Edition: May 2007

Technical Rules for Hazardous Substances	Restrictions on the use of anticorrosion agents whose use can lead to the formation of N-nitrosamines	Technical Rule 615

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 (GMBl).

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Annex

1 Scope

(1) This Technical Rule applies to the production and use of water-miscible, water-mixed and non-water-miscible anticorrosion agents, volatile corrosion inhibitors (VCI) and anticorrosion greases and waxes which are intended to provide temporary protection of metal objects (see also DIN EN ISO 8044 [1]). According to the meaning of this Technical Rule, anticorrosion agents are also materials from which volatile corrosion inhibitors are released (e.g. VCI films, VCI papers, VCI packaging as well as VCI oils) or those to which anticorrosion agents adhere.

(2) This Technical Rule is aimed at the employers in those companies where anticorrosion agents according to Section 1 are produced or used or in which metals with adherent anticorrosion agents are finished. This Technical Rule is also aimed at the producers and importers of such anticorrosion agents as well as at 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,
- to include in their safety data sheets the information demanded by this Technical Rule.

(3) Technical Rule 615 supplements Technical Rule 552 [2] for the special area that is described.

(4) Technical Rule 615 provides safety advice for the composition, production and use of anticorrosion agents intended for the temporary protection of metal objects. In accordance with the minimization rule stipulated in the Hazardous Substances Ordinance (GefStoffV) [3] (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 the production and use of anticorrosion agents and, as a result, largely exclude the exposure of workers during activities involving anticorrosion agents.

(5) Under certain circumstances, N-nitrosamines may form during the production of anticorrosion agents as well as during the use of anticorrosion agents [4,5].

(6) In order to reduce the risk of the formation of category 1 and 2 carcinogenic N-nitrosamines, restrictions are pronounced regarding the use of certain anticorrosion agents and protection and monitoring measures are stipulated for their production and use.

(7) 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 anticorrosion agents.

2 Definition of terms and explanations

(1) Anticorrosion agents are used in many areas (e.g. industry, skilled trades, service industries) for the purpose of preventing the corrosion of metal surfaces. This indeed occurs both with regard to the protection of metal input stock and metal products such as workpieces, vehicle parts, metal sheets, metal strips and other parts as well as in the protection of plant (store tanks, pipeline systems, circulation systems etc.). They are used, inter alia, in the form of

- liquids to be applied by dipping, spraying, brush application or rolling,
- greases and waxes,
- volatile corrosion inhibitors (e.g. as a component of VCI materials including VCI oils).

Subdivision is typically undertaken according to the following groups:

- non-water-miscible anticorrosion liquids containing solvents
- non-water-miscible, solvent-free anticorrosion liquids
- water-miscible anticorrosion liquids (concentrates)

- water-mixed anticorrosion liquids (emulsions and solutions)
- volatile corrosion inhibitors and VCI materials
- anticorrosion greases and waxes

Overview Table:

Type	Form in which used	Property	Type of application
Non-water-miscible anticorrosion liquids containing solvents	Oil	Low or medium viscosity	Dipping, spraying, brush application, rolling (preferably without heating)
e.g. non-water-miscible organic liquids which have a water-displacing effect and leave behind thin corrosion-protection films (dewatering anticorrosion fluids)	Oil	Medium viscosity	Dipping, spraying
Non-water-miscible, solvent-free anticorrosion liquids	Oil	Relatively high viscosity	Dipping, spraying, brush application, rolling (preferably with heating)
Water-miscible anticorrosion liquids	Liquid concentrate	Medium to high viscosity	Dipping, spraying, brush application, rolling (with and without heating)
Water-mixed anticorrosion liquids	Emulsion or solution	Low or very low viscosity	Dipping, spraying, brush application, rolling (preferably without heating)
Volatile corrosion inhibitors	Worked into powder, paper, polymer sheets, foams, moulded parts, oils etc. (different carrier substances), “VCI materials”	Packaging component with worked-in volatile corrosion inhibitors (protective effect from at least 10°C)	Packaging technology: covering, wrapping, in-laying, insertion etc. in airtight packaging,
Anticorrosion greases and waxes			

(2) The presence of nitrosatable secondary amines (including disguised secondary amines) and nitrosatable agents (including precursors) in anticorrosion agents, in store tanks, pipeline systems and circulation systems), in the workplace atmosphere as well as in VCI materials (e.g. VCI films, VCI papers, VCI packaging and VCI oils) results in an increased risk of the formation of carcinogenic N-nitrosamines.

(3) According to the meaning of this Technical Rule, N-nitrosamines are the category 1 and 2 carcinogenic N-nitrosamines cited in Number 1, Section 1 of Technical Rule 552 and other such carcinogenic N-nitrosamines which may form in a significant quantity within the framework of the production or use of anticorrosion agents and corresponding materials according to Number 1, Section 1 or which are present from the outset. On the basis of currently available knowledge, it can be assumed that, in this regard, essentially the formation of the following category 2 N-

nitrosamines cited in Technical Rule 552 is possible under certain conditions:

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

(No N-nitrosamines are currently classified as category 1 or 2 mutagens.)

(4) During the production or use of anticorrosion agents containing the secondary amine piperazine,

- N-nitroso-piperazine CAS No. 5632-47-3 and
- N,N'-dinitroso-piperazine CAS No. 140-79-4

may form. There is still no toxicological classification for N-nitroso-piperazine and N,N'-dinitroso-piperazine. As a precaution, they should be treated in the same way as the above-mentioned N-nitrosamines according to Number 2, Section 3.

(5) 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 tests have not revealed an indication of a carcinogenic effect, are to be regarded as non-carcinogenic N-nitrosamines.

(6) Category 3 mutagenic N-nitrosamines are not N-nitrosamines according to the meaning of Technical Rule 615 (see also Number 1, Section 3 of Technical Rule 552). As a matter of principle, on the basis of EU legislation on hazardous substances [6] and the Hazardous Substances Ordinance (see there 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 assessment of the risk 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. N-nitroso-dicyclohexylamine (dicyclohexylnitrosamine) is currently classified as a category 3 mutagen [7]. No N-nitrosamines are currently classified as category 3 carcinogens.)

(7) Inter alia, the following nitrosatable secondary amines have been named as constituents of anticorrosion agents [4,5]:

1. Secondary amines that form a category 2 carcinogenic N-nitrosamine:
   - diethanolamine (2,2'-iminodiethanol) CAS No. 111-42-2,
   - morpholine CAS No. 110-91-8,
2. Secondary amine forming two N-nitrosamines which have not yet been classified:

   piperazine CAS No. 110-85-0,
3. Secondary amine that forms a category 3 mutagenic N-nitrosamine:

   dicyclohexylamine CAS No. 101-83-7.

(8) According to the meaning of this Technical Rule, secondary amines are those secondary amines which, under the usual conditions of production or use of anticorrosion agents, 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) As a precaution, piperazine (CAS No. 110-85-0) should likewise be regarded as a secondary amine according to the meaning of Number 2, Section 8 (see also Number 2, Section 4).

(10) According to the meaning of this Technical Rule, disguised secondary amines are particular nitrogenous compounds which release secondary amines according to Section 8, for example, as a result of hydrolysis or thermal decomposition or other chemical reactions in the course of their production or use in anticorrosion agents (e.g. certain fatty acid alkanolamides which are produced from a fatty acid and a secondary alkanolamine - see also Technical Rule 611 [8]).

(11) With regard to the assessment of a possible release of secondary amines from such compounds, the crucial factor for the application of this Technical Rule is whether such a release occurs to a significant extent under the usual conditions that obtain in the production, storage or use of anticorrosion agents. 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 $\mu g/m^3$ - see Number 4.2, Section 3 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 anticorrosion agent) according to Technical Rule 905 (1 or 5 mg/kg) [7] 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.

(12) Secondary amines which are demonstrably not nitrosatable or are of only very low nitrosatability or whose nitrosation does not result in category 1 or 2 carcinogenic N-nitrosamines, e.g.

- dicyclohexylamine CAS No. 101-83-7,

are not secondary amines according to the meaning of this Technical Rule. Consequently, the restrictions on use according to Number 4.2 and the monitoring measures according to Number 5.2 and, possibly, 5.4 do not apply to anticorrosion agents that contain such secondary amines.

(13) Relevant nitrosatable agents or their precursors are, inter alia, [9-12]:

- certain nitrogen oxides (N_2O_3 and N_2O_4 as direct nitrosating agents as well as NO and NO_2 as precursors),
- nitrosyl halogenides (e.g. NOCl, NOBr),
- nitric acid (HNO_2) and its reaction patterns,

- nitrites, e.g. sodium nitrite ($NaNO_2$, CAS No. 7632-00-0) and potassium nitrite (KNO_2, CAS No. 7758-09-0)

  (nitrite frequently occurs in aqueous systems due to bacterial reduction of nitrate as the result of microbial attack).

(14) The following factors promote or influence the formation of N-nitrosamines [2, 8-12]:

- high concentrations of the co-reactants (nitrosating agent and 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 use temperatures,
- the presence of catalysts (e.g. formaldehyde, thiourea and individual thiols, halogenide and pseudohalogenide ions, individual metal ions),
- the activity of metal surfaces which can also have a catalytic effect,
- solvents in particular cases,
- uses involving the formation of aerosols.

(15) Inhibitors inhibit the formation of N-nitrosamines. Inter alia, the following compounds have been named as such in the literature: primary amines and aminoalcohols, primary amino acids, ascorbic acid and ascorbic acid derivates, certain thiols, sulphamates, p-aminobenzoic acid, alkane sulphonamide, 〈-tocopherol and 〈-tocopherol derivatives [2,8-12]. The effectiveness of an inhibitor must be tested under realistic conditions of use.

(16) In aqueous systems, a considerable part is played by the pH. Low pH values promote the formation of N-nitrosamines. The optimum pH range for N-nitrosamine formation is mostly located between 2 and 5. Nevertheless, under certain reaction conditions, N-nitrosamines can also be formed in an alkaline milieu, albeit with a lower yield [8-12].

(17) The formation of N-nitrosamines can be prevented or reduced by [2,8-12]

1. the absence or very low concentrations of co-reactants (nitrosating agents and nitrosatable secondary amines) including their precursors, preferably achievable by employing substitutes which are not co-reactants in the formation of N-nitrosamines (see also Number 4.4),
2. reaction conditions which are unfavourable for N-nitrosamine formation, 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),
3. absence of catalysts (see above),

4. presence of inhibitors (e.g. primary amines and primary alkanolamines, ascorbic acid and ascorbic acid derivatives, sulphamates, p-aminobenzoic acid, alkane sulphonamides, α-tocopherol and α-tocopherol derivatives, individual phenols); a number 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

The section “Information acquisition and risk assessment” is targeted particularly at the employers in companies which use anticorrosion agents and corresponding materials or finish metals with adherent anticorrosion agents.

3.1 Information acquisition

(1) Information acquisition includes the steps determination, assessment, examination and documentation (see also Technical Rule 440 [13]).

(2) The information acquisition process that is to be undertaken by the employer with regard to the composition of the anticorrosion agent or the VCI paper, the VCI film, VCI packaging as well as VCI oil etc. in the condition at the time of supply includes the determination of

- the content of N-nitrosamines that are already present,
- the content of nitrosating agents and their precursors,
- the content of secondary amines including disguised secondary amines.

(3) If no information in this regard is available in the safety data sheet, the employer must request it from the manufacturer of the utilized anticorrosion agent. If the information according to Number 3.1, Section 2 is not available, the anticorrosion agents must not be used.

(4) The information acquisition with regard to the use of anticorrosion agents concerns

- the possible presence of N-nitrosamines in the workplace atmosphere, in the anticorrosion agent, in VCI materials, on surfaces, in packaging or in or on other relevant materials,
- the possible presence of secondary amines (including disguised secondary amines) in store tanks, pipeline systems, circulation systems, in the workplace atmosphere, on surfaces, in packaging or in or on other relevant materials,
- the possible presence of nitrosating agents and their precursors (e.g. nitrite) in store tanks, pipeline systems, circulation systems, in the workplace atmosphere (here in particular nitrosating nitrogen oxides and their precursors - see Number 2, Section 13), on surfaces, in packaging or in or on other relevant materials.

(5) Special attention must be paid to the input stock and metal products (see Number 2, Section 1) for which the upstream supplier does not give any confirmation of the absence of N-nitrosamines, secondary amines (including disguised secondary amines) and nitrosating agents (including precursors) or for which the supply source is unknown or not clear (e.g. in some cases where supplies are from abroad).

(6) A particularly high risk of workers being exposed to N-nitrosamines and other dangerous constituents of anticorrosion agents exists in connection with those processes and applications in which considerable nebulization (aerosol formation) occurs.

3.2 Prohibition of mixing

(1) Anticorrosion agents containing secondary amines (including disguised secondary amines) according to Number 2, Section 8 or 10 must not be mixed with anticorrosion agents or other preparations that contain nitrosating agents or their precursors (e.g. nitrite).

(2) Attention must be paid here to ensuring that the other co-reactant that is in each case involved in N-nitrosamine formation (nitrosatable secondary amine or nitrosating agent) is not present on surfaces.

3.3 Carry-over of secondary amines

(1) Care must be taken to prevent secondary amines (including disguised secondary amines) according to Number 2, Section 8 or 10 as well as foreign substances and impurities which contain or release such secondary amines being carried over in considerable amounts into anticorrosion agents that are free of secondary amines or into work areas in which anticorrosion agents are handled.

(2) During the use of anticorrosion agents that contain nitrosating agents or their precursors (such as nitrite) according to Number 4.3, particularly careful attention must be paid to the exclusion of secondary amines according to Number 2, Section 8 or 10.

3.4 Carry-over or formation of nitrosating agents

(1) Avoid the penetration or carry-over of nitrosating agents or their precursors into anticorrosion agents (in particular into water-mixed anticorrosion liquids) which are free of nitrosating agents and their precursors or into work areas in which anticorrosion agents are handled.

(2) As far as possible, keep away external sources of nitrosating agents, in particular nitrosating nitrogen oxides and their precursors (as a result of the operation of combustion engines, gas or diesel-powered forklift trucks, welding equipment or similar as well as cigarette and other tobacco smoke).

(3) As far as possible, avoid the carry-over of nitrite-containing cleaning agents, nitrite-containing hardening salts, nitrite-containing pre-preserved parts and similar into anticorrosion agents or into workplaces in which anticorrosion agents are handled. Particular attention should be paid to this in the case of the import of pre-preserved parts from abroad.

(4) As far as possible, the formation of nitrite from nitrate as a result of bacterial reduction in aqueous systems (emulsions and solutions) must be avoided by taking suitable measures.

(5) In areas in which anticorrosion agents containing secondary amines according to Number 4.2 are employed, strict attention must be paid to the avoidance of the carry-over or formation of nitrosating agents and their precursors.

3.5 Temperature during the employment of anticorrosion agents

Elevated temperatures promote the formation of N-nitrosamines and the transfer of N-nitrosamines to the workplace atmosphere and should therefore be avoided as far as possible. This applies in particular to anticorrosion agents that still contain secondary amines according to Number 4.2 or nitrite or other nitrosating agents according to Number 4.3.

3.6 Avoidance of dermal contact

Dermal contact with the anticorrosion agent or the VCI material (see Number 1, Section 1) must be limited to the unavoidable level by means of technical measures. In the case of dermal contact, suitable protective gloves which ensure protection against the anticorrosion agent must be worn. Attention is drawn in this connection to Technical Rule (TRGS) 401 [14]. Considerable skin absorption is to be expected in connection with a number of N-nitrosamines.

4 Restrictions on the use of anticorrosion agents, substitutes

The following section describes anticorrosion agents which either must not be used at all or only in compliance with special monitoring measures, as well as corresponding substitutes.

4.1 Absence of nitrosating agents and secondary amines

(1) In accordance with the Hazardous Substances Ordinance, in particular its § 18 , Section 1 and Annex IV, Number 31 [15], anticorrosion agents that simultaneously contain secondary amines (including disguised secondary amines) according to Number 2, Section 8 or 10 and nitrosating agents (including precursors) must not be employed.

(2) A very low content of such secondary amines occurring as a result of by-products and impurities in technical products (components and constituents of anticorrosion agents) is permitted up to the maximum value cited in Number 4.2, Section 6. Consequently, anticorrosion agents whose content of such secondary amines is below the concentration limits cited in Number 4.2, Section 6 (related to the finished product) are not subject to this rule.

4.2 Anticorrosion agents containing secondary amines

(1) Anticorrosion agents that contain free or disguised secondary amines according to Number 2, Section 8 or 10 must be monitored during their employment according to Number 5.2 and, if appropriate, 5.4 in connection with the formation of N-nitrosamines.

(2) With regard to the concentration of category 1 and 2 carcinogenic N-nitrosamines in the workplace atmosphere, the state of technology shall be adhered to during the production or the employment of such anticorrosion agents (see Number 5.2 and 5.3).

(3) A value of 0.2 $\mu g/m^3$ (category 1 and 2 carcinogenic N-nitrosamines in the workplace atmosphere) is to be regarded as the state of technology (see Technical Rule (TRGS) 552 Number 4.3).

(4) In preparations or materials, the concentration limits for category 1 or 2 carcinogenic N-nitrosamines according to Technical Rule (TRGS) 905 Number 4 must be adhered to (see Number 5.4).

(5) When employing tertiary and primary amines whose technical qualities include such secondary amines (including disguised secondary amines), a highest possible purity on the part of the technical products must be ensured.

(6) The content of secondary amines in the finished product must not exceed

- 0.02 % in the case of VCI packaging materials (with an active-substance content of up to 10 %) ,
- 0.2 % in the case of all other anticorrosion agents and VCI materials

This content must not be achieved by targeted addition of secondary amines.

(7) The information on the content of secondary amines or the purity of technical products (e.g. technical primary and tertiary amines) must be included in the safety data sheet that is to be provided by the manufacturer (e.g. its section 3) even if these secondary amines are not to be classified as hazardous substances. Otherwise it is to be acquired from the manufacturer in accordance with § 7 of the Hazardous Substances Ordinance.

4.3 Anticorrosion agents containing nitrosating agents or their precursors

(1) VCI materials (including VCI oils), anticorrosion greases and waxes and non-water-miscible anticorrosion liquids containing more than 1.0 % nitrite (determined as sodium nitrite) or more than 0.1 % of other nitrosating agents (e.g. nitrophenols, dinitrophenols or nitrosophenols) or their precursors may only be employed if the monitoring measures according to Number 5.3 are adhered to.

(2) Every effort should be made to reduce the nitrite content to below 0.5 %.

(3) At the time of supply, water-miscible and water-mixed anticorrosion agents must not contain any nitrite or any other nitrosating agents, including their precursors (see the Hazardous Substances Ordinance, in particular its § 18, Section 1 and Annex IV, Number 31).

(4) The information required with regard to the content of nitrite and other nitrosating agents and their precursors must be included in the safety data sheet that is to be provided by the manufacturer, even if these substances are not to be classified as hazardous substances. Otherwise it is to be acquired from the manufacturer in accordance with § 7 of the Hazardous Substances Ordinance.

4.4 Substitutes

(1) If anticorrosion agents are employed which include secondary amines (including disguised secondary amines) according to Number 2, Section 8 or 10 or nitrosating agents or their precursors, it must be examined whether they can be substituted by technical products of equal quality which are free of such secondary amines (including disguised secondary amines) or free of nitrosating agents and their precursors and which do not include any other risks.

(2) Primary amines or primary alkanolamines are regarded as suitable substitutes for secondary amines or secondary alkanolamines since primary amines and primary alkanolamines do not form any stable N-nitrosamines (see also Technical Rule (TRGS) 611). According to current scientific knowledge, it can be assumed that, due to their inhibitory effect, primary amines and primary alkanolamines inhibit the formation of N-nitrosamines (see also Number 2, Section 15).

5 Monitoring measures that apply to the use of anticorrosion agents

(1) The following monitoring measures are to be adhered to in particular by the employers at those companies which employ and handle anticorrosion agents and corresponding materials (see Number 1, Section 1).

(2) In addition, they also apply to the production of anticorrosion agents and VCI materials. They are therefore also directed at the employers of the manufacturing companies.

5.1 Anticorrosion agents that are free of secondary amines and nitrosating agents

(1) No obligation to undertake monitoring measures applies in the case of anticorrosion agents that contain neither secondary amines according to Number 2, Section 8 or 10 nor nitrosating agents.

(2) The following concentration limits apply to this exemption from the monitoring measures:

- In accordance with Number 4.2, Section 6, the content of secondary amines according to Number 2, Section 8 and 10 in VCI packaging materials (with an active-substance content of up to 10 %) must not exceed 0.02 % (related to the finished product) and in all other anticorrosion agents and VCI materials 0.2 % (related to the finished product).
- In accordance with Number 4.3, Section 1, in VCI materials, anticorrosion greases and waxes and non-water-miscible anticorrosion liquids, the nitrite content must not exceed 1.0 % (determined as sodium nitrite and related to the preparation or the VCI material) or the content of other nitrosating agents must not exceed 0.1 % (related to the preparation or the VCI material).

5.2 N-nitrosamine content in the workplace atmosphere in the case of anticorrosion agents that contain secondary amines

(1) Regular N-nitrosamine examinations must be performed in the workplace atmosphere during the use of anticorrosion agents with components and constituents that contain secondary amines according to Number 4.2. It is necessary to measure the N-nitrosamine that can be formed as a result of nitrosation of the utilized secondary amine (e.g. N-nitroso-morpholine in the case of the presence of morpholine or morpholine derivatives).

(2) This measurement obligation does not apply if, in the finished product, the secondary amine content (including disguised secondary amines) according to Number 2, Section 8 and 10 does not exceed the concentration limits cited in Number 4.2, Section 6.

(3) During the production or the use of such anticorrosion agents, the state of technology with regard to the concentration of category 1 and 2 carcinogenic N-nitrosamines in the workplace atmosphere shall be adhered to. A value of 0.2 $\mu g/m^3$ is to be considered as the state of technology in this regard (see Number 4.3 of Technical Rule (TRGS) 552).

(4) In all other cases, the rules and provisions contained in Technical Rule 402 [16] apply to the N-nitrosamine measurements in the workplace atmosphere.

5.3 N-Nitrosamine measurements in the workplace atmosphere in the case of anticorrosion agents that contain nitrosating agents and their precursors (e.g. nitrite)

(1) During the use of VCI materials (including VCI oils), anticorrosion greases and waxes and non-water-miscible anticorrosion liquids containing more than 1.0 % nitrite or more than 0.1 % of other nitrosating agents according to Number 4.3 it is likewise necessary to ensure, on the basis of measurements performed in the workplace atmospheres according to Technical Rule 402, that no significant N-nitrosamine formation takes place.

(2) With regard to the concentration of category 1 and 2 carcinogenic N-nitrosamines in the workplace atmosphere, the state of technology shall be adhered to during the production or use of such anticorrosion agents. A value of 0.2 $\mu g/m^3$ is to be considered as the state of technology in this regard (see Number 4.3 of Technical Rule 552).

5.4 N-nitrosamine content of anticorrosion liquids that contain secondary amines and are employed in circulation processes

(1) Anticorrosion liquids (e.g. emulsions and solutions) that contain secondary amines according to Number 2, Section 8 and 10 or according to Number 4.2 and are employed in circulation processes (e.g. in spraying or dipping plant) must be regularly monitored with regard to their N-nitrosamine content. It is necessary to measure the concentration of the N-nitrosamine which can be formed by nitrosation of the secondary amine contained in the anticorrosion agent (see Number 5.2).

(2) The following examination intervals apply:

- If the N-nitrosamine concentration is below half the concentration limit according to Number 4 of Technical Rule 905 (see Section 3), the next examination takes place after 6 months.
- If the N-nitrosamine concentration is between half the concentration limit and the concentration limit according to Number 4 of Technical Rule 905, the next examination takes place after 3 months.

(3) The concentration limits for category 1 or 2 carcinogens in preparations and materials according to Number 4 of Technical Rule 905 amount to

- 0.0005 % (5 mg/kg) for N-nitroso-diethanolamine CAS No. 1116-54-7,
- 0.0001 % (1 mg/kg) for N-Nitroso-morpholine CAS No. 59-89-2 .

(4) If this concentration limit is exceeded, the preparation or material concerned is to be regarded as a category 1 or 2 carcinogen. In this case, the provisions of § 11 of the Hazardous Substances Ordinance apply, i.e. the measures relating to protection level 4 must be adhered to.

(5) In the case of N-nitroso-piperazine and N,N‘-dinitroso-piperazine, no substance-specific concentration limits have yet been laid down for the classification of preparations. Until the substance-specific concentration limits have been laid down, orientation towards the level of the concentration limit for N-nitroso-morpholine is recommended.

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[13] Technische Regel für Gefahrstoffe TRGS 440: „Ermitteln und Beurteilen der Gefährdungen durch Gefahrstoffe am Arbeitsplatz“

[14] Technische Regel für Gefahrstoffe TRGS 401: „Gefährdung durch Hautkontakt - Ermittlung, Beurteilung, Maßnahmen“

[15] Verordnung zur Umsetzung der EG-Richtlinien 2002/44/EG und 2003/10/EG, Artikel 4 (Änderung der Gefahrstoffverordnung) vom 6.3.2007, BGBl. I Nr. 8 S. 261, S. 276

[16] Technische Regel für Gefahrstoffe TRGS 402: „Ermittlung und Beurteilung der Konzentration gefährlicher Stoffe in der Luft in Arbeitsbereichen“

Annex

Annex: Examination methods for the monitoring of anticorrosion agents

Annex to Technical Rule 615

Examination methods for monitoring anticorrosion agents

N-nitroso-diethanolamine (NDELA)

-	in the workplace atmosphere	BGI (Information on occupational safety and health from the Statutory Accident Insurance Institutions) 505-36 (BIA - The BG Institute for Occupational Safety - 8183)
-	in emulsions and solutions	BGI (Information on occupational safety and health from the Statutory Accident Insurance Institutions) 505-36, Annex
-	in VCI papers/films	BGIA (BG-Institute for Occupational Safety and Health) work folder, 30th loose-leaf version IV/03

N-nitroso-morpholine (NMOR)

-	in the workplace atmosphere	BGI (Information on occupational safety and health from the Statutory Accident Insurance Institutions) 505-23 (BIA - The BG Institute for Occupational Safety and Health - 8196)*
-	in emulsionen and solutions	BGIA (BG-Institute for Occupational Safety and Health) method, 30th loose-leaf version IV/03
-	in VCI papiers/films	BGIA (BG-Institute for Occupational Safety and Health) method, 30th loose-leaf version IV/03*

* These methods are also suitable for other highly volatile N-nitrosamines (see also [4]).

N-nitroso-dicyclohexylamine

N-nitroso-piperazine

N,N‘-dinitroso-piperazine

Total N-nitrosamines

no valid and publicly published method is currently available