

**Edition: May 2007**

|  |  |                                  |
|--|--|----------------------------------|
| <p><b>Technical Rules for Hazardous Substances</b></p> | <p><b>Restrictions on the use of water-miscible or water-mixed cooling lubricants whose employment can result in the formation of N-nitrosamines</b></p> | <p><b>Technical Rule 611</b></p> |
|--|--|----------------------------------|

The Technical Rules for Hazardous Substances (TRGS) reflect the state of technology, occupational safety and health and occupational hygiene as well as other definite knowledge relating to activities involving hazardous substances including their classification and labelling. The

**Committee on Hazardous Substances (AGS)**

establishes the rules and adapts them to the current state of development accordingly.

The Technical Rules are announced by the Federal Ministry of Labour and Social Affairs in the Joint Ministerial Gazette (GMBI).

**Contents**

- 1 Scope
- 2 Definition of terms and explanations
- 3 Information acquisition and risk assessment
- 4 Demands made on water-miscible cooling lubricants in the condition in which they are supplied
- 5 Protection and monitoring measures that apply during the employment of water-mixed cooling lubricants

Annex

**1 Scope**

(1) Technical Rule 611 applies to the use of water-miscible cooling lubricants or the employment of water-mixed cooling lubricants in the skilled-trade area concerned with the shaping and finishing of workpieces, i.e. above all in the metal-working industry. As a rule, N-nitrosamines are neither produced nor used in the skilled-trade area named here. They are also not included in water-miscible cooling lubricants or, at most, only in extremely low amounts (as an impurity). Instead, they only form under certain conditions during the employment of certain water-mixed cooling lubricants as a result of the nitrosation of secondary amines.

(2) This Technical Rule is aimed at the employers in those companies in which water-miscible cooling lubricants are used or in which water-mixed cooling lubricants are employed.

(3) In addition, this Technical Rule is aimed at the producers and importers of water-miscible cooling lubricants as well as those responsible for placing them on the market since they are required to

- only place on the market products that meet the demands of this Technical Rule,
- include in their safety data sheets the information demanded by this Technical Rule.

(4) Technical Rule 611 follows on from Technical Rule 552 “N-nitrosamines” [1] and supplements it with regard to the special area described here.

(5) Technical Rule 611 provides safety advice for the composition and the use of water-miscible or water-mixed cooling lubricants during production processes involving metal removal and the reshaping of workpieces, in particular in the metal-working industry. In accordance with the minimization rule stipulated in the Hazardous Substances Ordinance (GefStoffV) [2] (see, in particular, § 8, Section 2 and § 11 of the Hazardous Substances Ordinance), application of this Technical Rule is intended to largely exclude the risk of N-nitrosamine formation during use of these cooling lubricants and, as a result, largely exclude the exposure of workers in the metal-working industry [3].

(6) N-nitrosamines are either not included at all in water-miscible cooling lubricants without nitrosating agents (such as nitrite) or are at most included in extremely low quantities (as a result of impurities). In certain circumstances, they can form during the employment of water-mixed cooling lubricants.

(7) In order to reduce the risk of N-nitrosamines forming, a series of restrictions on use based on keeping away nitrosating agents and replacing nitrosatable secondary amines with suitable substitutes, e.g. primary amines, are announced.

(8) Attention is drawn to Technical Rule 552 with regard to the general aspects relating to the topic complex N-nitrosamines and the general rules and regulations that already exist and go beyond the area concerned with cooling lubricants.

## **2 Definition of terms and explanations**

(1) According to the meaning of this Technical Rule, cooling lubricants are the water-miscible cooling lubricants (cooling lubricant concentrates) supplied by the producer, importer or person placing them on the market and the water-mixed cooling lubricants (cooling lubricant emulsions and solutions) employed by the user during material-removal production processes and the reshaping of workpieces.

(2) N-nitrosamines are organic nitrogen compounds which, under certain reaction conditions, can form from nitrosating agents and nitrosatable secondary amines [4-9].

(3) According to the meaning of this Technical Rule, N-nitrosamines are the category 1 and 2 carcinogenic N-nitrosamines named in Number 1, Section 1 of Technical Rule 552 and other such carcinogenic N-nitrosamines which can form during the employment of water-mixed cooling lubricants.

(4) On the basis of currently available knowledge it can be assumed that, essentially, the formation of the following category 2 carcinogenic N-nitrosamines named in Technical Rule 552 is possible during the employment of particular water-mixed cooling lubricants in certain circumstances:

- N-nitroso-diethanolamine (2,2'-(nitrosoimino)bisethanol) CAS No. 1116-54-7,
- N-nitroso-morpholine CAS No. 59-89-2.

(5) The currently available results and publications clearly reveal that, in this connection, N-nitroso-diethanolamine (NDELA) is by far the most frequently occurring N-nitrosamine [5,6,10-13]. N-nitroso-diethanolamine (NDELA) is therefore regarded as the lead substance according to the meaning of this Technical Rule.

(6) This Technical Rule does not apply to non-carcinogenic N-nitrosamines. According to the meaning of this Technical Rule, the N-nitrosamines listed in Number 1, Section 2 of Technical Rule 552, inter alia, N-nitroso-dicyclohexylamine (dicyclohexylnitrosamine, CAS No. 947-92-2) as well as other N-nitrosamines for which an indication of a carcinogenic effect has not been revealed in tests, are to be regarded as non-carcinogenic N-nitrosamines.

(7) Category 3 mutagenic N-nitrosamines are not N-nitrosamines according to the meaning of Technical Rule 611 (see also Number 1, Section 3 of Technical Rule 522). As a matter of principle, on the basis of EU legislation on hazardous substances [14] and the Hazardous Substances Ordinance (see, in particular, §§ 7-11), category 3 carcinogenic and mutagenic substances are to be assessed differently from category 1 and 2 carcinogenic and mutagenic substances. Should the risk assessment reveal a risk of the formation or release of a category 3 mutagenic N-nitrosamine, as a rule, the measures at protection level 2 according to § 9 of the Hazardous Substances Ordinance must be followed. (Currently, N-nitroso-dicyclohexylamine (dicyclohexylnitrosamine) is classified as a category 3 mutagen [15]. No N-nitrosamines are currently classified as category 3 carcinogens.)

(8) According to the meaning of this Technical Rule, secondary amines are those secondary amines which, under the usual conditions for the employment of water-mixed cooling lubricants, form category 1 or 2 carcinogenic N-nitrosamines. Such nitrosatable secondary amines are, in particular,

- diethanolamine (2,2'-iminodiethanol) CAS No. 111-42-2,
- morpholine CAS No. 110-91-8.

(9) According to the meaning of this Technical Rule, disguised secondary amines are certain nitrogen-containing compounds which release nitrosatable secondary amines according to Section 8 on a significant scale under usual conditions of use or employment, e.g. as a result of hydrolysis or thermal decomposition or other chemical reactions in the course of their use in water-miscible cooling lubricants or as a result of their employment in water-mixed cooling lubricants, e.g.

- certain fatty acid alkanolamides (corrosion inhibitors) which are produced from a fatty acid and a secondary alkanolamine,
- bismorpholinomethane (4,4'-methylene-bis-morpholine), CAS No. 5625-90-1

The release of a secondary amine is to be regarded as significant if, during the resulting formation of the corresponding category 1 or 2 carcinogenic N-nitrosamine, the state of technology in the workplace atmosphere ( $0.2 \mu\text{g}/\text{m}^3$  - see Number 5.4, Section 4 of this Technical Rule and Number 4.3 of Technical Rule 552) is not adhered to or if the concentration limit in preparations (i.e. in the water-miscible or water-mixed cooling lubricant) according to Technical Rule 905 (1 and 5 mg/kg respectively) [15] is exceeded. In the course of this Technical Rule, such disguised secondary amines are to be treated in the same way as secondary amines according to Section 8.

(10) Secondary amines proven to be non-nitrosatable or of very low nitrosatability or whose nitrosation does not result in category 1 or 2 carcinogenic N-nitrosamines, such as dicyclohexylamine (see Sections 6 and 7, CAS No. 101-83-7), are not secondary amines according to the meaning of this Technical Rule.

(11) Relevant nitrosating agents or their precursors (from which readily nitrosating agents form) are, inter alia, [4-7]:

- certain nitrogen oxides ( $\text{N}_2\text{O}_3$  and  $\text{N}_2\text{O}_4$  as directly nitrosating agents as well as NO and  $\text{NO}_2$  as precursors),
- nitrosylhalogenides (e.g. NOCl, NOBr),
- organic nitro- and nitroso compounds,
- nitrous acid ( $\text{HNO}_2$ ) and its reaction forms,
- nitrites, e.g. sodium nitrite ( $\text{NaNO}_2$ , CAS No. 7632-00-0) and potassium nitrite ( $\text{KNO}_2$ , CAS No. 7758-09-0),  
(Nitrite forms in water-mixed cooling lubricants in the case of microbial attack, frequently as a result of bacterial reduction of nitrate. In addition, it can, for example, be carried over, for example, from hardening shops or anti-corrosion agents).

(12) The following factors promote the formation of N-nitrosamines [4-9]:

- high concentrations of the co-reactants (nitrosating agent and nitrosatable secondary amine) in liquid and solid systems,
- high vapour pressure of volatile co-reactants or high partial pressure of gaseous co-reactants in the case of gas-phase reactions,
- high process or application temperatures,
- the presence of catalysts (e.g. formaldehyde, thiourea and individual thiols, halogenide and pseudohalogenide ions, individual metal ions),
- Applications in which aerosols form.

(13) In aqueous systems a considerable part is played by the pH. Low pH values promote the formation of N-nitrosamines. The optimal pH range for the formation of N-nitrosamines is mostly between 2 and 5 [4-7]. Nevertheless, under certain reaction conditions, N-nitrosamines can also be formed during the employment of water-

mixed cooling lubricants in the alkaline milieu up to a pH of approx. 9.5, albeit with a lower yield.

(14) The formation of N-nitrosamines can be prevented or reduced by [4-9,16-19]

1. The absence or very low concentrations of the co-reactants (nitrosating agents and nitrosatable secondary amines) including their precursors. This is preferably to be achieved by employing substitutes that are not co-reactants in N-nitrosamine formation (see also Number 4.2, Section 3).
2. Reaction conditions that are unfavourable for the formation of N-nitrosamines, e.g.
  - low temperatures,
  - avoidance of the formation of aerosols,
  - high pH (in aqueous systems),
  - avoidance of the microbial formation of nitrite (in aqueous systems), e.g. through preventive preservation of water-mixed cooling lubricants,
3. Absence of catalysts (see above),
4. Absence of inhibitors (e.g. primary amines and primary alkanol amines, ascorbic acid and ascorbic acid derivatives, sulphamates, p-aminobenzoic acid, alkansulphonamides,  $\alpha$ -tocopherol and  $\alpha$ -tocopherol derivatives, individual phenols). A series of primary amines and primary alkanolamines have proven to be particularly suitable inhibitors in aqueous systems.
5. UV light.

### **3 Information acquisition and risk assessment**

(1) The provisions on information acquisition and risk assessment according to § 7 of the Hazardous Substances Ordinance apply in work areas in which water-miscible cooling lubricants are used or water-mixed cooling lubricants are employed.

(2) Attention is drawn to the obligation on the part of the producer, importer or person placing the water-miscible cooling lubricant on the market to provide information to the user in accordance with § 5 and § 6 of the Hazardous Substances Ordinance as well as to the provisions on co-operation between companies in accordance with § 17 of the Hazardous Substances Ordinance.

(3) As a rule, the key demands of the Hazardous Substances Ordinance in relation to the risk described here (risk of the formation of carcinogenic N-nitrosamines - see Numbers 1 and 2) are considered to be met if use is made exclusively of water-miscible cooling lubricants according to Number 4 and if, during the employment of water-mixed cooling lubricants, the protection and monitoring measures laid down in Number 5 are followed.

(4) The employer must accordingly make sure that the utilized water-miscible cooling lubricant meets the demands laid down in Number 4 of this Technical Rule.

## **4 Demands made on water-miscible cooling lubricants in the condition in which they are supplied**

### **4.1 Absence of nitrosating agents**

In accordance with § 18, Section 1 and Annex IV, Number 19 of the Hazardous Substances Ordinance, water-miscible cooling lubricants must not include any nitrosating agents or their precursors (such as nitrites or nitrite-cleaving substances, for example, certain organic nitro compounds such as 2-methyl-2-nitro-1,3-propandiol, 2-ethyl-2-nitro-1,3-propandiol, 2-bromo-2-nitro-1,3-propandiol, 2-hydroxymethyl-2-nitro-1,3-propandiol, 4-(2-nitrobutyl)morpholine, 4,4'-(2-ethyl-2-nitro-trimethylene)dimorpholine and 5-methyl-5-nitro-1,3-dioxane).

### **4.2 Secondary-amine content**

(1) Water-miscible cooling lubricants (cooling lubricant concentrates) must not include as components any secondary amines according to Number 2, Section 8 or 9.

(2) The content of such secondary amines in water-miscible cooling lubricants resulting from impurities or minor constituents must not exceed 0.2 % by mass (related to the cooling lubricant concentrate). By analogy, this limit value also applies to disguised secondary amines (see Number 2, Section 9).

(3) Primary amines and primary alkanol amines are regarded as the preferred suitable substitutes for secondary amines because their nitrosation does not result in stable N-nitrosamines. In addition, according to current scientific knowledge, it can be assumed that, due to their inhibitory effect, primary amines and primary alkanol amines inhibit the formation of N-nitrosamines from secondary amines [4-7,9,16-19].

(4) In the case of the employment of tertiary amines which currently still contain secondary amines in the form of impurities, attention must be paid to the technical product possessing the highest possible purity.

### **4.3 Amine-free cooling lubricants**

(1) The so-called amine-free cooling lubricants also meet the demands according to Number 4 of Technical Rule 611. The water-miscible cooling lubricants that include neither free nor disguised amines in the condition in which they are supplied are described as amine-free cooling lubricants.

(2) During the employment of water-mixed amine-free cooling lubricants, particular attention must be paid to the constancy of the pH. In addition, the use of suitable inhibitors for the purpose of inhibiting N-nitrosamine formation is specially recommended when employing water-mixed amine-free cooling lubricants in order to avoid an increased risk of N-nitrosamine formation in the case of carry-over, impurities or the formation of certain microbial reaction products (see Number 5.6 and 5.7).

#### **4.4 Cooling lubricants containing secondary amines / inhibitors of the formation of N-nitrosamines**

Cooling-lubricant recipes containing inhibitors to an extent that demonstrably prevents the formation of N-nitrosamines during employment are excluded from the restrictions on secondary amines listed in number 4.2. However, in the case of a secondary-amine content in the cooling-lubricant concentrate of more than 0.2 %, in accordance with the extended scope of testing according to Number 5.5 and Table 2 of the Annex to Technical Rule 611, the water-mixed cooling lubricant must be examined during its employment on a case-by-case basis.

### **5 Protection and monitoring measures that apply during the employment of water-mixed cooling lubricants**

#### **5.1 Avoidance of dermal contact**

In the case of cooling lubricants, considerable importance attaches to the dermal absorption of the N-nitrosamines. For this reason, dermal contact with the water-mixed cooling lubricant must be reduced to the unavoidable minimum. In this connection, attention is drawn to compliance with Technical Rule 401 [20].

#### **5.2 Nitrate content of the preparation water**

(1) Care must be taken to ensure that the water used in the preparation of cooling-lubricant emulsions and solutions or replenishment does not exceed a nitrate content of 50 mg/l (in accordance with the maximum value for nitrate in the Drinking Water Ordinance [21]). A lower nitrate content must be striven for. The nitrate content of the preparation or replenishment water must be checked from time to time or inquired about at the responsible waterworks.

(2) If the nitrate content of the preparation water exceeds 50 mg/l, a nitrate content of the preparation water that is below this limit value must be achieved by mixing it with demineralized or other low-nitrate water.

#### **5.3 Monitoring the nitrite content**

(1) As a matter of principle, nitrite must be measured on a weekly basis in the used water-mixed cooling lubricant.

(2) If regular checking of the used emulsion or solution and corresponding documentation of the measured values are ensured, in the case of continued low nitrite values (three times in succession under 10 mg nitrite/l), a longer measurement interval (maximum 4 weeks) can be laid down for the measurement of nitrite. In the case of values above 10 mg nitrite/l, it is necessary to revert to the weekly

measurement interval. Attention is drawn to the recommendations for tests to check used water-mixed cooling lubricants that are provided in Rule 143 of the German Statutory Accident Insurance Institutions [22].

(3) If a value of 20 mg nitrite/l is exceeded, the water-mixed cooling lubricant must be changed in full or in part. Alternatively, in consultation with the manufacturer of the cooling lubricant, a suitable inhibitor (for the purpose of inhibiting N-nitrosamine formation) must be added. If the water-miscible cooling lubricant (i.e. the cooling-lubricant concentrate) contains a sufficient quantity of a suitable inhibitor, this is equivalent to the addition of a suitable inhibitor to the used emulsion or solution.

(4) Dependent on the degree of contamination and microbial attack, the cooling-lubricant system must be cleaned effectively with a full change of the emulsion or solution. In this connection, attention is drawn to the cleaning measures described in Rule 143 of the German Statutory Accident Insurance Institutions.

#### **5.4 N-nitrosamine content in the water-mixed cooling lubricant and in the workplace atmosphere**

(1) If the exchange, partial exchange or the addition of an inhibitor cited in Number 5.3 is not undertaken or the water-miscible cooling lubricant (i.e. the cooling lubricant concentrate) does not contain a sufficient quantity of a suitable inhibitor, the N-nitroso-diethanolamine (NDELA) content in the used water-mixed cooling lubricant and the NDELA concentration in the workplace atmosphere must be determined.

(2) The N-nitroso-diethanolamine (NDELA) content in the used water-mixed cooling lubricant must not exceed the special concentration limit in preparations for “category 1 or 2 carcinogens” according to Number 4 of Technical Rule 905 of 0.0005 % (5 mg/kg) [15]. Providing that Number 3, Section 4 and Number 4 are observed, the NDELA content is considered to be adhered to if the used water-mixed cooling lubricant does not contain more than 20 mg/l nitrite or if the conditions according to Number 5.3, Section 3 are met.

(3) The N-nitrosomorpholine (NMOR) content in the used water-mixed cooling lubricant must not exceed the special concentration limit in preparations for “category 1 or 2 carcinogens” according to Number 4 of Technical Rule 905 of 0.0001 % (1 mg/kg) [15]. Providing that Number 3, Section 4 and Number 4 are observed, the NMOR content is considered to be adhered to if the used water-mixed cooling lubricant does not contain more than 20 mg/l nitrite or if the conditions according to Number 5.3, Section 3 are met.

(4) In the case of the employment of water-mixed cooling lubricants, a value of 0.2 µg/m<sup>3</sup> is considered to represent the current state of technology for the concentration of category 1 and 2 carcinogenic N-nitrosamines (such as NDELA and NMOR) in the workplace atmosphere (see Technical Rule 552, Number 4.3.). This state of technology is regarded as being adhered to if the used water-mixed cooling lubricant does not include more than 20 mg/l nitrite or if the conditions according to Number 5.3, Section 3 are met.

## 5.5 Extended scope of testing in the special case of cooling lubricants containing secondary amines according to Number 4.4

(1) Regular N-nitrosamine tests must be performed in the used water-mixed cooling lubricants and in the workplace atmosphere in the case of water-mixed cooling lubricants which, in accordance with Number 4.4, contain more than 0.2 % secondary amines according to Number 2, Section 8 or 9 and which, therefore, do not meet the demands according to Number 4.2. Measurement must be performed for the N-nitrosamine which can be formed as a result of nitrosation of the utilized secondary amine (e.g. N-nitroso-diethanolamine in the case of the presence of diethanolamine or diethanolamine derivatives [23], N-nitroso-morpholine in the case of the presence of morpholine or morpholine derivatives such as bismorpholinomethane). Here attention must focus on the measurements in the atmosphere in the case of volatile N-nitrosamines (e.g. N-nitroso-morpholine) and on the measurements in the used water-mixed cooling lubricant in the case of non-volatile N-nitrosamines (e.g. N-nitroso-diethanolamine).

(2) The special concentration limits for “category 1 or 2 carcinogens” in preparations according to Number 4 of Technical Rule 905 amount to:

- N-nitroso-diethanolamine (NDELA)            0.0005 % (5 mg/kg),
- N-nitroso-morpholine (NMOR)                0.0001 % (1 mg/kg).

(3) With regard to the N-nitrosamine measurements in the water-mixed cooling lubricant containing secondary amines, initially (after the replenishment of the cooling-lubricant system), the following test interval applies: at least every two weeks.

(4) Should the results of three consecutive N-nitrosamine measurements be below half of the special concentration limit in preparations for “category 1 or 2 carcinogens” according to Number 4 of Technical Rule 905 and the N-nitrosamine concentration in the water-mixed cooling lubricant not reveal any further clear increase, the test interval can be extended to two months.

(5) In the case of non-volatile N-nitrosamines (e.g. N-nitroso-diethanolamine), an N-nitrosamine measurement must be performed in the workplace atmosphere six weeks after replenishing the cooling lubricant system.

(6) In the case of volatile N-nitrosamines (e.g. N-nitroso-morpholine) the measurement in the workplace atmosphere must initially be performed every two weeks after the replenishment of the cooling lubricant system.

(7) Further N-nitrosamine measurements must be undertaken in the workplace atmosphere if adherence to the state of technology is not permanently ensured or if a clear increase in the N-nitrosamine values in the water-mixed cooling lubricant was determined. In the case of volatile N-nitrosamines, an N-nitrosamine measurement must be performed in the workplace atmosphere parallel to each determination of the N-nitrosamine concentration in the water-mixed cooling lubricant.

(8) With regard to the concentration of category 1 and 2 carcinogenic N-nitrosamines (such as NDELA and NMOR) in the workplace atmosphere, the state of technology is considered to be adhered to if a value of 0.2 µg/m<sup>3</sup> for the concentration of category 1 and 2 carcinogenic N-nitrosamines is not exceeded.

(9) The regular tests (extended scope of testing) listed in Table 2 of the Annex to Technical Rule 611 must be additionally performed.

(10) N-nitrosamine measurements must be performed immediately in the water-mixed cooling lubricant and in the workplace atmosphere should there be any indications of N-nitrosamine formation (considerable microbial attack and/or clear increase in the nitrite content and/or considerable decrease in the pH).

(11) All of the measurements performed within the framework of the employment of such a water-mixed cooling lubricant containing secondary amines must be documented by the employer.

(12) The manufacturer must include the following warning in the safety data sheet of the cooling lubricant: "This cooling lubricant must only be used under the conditions laid down in Numbers 4.4 and 5.5 of Technical Rule 611. Contact the manufacturer to inquire about available knowledge."

## **5.6 Avoiding the carry-over or formation of nitrosating agents**

(1) The entry of nitrosating agents into the water-mixed cooling lubricant and the formation of nitrosating agents in the water-mixed cooling agent increase the risk of the formation of N-nitrosamines and should therefore be avoided as far as possible.

(2) Keep away external sources of nitrosating agents, e.g. nitrogen oxides (as a result of the operation of combustion engines, gas or diesel-operated forklift trucks, welding equipment and similar as well as smoke from cigarettes and other tobacco).

(3) The carry-over of nitrite-containing anti-corrosion agents, cleaning agents, hardening salts and similar as well as food, drinks and tobacco and other such organic substances into cooling lubricant systems should be prevented as far as possible. The cleaning units (e.g. rinsing baths) must be regularly examined for any residual nitrite content.

(4) Components added to water-mixed cooling lubricants during their employment must also not contain any nitrosating agents.

(5) The microbial reduction of nitrate to nitrite can play a considerable part in some cases. It should be avoided as far as possible, i.e. through the use of cooling lubricants that are as resistant as possible to microbes, through regular checking and care of the used emulsions or solutions and through relevantly conceived circulation systems for emulsions and solutions.

(6) Breaches of cooling lubricant systems by foreign oils should also be avoided as far as possible. Penetrating foreign oils should be removed by suitable measures (e.g. by skimming off, filtering off by suction or centrifuging).

## **5.7 Preventing the carry-over of secondary amines**

The carry-over of foreign matter and impurities which contain or release in considerable quantity secondary amines according to Number 2, Section 8 or 9 (e.g. certain anti-corrosion agents and vapour-phase corrosion inhibitors, system cleaners

or other cleaning agents as well as hydraulic liquids or lubricants which contain phosphoric acid ester neutralized by means of secondary amines) must be prevented. This also applies to components added to water-mixed cooling lubricants during their employment.

## **5.8 Temperature in the emulsion or solution system**

Elevated temperatures promote the formation of N-nitrosamines and should therefore be avoided. The temperature in emulsion and solution systems should not exceed certain limit values determined by the application technology, e.g. 40°C for many material-removal operations and 60°C in the case of the hot-rolling of aluminium.

## **5.9 pH**

(1) The pH of the used water-mixed cooling lubricant must be checked weekly, during the processing of glass and ceramics (due to the cross-over of alkaline inorganic substances and the resultant higher pH values) on a monthly basis.

(2) Low pH values promote the formation of N-nitrosamines. A considerable drop in the pH (i.e. a prolonged drop of more than 0.5 pH points compared to the pH of the corresponding freshly prepared emulsion or solution) must therefore be avoided.

(3) As a rule, the manufacturer of the cooling lubricant should be consulted with regard to suitable counter measures. Possible measures to raise the pH include, for example, the addition of a suitable alkaline biocide (in the case of considerable microbial attack), the addition of a suitable organic base or the subsequent filling of a fresh emulsion or solution at a higher concentration within the framework of a partial exchange.

## **5.10 Random-sampling rule for individual machines**

(1) In the case of the employment of a larger number of individual machines, the measurement obligations laid down in Numbers 5.3, 5.4, 5.8 and 5.9 are also regarded to have been fulfilled if, in a proper manner, random samples of used water-mixed cooling lubricants from one or some individual machines are taken in each case and examined accordingly. During this procedure it must be ensured that the random-sampling system is in each case applied to groups of individual machines in which the same cooling lubricant is used and which work under the same, or at least similar, processing and operating conditions.

(2) It must be ensured that the individual machines operating under the most difficult conditions in each case or that the water-mixed cooling lubricants subject to the relatively most difficult conditions are appropriately represented in the random-sample selection. From time to time it is necessary to check whether the random-sampling system continues to meet the above-mentioned demands.

(3) For example, a random-sample rule can be laid down by first examining in a risk-determination process all of the parameters that are relevant for the possible formation of N-nitrosamines, in addition to those already cited in Number 2, Number 4 and in Numbers 5.2, 5.3, 5.6, 5.7, 5.8 and 5.9, for example, the extent and type of carried-over substances (e.g. foreign oils) and of the formed reaction products, the plant operating times, the life of the cooling lubricant as well as the presence of catalysts.

(4) Subsequently, the nitrite content and the pH are regularly measured on a weekly basis for three months. A decision is then taken on whether the measurement results from selected items of plant can be transferred to other workplaces.

(5) If only one of several items of plant is monitored, the one with the most unfavourable measurement results (i.e. the highest nitrite value or the lowest pH) must be selected. It must be ensured in the risk-determination process that a sufficient correlation exists between the measured item of plant and the further items of plant. The time and place of measurement must be selected so that the higher risk is determined (apart from the above-mentioned measurement results for nitrite and the pH, for example, the item of plant with the higher temperature or the longer dwell time of the cooling lubricant).

(6) Other appropriate methods for the establishment of a random-sampling rule are permitted if these methods also ensure the inclusion of the items of plant with the highest risk level in each case in terms of the possible formation of N-nitrosamines.

## 5.11 Test methods

Methods for the above-mentioned checks are listed in the Annex to this Technical Rule.

### Literature

- [1] Technical Rule for Hazardous Substances TRGS 552 "N-nitrosamines"
- [2] Ordinance on protection against hazardous substances (Hazardous Substances Ordinance - GefStoffV) of 23.12.2004
- [3] D. Breuer, R. van Gelder, Keeping the air free from hazardous substances (Gefahrstoffe-Reinhaltung der Luft), 61, p. 49-55 (2001)
- [4] M. L. Douglass, B. L. Kabacoff, G. A. Anderson, M. C. Cheng, J. Soc. Cosmet. Chem., 29, p. 581-606 (1978)
- [5] R. Preussmann (editor): The nitrosamine problem, report by the German Research Foundation, Verlag Chemie, Weinheim (1983)
- [6] M. J. Hill (publisher), Nitrosamines, VCH Verlagsgesellschaft, Weinheim (1988)
- [7] R. N. Loeppky, C. J. Michejda (Herausgeber), Nitrosamines and Related N-Nitroso Compounds - Chemistry and Biochemistry, ACS Symposium Series 553, Washington D.C. (1994)

- [8] E. O. Bennett, D. L. Bennett, *Tribology International*, 17, p. 341-346 (1984)
- [9] R. O. Sköld, L. C. Svensson, B. C. Challis, *Proceedings of the 8th International Tribology Colloquium*, Technische Akademie Esslingen, p. 18.6-1 – 18.6-12, Ostfildern (1992)
- [10] Nitrosamines, Conference transcript (Tb 57), Series of publications from the Federal Institute for Occupational Safety and Health, Dortmund (1992)
- [11] H. Blome, D. Breuer, W. Pfeiffer, D. Wolf, *Staub/Keeping the air clean*, p. 3-6 (1990)
- [12] S. Fadlallah, S. F. Cooper, M. Fournier, D. Drolet, G. Perrault, *J. Chromat. Science*, 28, p. 517-523 (1990)
- [13] Report from the BG Institute for Occupational Safety (BIA) 6/95 "Cooling lubricants", p. 51, St. Augustin (1995)
- [14] Directive 67/548/EEC of 27.6.1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances, Official Journal EC L 196 p. 1 of 16.8.1967, including the Adaptation Directives
- [15] Technical Rule for Hazardous Substances TRGS 905 "Register of carcinogenic, mutagenic or reproductive toxic substances"
- [16] J. Hübner, *Proceedings of the 9th International Tribology Colloquium*, Technische Akademie Esslingen, p. 4.8-1 – 4.8-18, Ostfildern (1994)
- [17] M. Blankart, *N-nitroso compounds in cosmetic agents*, Dissertation, Kaiserslautern (1989)
- [18] G. Eisenbrand, *Avoiding nitrosamine formation in cosmetic agents*, study for IKW/TEGEWA, Kaiserslautern (1994)
- [19] H. Sommer, *Formation and occurrence of N-nitrosodialkanolamines in cosmetic agents as well as prevention measures*, Dissertation, Kaiserslautern (1988)
- [20] Technical Rule for Hazardous Substances (TRGS) 401: "Risk as a result of dermal contact - ascertainment, assessment, measures"
- [21] Drinking-water Ordinance of 21.5.2001, Federal Law Gazette I, p. 959, last amended on 25.11.2003, Federal Law Gazette I, p. 2304
- [22] German Statutory Accident Insurance Institution Rule (BGR) 143, "Activities involving cooling lubricants", Main Association of German Statutory Accident Insurance Institutions, St. Augustin (2006)
- [23] H. Hobelsberger, W. Illi, A. Kiechle, H. Kreilinger, I. Sadorf, W. Angerer, C. Eckert, R. Freitag, M. Rocker, D. Breuer, *Hazardous Substances - Keeping the air clean*, 60, p. 159-166 (2000)
- [24] D. Breuer, C. Lützenkirchen, M. Böckler, T. Rabente, *Hazardous Substances - Keeping the air clean*, 64, p. 473-479 (2004)
- [25] The BG Institute for Occupational Safety Report 7/96, "Cooling Lubricants", p. 80-83, St. Augustin (1996)

[26] CD-ROM "Safe handling of cooling lubricants", The BG Institute for Occupational Safety, St. Augustin (2007)

**Annex**

Annex: Test methods for monitoring the employment of water-mixed cooling lubricants

## Annex to Technical Rule 611

### Test methods for monitoring the employment of water-mixed cooling lubricants

(1) Nitrate (in the water added initially or replenishment water)

DIN 38405, Part 9 : Anions (Group D), determination of the nitrate ion (D 9)

or

test rods for the detection and semi-quantitative determination of nitrate ions

(2) Nitrite

DIN EN 26777:1993-04 : Water quality, determination of nitrite; spectrometric method/photometry (ISO 6777:1984), Beuth-Verlag, Berlin (1993)

or

test rods for the detection and semi-quantitative determination of nitrite ions

(3) N-nitroso-diethanolamine (NDELA)

*NDELA in the workplace atmosphere:*

Methods for the determination of N-nitrosodiethanolamine. In BGI (Information on occupational safety and health from the Statutory Accident Insurance Institutions) 505: Analysis methods for the determination of the concentration of carcinogenic working substances in the workplace atmosphere recognized by the German Statutory Accident Insurance Institutions, method No. 36 (Sept. 1992). Carl Heymanns Verlag KG, Luxemburger Straße 449, 50939 Cologne

N-Nitrosodiethanolamine, In: Work folder of the BG-Institute for Occupational Safety and Health, Measurement of Hazardous Substances, sheet No. 8183, (24th loose-leaf version, 2000), Erich Schmidt Verlag, Bielefeld

*NDELA in cooling-lubricant solutions:*

Annex BGI (Information on occupational safety and health from the Statutory Accident Insurance Institutions) 505: Determination of N-nitrosodiethanolamine in cooling-lubricant solutions, (Sept. 1992), Carl Heymanns Verlag KG, Luxemburger Straße 449, 50939 Cologne

Analysis of water-mixed cooling lubricants, Part 2: N-nitrosodiethanolamine. In: Work folder of the BG-Institute for Occupational Safety and Health, Measurement of Hazardous Substances, sheet No. 7748/2, (30th loose-leaf version, 2003), Erich Schmidt Verlag, Bielefeld

(4) N-nitrosomorpholine (NMOR)

*NMOR in the workplace atmosphere:*

Method for the determination of N-nitrosamines. In BGI (Information on occupational safety and health from the Statutory Accident Insurance Institutions) 505: Analysis methods for the determination of the concentration of carcinogenic working substances in the workplace atmosphere recognized by the German Statutory Accident Insurance Institutions, method No. 23 (Sept. 1992). Carl Heymanns Verlag KG, Luxemburger Straße 449, 50939 Cologne

N-nitrosamines, In: Work folder of the BG-Institute for Occupational Safety and Health, Measurement of Hazardous Substances, sheet No. 8172, (35th loose-leaf version, 2005), Erich Schmidt Verlag, Bielefeld

*NMOR in cooling-lubricant solutions:*

Analysis of water-mixed cooling lubricants, Part 3: Volatile nitrosamines in cooling lubricants (NMOR). In: Work folder of the BG-Institute for Occupational Safety and Health, Measurement of Hazardous Substances, sheet No. 7748/3, (30th loose-leaf version, 2003), Erich Schmidt Verlag, Bielefeld

(5) pH

DIN 51369 : Determination of the pH of water-mixed cooling lubricants. Analysis of water-mixed cooling lubricants, Part 7: pH. In: Work folder of the BG-Institute for Occupational Safety and Health, Measurement of Hazardous Substances, sheet No. 7748/3, (31st loose-leaf version, 2003), Erich Schmidt Verlag, Bielefeld

The use of pH special indicator paper or pH special indicator rods is permitted if a comparable degree of precision is achieved.

(6) Alkanolamines [24]

Analysis of water-mixed cooling lubricants, Part 4: Alkanolamines. In: Work folder of the BG-Institute for Occupational Safety and Health, Measurement of Hazardous Substances, sheet No. 7748/3, (30th loose-leaf version, 2003), Erich Schmidt Verlag, Bielefeld

A list of the measurement units accredited according to § 9, Section 6 of the Hazardous Substances Ordinance is published on the internet under

[www.bua-verband.de/gefahrstoffmessstellen.html](http://www.bua-verband.de/gefahrstoffmessstellen.html).

**Overview of the above-mentioned test methods**

**Table 1 Standard programme of testing for cooling lubricants that meet the demands according to Number 4.2**

| <b>Test</b>  | <b>Method</b>  | <b>Frequency</b>                                | <b>Limit value</b>                         | <b>Comments</b>                            |
|--|--|---|--|--|
| Nitrate content of the water added initially or replenishment water    | DIN 38405, Part 9, or test rods  | from time to time, see Number 5.2               | max. 50 mg/l                               |  |
| Nitrite content of the water-mixed cooling lubricant                   | DIN EN 26777 or test rods  | always weekly, see Number 5.3                   | max. 20 mg/l                               |  |
| N-nitroso-diethanol-amine (NDELA) in the water-mixed cooling lubricant | BGI 505, method No. 36, Annex  | as required, see Number 5.4                     | max. 0.0005 % (5 mg/kg) [15]               |  |
| N-nitrosodiethanol-amine (NDELA) in the workplace atmosphere           | BGI 505, method No. 36   | as required, see Number 5.4                     | For the state of technology see Number 5.4 |  |
| Temperature in the system of the water-mixed cooling lubricant         | Indication of temperature  | regularly                                       | -  | Avoidance of elevated temperature          |
| pH of the water-mixed cooling lubricant                                | DIN 51369 pH special indicator paper/rods are permitted if they achieve the same precision as DIN 51369. | weekly (glass and ceramics processing: monthly) | -  | Avoidance of a considerable drop in the pH |

**Table 2 Extended scope of testing for the special case of cooling lubricants containing secondary amines (according to Numbers 4.4 and 5.5)**

| Test  | Method   | Frequency                         | Limit value                                | Comments  |
|---|--|-----------------------------------|--|---|
| N-nitrosamines in the water-mixed cooling lubricant   | BGI 505, No. 36, Annex (NDELA)   | see Number 5.5                    | see Technical Rule 905, Number 4 [15]      |   |
| N-nitrosamines in the workplace atmosphere  | BGI 505, No. 36 (NDELA), No. 23 (NMOR)   | see Number 5.5                    | For the state of technology see Number 5.5 |   |
| Nitrate content of the water added initially or replenishment water   | DIN 38405, Part 9, or test rods  | from time to time, see Number 5.2 | max. 50 mg/l                               |   |
| Nitrite content of the water-mixed cooling lubricant  | DIN EN 26777 or test rods  | weekly                            | max. 20 mg/l                               |   |
| pH of the water-mixed cooling lubricant Drop in the pH (compared to the pH of the freshly prepared water-mixed cooling lubricant) | DIN 51369 pH special indicator paper/rods are permitted if they achieve the precision of DIN 51369 | weekly                            |  | max. 0.5 pH points                              |
| Microorganisms  | Suitable laboratory methods [25,26] or dip slides  | weekly                            | -  | Avoidance of considerable microbial attack      |
| Concentration of the water-mixed cooling lubricant  | e.g. titration to alkaline cooling-lubricant constituents  | weekly                            | -  | Avoidance of considerable drop in concentration |
| Temperature in the system of the water-mixed cooling lubricant  | Indication of temperature  | regularly                         | -  | Avoidance of elevated temperature               |