Amine-free coolants from Rhenus Lub.

Better protection at the same level of performance.

Amines are the important constituents of many water-miscible coolants. In the interplay with boric acid and other coolant components, they are e.g. responsible for corrosion protection, bacterial resistance as well as the adjustment of the pH-value to 9.0 - 9.3 in the water-mixed state. However, nitrosamines can be generated when using such products during the application of coolants, most of which have clearly been shown to be carcinogenic in animal trials. Their formation is based in general on the reaction between an amine and a nitrosing agent. Both components must be present.

Amine + Nitrosing agent --------> Nitrosamine

Coolants used today are free of nitrites. One of the reaction partners is thus missing. However, investigations with used solutions/emulsions show that nitrite ions can occur in slight amounts. Possible sources of nitrite are: bacterial break-down of nitrate from the mixing water, impurities in coolant emulsions (e.g. food residues) or introduction via pre-treated parts (e.g. from nitrite-containing rust protection agents or hardening salts). In addition, nitrogen oxides (NOx) from the ambient air may also come into question as nitrosing agents. Additional nitrogen oxide sources are: combustion motors (e.g. fork-lift trucks), gas burners or a busy road nearby.

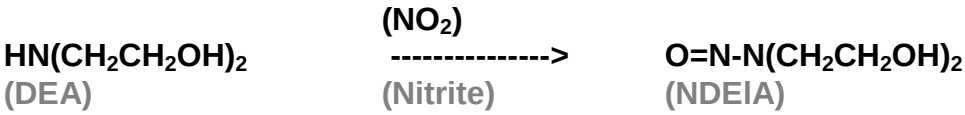
As a matter of principle, all amines can undergo nitrosation in the presence of nitrosing agents. Decisive is, however, the type of end product arising according to the nature of the amines used. In general, the following tendency applies in nitrosamine formation:

Sec. amines >>	**Tert. amines >**	**Prim. amines**
(DEA)	**(TEA)**	**(MEA)**

The tendency to form stable nitrosamines is by far the strongest in the case of secondary amines. This is followed by tertiary amines - primary amines behave the most favourable of all in this respect.

This led to the TRGS 611 - which came into force in 1993 - and declared the usage of secondary amines. The consequence was that diethanolamine (DEA) which was normally used in coolants up to this day was replaced, because this resulted in the formation of stable N-nitrosodiethanolamine (NDElA).

Schematic: The formation of NDElA



There are a number of basic rules, which concern themselves with the nitrosamine problem in coolants.

Two ways of solving the nitrosamine problem were considered: The use of alternative amines such as monoethanolamine (MEA) and/or triethanolamine (TEA). Or the development of new amine-free coolants, which are not comparable in particular to the "drilling fluids" of earlier years with regard to their biostability.

Long before the TRGS 611 came into force, Rhenus Lub decided to go both ways. The degree of success, in particular with amine-free varieties, justifies the concept.

Many years of experience with amine-free varieties have shown that these products are at least equal to the amine-containing coolants for technical applications, but offer considerable advantages from the point of view of occupational health.

Besides the clearly more favourable pH-levels of 8.0 - 8.8 of the used emulsions (= better skin tolerability), for example, there is also no nitrosamine problem during use. If one looks at the formation of nitrosamines, both reaction partners are thus missing from the amine-free coolants. Even if nitrite is introduced into the used emulsions, the occurrence of nitrosamines is not possible, as the amine required is likewise not present. From an occupational health point of view, one is practically working in this case with both “belt and braces”. The frequently heard argument that in the case of contamination with operating substances containing secondary amines (e.g. DEA-containing cleaners are to be avoided according to the TRGS 611) is not sound, as no corresponding inhibitors are present.

- The only inhibitors with practical relevance are currently the primary amines. But they themselves can form otherwise structured, stable nitrosamines in low concentrations. This has been verified with the example of MEA. This likewise applies to tertiary amines such as TEA. However, these nitrosamines cannot be analytically determined at the moment, as NDEIA is not involved, for which a validated procedure is available. Naturally, several orders of magnitude lie between the formation of these nitrosamines and the occurrence of NDEIA from DEA-containing coolants.

- However, it is precisely these orders of magnitude when one speaks about contamination with DEA-containing media. **Assumption:** The used emulsion contains 0.1 % of a cleaner with 15 % DEA, i.e. 150 ppm. DEA-containing products previously contained e.g. up to 30 % DEA. At a 5 % application concentration, this corresponds to 15000 ppm, i.e. a factor of 100.

- Naturally, NDEIA can also be introduced with DEA-containing external media. The already mentioned inhibitors do not affect this. They are by no means in a position to destroy the NDEIA which has already formed.

- More and more operating materials such as corrosion protection agents, system cleaners and other cleaners are formulated free of secondary amines. This applies without restriction to the auxiliaries and additives manufactured by Rhenus Lub. Numerous amine-free used emulsions have been examined in the last few years for their NDEIA content.

The data obtained clearly demonstrates that despite a relatively broad scatter of nitrite and nitrate concentrations and even at relatively low pH-levels – i.e. conditions which are actually beneficial for the formation of NA – the NDEIA limits and/or orientation values of 5 ppm for emulsions and/or 0.001/ 0.00025 mg/m^3 for air clearly fall short of these values for amine-free coolants.

In other words: Nitrosamines – amine-free no problem!

Why boron and amine-free coolants from Rhenus Lub?

The individual is the central focus

- Best levels of tolerability in man, raw materials of the highest purity
- Modern well-tolerated inhibitor concept without boron and bactericides
- Free of ethanolamines, which are classified as sensitising
- Low uptake of heavy metals (Cu, Co, Ni, etc.)
- Best possible skin tolerability (TEWL and chromametric measurements) thanks to
- Low pH-level – pH 8 ± 0.5
- No nitrosamine formation by coolants
- No bacterial transformation from amine to nitrite

High performance, low costs

- Universal application
- No loss of corrosion protection and stability by volatile amines
- High emulsion stability, permanent corrosion protection

  at low pH-values
- Low emissions = low top-up amounts = **low consumption**
- Good foreign oil separation = simple care
- Favourable process costs