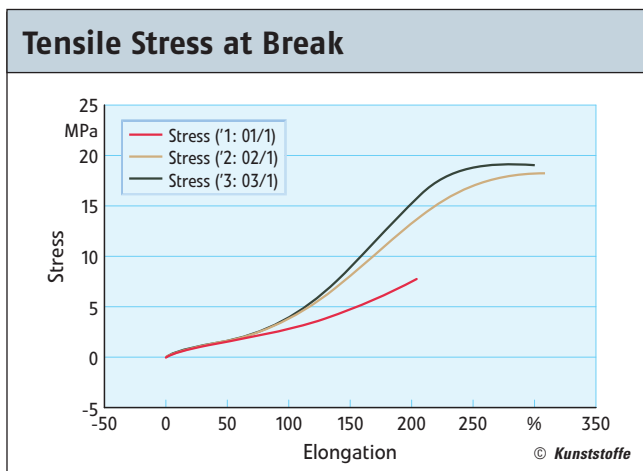
Linchpin of the SCR catalytic process is the catalytic conversion of the nitrogen oxides by ammonia into water and nitrogen. The method is highly selective, which means that only the nitrogen oxides are removed. The disadvantage is that ammonia is an aggressive gas, which even in aqueous solution has a noticeable pungent odor and can form explosive mixtures with air.

SCR technology circumvents these problems by using urea as the source of the ammonia. Urea is a naturally occurring, non-toxic, biodegradable chemical that is colorless, odorless and does not require labeling. It is manufactured cost-effectively on a large scale and decomposes to ammonia in the solid state above 132.5°C. The SCR process, however, does not employ solid urea, but rather a 32.5 %, aqueous urea solution (AdBlue, whose composition and purity is regulated in accordance with DIN 70070). The urea burden of this solution is converted into ammonia in a reaction stage that is upstream of the SCR catalyst. Depending on the volume of nitrogen oxide per liter of diesel, 20 to 80 ml AdBlue solution is enough to make a significant reduction in NO<sub>x</sub> emissions: the potential for reduction is around 80 %. If SCR denitrification is combined with an intelligent engine controller, it is even possible to reduce the fuel consumption of the vehicle. Strong growth is forecast for consumption of AdBlue (Fig. 4).

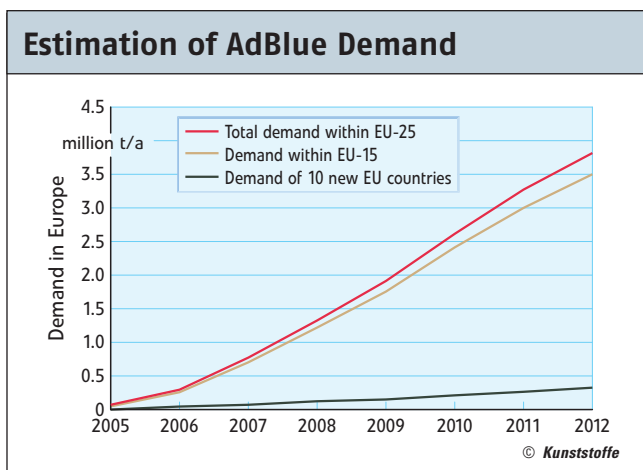


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**Fig. 3. Tensile stress at break tests on samples (for order refer to Fig. 2) conditioned for 30 days in AdBlue solution (95°C). The samples show a property level similar to that before conditioning (source: Lanxess)**



**Fig. 4. The Association of the Automotive Industry (Verband der Automobilindustrie, VDA), proprietary owner of the AdBlue brand, reckons with steadily growing demand for SCR systems in Europe (source: VDA, 2005)**

tommer, due to its higher polarity, is characterized by greater swelling resistance in oil in a direct comparison of the two materials, so far “only” EPDM hoses have managed to break into the market: ContiTech Schlauch GmbH, Northeim, Germany, manufactures hoses from Buna EP for the SCR systems of a major OEM.

This example clearly shows that the extent to which the innovative products at the cutting edge of technology can be realized nowadays depends on the availability of suitable materials. In particular, it is no rarity for specialty elastomers to play a key role, because “conventional” rubber grades have often been identified as the weakest link in the chain.

A lot is expected of these materials in the area of “green” technologies and from the point of view of resource conservation: keywords are minimized spare-parts and maintenance requirements due to longer service lives, even at elevated temperatures and under harsh conditions, as well as increased resistance to alternative fuels, such as biodiesel. Modern high-performance elastomers open up tantalizing prospects in this regard. ■

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