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Technical Rules for Hazardous Substances	Substitute substances, substitute processes and restrictions on the use of methylene chloride-based paint strippers	TRGS 612
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The Technical Rules for Hazardous Substances (TRGS) provide information on the current state of the art, occupational medicine and hygiene requirements and other established knowledge relating to work with hazardous substances, including classification and labeling. They are compiled by the

Committee for Hazardous Substances (AGS)

and regularly updated to take account of current developments.

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1 Scope

This TRGS applies to paint stripping and removal with methylene chloride-based and methylene chloride-free paint strippers. It does not apply to closed systems.

2 Definition of terms

(1) Paint strippers are alkaline, acid or neutral preparations that, when applied onto a coating, soften it in such a way that it can be removed from its substrate. Paint strippers may be in liquid or pasty form. Alkaline paint strippers are also known as “caustic paint strippers”, while solvent-based paint strippers are sometimes called “stripping fluids”. Paint strippers are marketed for a number of uses, including paint removal, façade cleaning and graffiti removal. A distinction is made between methylene chloride-based and methylene chloride-free paint strippers.

(2) Methylene chloride-based paint strippers contain about 80% methylene chloride, 2-5% thickener (cellulose or cellulose derivatives), 15% alcohols as cosolvents (e.g. ethanol, isopropanol or, in exceptional cases, methanol) as well as emulsifiers and wetting agents.

(3) Methylene chloride-free paint strippers contain no methylene chloride. They can be sub-divided into:

- Aqueous solutions of alkalis, such as potassium or sodium hydroxide and alkaline salts (caustic paint strippers), or
- Mixtures of organic solvents, if necessary also containing acids or alkalis.

(4) Substitute substances within the meaning of this TRGS are substances, preparations or products that can replace methylene chloride-based paint strippers and are not hazardous or are less hazardous to the health and safety of employees under application conditions.

(5) Substitute processes are processes that can achieve the same or a comparable technical result without the use of paint strippers and that are not hazardous or are less hazardous to the health and safety of employees.

3 Risk determination and assessment

3.1 Methylene chloride-based paint strippers

(1) Methylene chloride-based paint strippers contain the ingredients listed in Table 1, with methylene chloride accounting for approximately 80% of the contents and the other ingredients at least 1%. Thickeners, emulsifiers and wetting agents are not included.

Table 1: Ingredients of methylene chloride-based paint strippers (as at: April 2005)

	CAS	Classification	MAC according to TRGS 900 [mg/m ³]	Vapor pressure [hPa] at 20°C
Ethanol	64-17-5	F, R11	960	57.3
Isobutanol	78-83-1	Xi, R10-37/38-41-67	310	11.7
Isopropyl alcohol	67-63-0	F, Xi, R11-36-67	500	42
Methanol	67-56-1	F, T, R11-23/24/25-39/23/24/25	270	128
Methylene chloride	75-09-2	Xn, R40		475
(2-Methoxymethyl ethoxy) propanol (isomer mixture)	34590-94-8		310	0.5
1-Methoxy-2-propanol	107-98-2	R10	370	13
Solvent naphtha	---	Xn, R65-66-67-51/53		< 1 to 5

(2) The hazard potential of methylene chloride-based paint strippers is not fully apparent from the classification and labeling information. In terms of human toxicology, the hazard potential of methylene chloride lies primarily in its narcotic effect and subsequent depression of the central nervous system at high concentrations [1]. Given the high volatility of methylene chloride, high workplace concentrations of methylene chloride can be expected in using methylene chloride-based paint strippers.

(3) On inhalation, particularly at high concentrations, methylene chloride can cause loss of consciousness and death by asphyxiation. For this reason, the use of methylene chloride-based paint strippers without wearing a respirator that provides breathing air from a source independent of the surrounding atmosphere has already resulted in a number of serious accidents, some with fatal outcome [2, 9].

(4) Methylene chloride is classified by the EC Commission as a category 3 carcinogen: »substance which causes concern for humans owing to possible carcinogenic effects ...«

(5) When working with methylene chloride-based paint strippers, protective measures in accordance with §§ 8 and 9 of the German Hazardous Substance Regulations (GefStoffV) (protection level 2) should be taken as a general rule. Owing to the high volatility of methylene chloride, such high workplace concentrations can occur that a very high risk to users may be assumed, particularly as a result of the narcotic effect [2]. Therefore, in addition, suitable protective measures in accordance with § 10 of the German Hazardous Substance Regulations (GefStoffV) (protection level 3) should be employed. The technical, organizational and personal protective measures that should be taken when using methylene chloride-based paint strippers in the trades sector are detailed in Appendices 1 and 3.

(6) When carrying out paint stripping or removal with methylene chloride-based paint strippers without suitable extraction and ventilation equipment, a very high risk to health may be assumed. This applies, even when working outdoors [3, 4, 9].

(7) At temperatures above about 160°C, methylene chloride decomposes with the

formation of toxic gases (phosgene and hydrogen chloride). For this reason, when using methylene chloride-based paint strippers, temperatures exceeding 100°C should be avoided as a general rule (see also Appendix 1). It should also be noted that methylene chloride has an explosive range (lower explosive limit = 13% v/v, upper explosive limit = 22% v/v). In mixtures with flammable solvents, the lower explosive limit can even be reduced. As a result, under unfavorable circumstances, the lower explosive limit can be exceeded and an explosive atmosphere formed.

3.2 Methylene chloride-free paint strippers

(1) Methylene chloride-free paint strippers contain the ingredients listed in Table 2, which are used in paint strippers for their stripping action and as cosolvents in concentrations of more than 1%. Thickeners, emulsifiers and wetting agents are not included.

Table 2: Ingredients of methylene chloride-free paint strippers (as at January 2005)

	CAS	Classification	MAC according to TRGS 900 [mg/m ³]	Vapor pressure [hPa] at 20°C
Acetone	67-64-1	F, Xi, R11-36-66-67	1200	233
2-Amino-ethanol	141-43-5	Xn, R20/21/22-34	5.1	0.3
2-(2-Aminoethoxy) ethanol	929-06-6	C, R21-34	-	< 0.1
Benzyl alcohol	100-51-6	Xn, R20/22	-	< 0.1
Benzyl formate	104-57-4	Xn, R 22	-	0.31
1-Butanol	71-36-3	Xn, R10-22-37/38-41-67	310	6.7
2-Butoxy-ethanol	111-76-2	Xn, R20/21/22-36/38	98	0.01
2-(2-Butoxyethoxy) ethanol	112-34-5	Xi, R36	100	0.3
n-Butyl acetate	123-86-4	R10-66-67	-	9.6
Butyl diglycol acetate	124-17-4	-	-	0.05
Dearomatized white spirit	-	Xn, R65	-	< 1 - 8
Dibasic ester	95481-62-2	-	-	0.3
Dimethyl adipate	627-93-0	-	-	0.06
Dimethyl glutarate	1119-40-0	-	-	0.008
Dimethyl succinate	106-65-0	-	-	0.3
Dimethyl sulfoxide	67-68-5	-	-	0.55
1,3-Dioxolan	646-06-0	R11	-	93
Dipropylene glycol dimethyl ether	111109-77-4	-	-	0.7
Ethanol	64-17-5	F, R11	960	57.3
1-Ethoxypropane-2-ol	1569-02-4	R10-67	-	10
2-Ethylhexyl acetate	103-09-3	Xi, R36/38	-	17.6 (at 25°C)

Ethyl diglycol	111-90-0	-	-	0.1
Ethylene carbonate	96-49-1	Xi, R41	-	< 0.09
Formic acid	64-18-6	C, R35	9.5	43
gamma-butyrolactone	96-48-0	Xn, R22-36	-	0.4
Hydrogen peroxide	7722-84-1	O ,C, Xn R5-8-20/22-35	-	6.67 (at 30°C)
3-Methoxy-n-butyl acetate	4435-53-4	-	-	1.5
(2-Methoxymethyl ethoxy) propanol (isomer mixture)	34590-94-8	-	310	0.5
1-Methoxy-2-propyl acetate	108-65-6	Xi, R10-36	270	5
1-Methoxy-2-propanol	107-98-2	R 10	370	13
Methyl decanoate	110-42-9	Xi, R36/38	-	0.475
2-Methylpropane-1-ol	78-83-1	Xi, R10-37/38-41-67	310	11.7
N-Methyl-2-pyrrolidone (vapor)	872-50-4	Xi, R36/38	80	0.32
Orange terpene (dipentene)	138-86-3	Xi,N, R10-38-43-50/53	-	
Orange terpene/ citrus terpene	8028-48-6	Xn, R10-38-65	-	1.9
Potassium hydroxide	1310-58-3	C, R22-35	-	0
Propylene carbonate	108-32-7	Xi, R36	-	0,09
1,2-Propylene glycol	57-55-6	-	-	0.11
Solvent naphtha light to heavy	---	Xn, R65-66-67-51/53	-	< 1 – 5
Triethanolamine	102-71-6		-	0.00005

(2) For work involving the use of methylene chloride-free paint strippers, too, employers should as a general rule take protective measures in accordance with the German Hazardous Substance Regulations §§ 8 and 9 (protection level 2) (see Appendices 1 and 2).

(3) In comparison with methylene chloride-based paint strippers, the solvent-based methylene chloride-free paint strippers pose an increased fire and explosion risk if the methylene chloride-free strippers are labeled with phrases R 10 or R 11, or if they are sprayed. In such cases, the formation or presence of explosive vapor/air mixtures must be expected throughout the duration of work. During spraying, explosive mist/air mixtures must be expected. In all these cases, appropriate protective measures in accordance with § 12 of the German Hazardous Substance Regulations must be taken (see Appendix 1).

4 Substitution of methylene chloride-based paint strippers

(1) Under the German Hazardous Substance Regulations, employers have to ensure that the risk posed by methylene chloride-based paint strippers to the health and safety of employees is eliminated or reduced to a minimum. If technically

possible, employers should replace methylene chloride-based paint strippers with substances, preparations, products or processes, which under the relevant conditions of use are not hazardous or are less hazardous to the health and safety of employees.

4.1 Substitute substances (methylene chloride-free paint strippers)

(1) Generally speaking, suitable, effective, methylene chloride-free paint strippers can be obtained (and readily used from a technical viewpoint) for all coatings that are removable with methylene chloride-based strippers. A list of methylene chloride-free paint strippers can be downloaded from www.gisbau.de.

(2) Employers must carry out tests to determine which substitute substance will be most effective in each individual case. If such tests fail (at least 3 stripping trials with potentially suitable substitute substances), then the use of substitute substances may be deemed technically unsuitable. Manufacturers or dealers can be asked for information on suitable products. The result of the tests should be documented in the risk assessment.

(3) All ingredients of methylene chloride-free paint strippers, except for acetone (see Table 2), have a far lower vapor pressure than methylene chloride. In view of their lower vapor pressures and better toxicological properties, the methylene chloride-free paint strippers pose a lower acute health risk in the workplace.

(4) Dimethyl sulfoxide or N-methyl-2-pyrrolidone are very readily absorbed into the body through the skin and also aid skin resorption of substances such as polycyclic aromatic hydrocarbons (PAHs). Paint strippers containing these substances should not be used.

(5) The use of technically suitable methylene chloride-free paint strippers as substitutes for methylene chloride-based paint strippers makes good economic sense according to TRGS 440 "Risk determination and assessment duties" [5] – particularly if the protective measures that would otherwise be necessary are taken into account.

4.2 Substitute processes

(1) Paint removal with abrasive blasting equipment (e.g. dry, wet and slurry blasting; high-pressure water jet blasting) should always be considered as an alternative and is often suitable and technically feasible for outdoor use. Since the parameters that need to be considered (pressure, jet geometry, blasting media, additives, temperature) depend very much on the nature, shape and condition of the coated substrate and the coating to be removed, no generally applicable recommendations can be given. For working with abrasive blasting equipment, reference should be made to the Employers' Liability Insurance Association (Berufsgenossenschaft) standard (BG Regel) on "Operation of work equipment" (BGR 500) (Part 2, Section 2.36 Working with wet abrasive blasting equipment and Part 2, Section 2.24 Working with dry abrasive blasting equipment (abrasive blasting)).

(2) The other method of mechanical paint removal that has mainly been used is

sanding. For mineral and wood substrates, other proven machines are now available that operate with carbide- or diamond-tipped milling cutters. A milling cutter that works on the principle of a plane can be specially used for wood substrates. Like abrasive blasting methods, however, these mechanical processes remove some of the substrate along with the coating. It is important to check in each individual case whether explosion-proof separation systems should be used.

(3) The health risk posed by the dusts or spray mists produced in mechanical coating removal depends on the particular substrate and coating involved. As a general rule, it is advisable to choose and operate machinery and equipment that produces the minimum amount of dust or spray mist. If the risk assessment shows that the maximum allowable workplace concentrations (MACs) will be exceeded, the employer must provide suitable personal protective equipment, particularly respirators. When removing lead- or tar-based coatings, it is important to observe TRGS 505 "Lead and lead-containing hazardous substances" and TRGS 551 "Tar and other pyrolysis products of organic material".

(4) In certain individual cases, hot air or other thermal treatment can be used for coating removal. However, in view of the possible formation of thermal decomposition products, particularly with chlorine- or lead-containing coating materials [2], and the risk of fire, these processes should only be used if no other alternatives are feasible.

5) The use of technically suitable abrasive blasting equipment generally makes good economic sense for coating removal work on facades. Other mechanical removal methods may also be economic.

5. Restrictions on use

(1) Methylene chloride-based paint strippers should no longer be used in view of the availability in principle and comparable effectiveness of substitute substances (see 4.1) and substitute processes (see 4.2). If employers depart from this advice, they must take other measures to ensure that the health and safety of employees is at least as well protected.

(2) Alkaline strippers labeled as "corrosive" should not be sprayed because of the risk of chemical burns.

(3) In the risk assessment documentation, employers should give their reasons for not implementing a substitution (replacement of methylene chloride-based paint strippers by substitute substances or substitute processes) and should detail the protective measures taken instead of substitution.

Literature

- [1] BUA-Stoffbericht No. 6 'Dichlormethan'. VCH Verlagsgesellschaft, 69469 Weinheim
- [2] Rühl, R. and Kluger, N.: Section IV-8 'Entschichtungsarbeiten' in the Handbuch Bau-Chemikalien. Ecomed-Verlagsgesellschaft, Landsberg, 9th Revision, 10/98

- [3] Rühl, R., Höber, D., Bredendiek-Kämper, S.: European measurements confirm high exposure during paint stripping. Gefahrstoffe-Reinhaltung der Luft 64 (2004) Nos. 11/12, 467-470
- [4] Expositionsbeschreibung 'Einsatz von dichlormethanhaltigen Abbeizmitteln'. Handbuch Bau-Chemikalien, ecomed verlag, Landsberg, 32nd Revision, 09/04
- [5] Technische Regel für Gefahrstoffe (TRGS) 440: Ermitteln und Beurteilen der Gefährdungen durch Gefahrstoffe am Arbeitsplatz: Ermitteln von Gefahren und Methoden zur Ersatzstoffprüfung
- [6] Effectiveness of vapor retardants in reducing risks to human health from paint strippers containing dichloromethane. Scientific committee on Health and environment risks (SCHER), European Commission, March 18, 2005
- [7] Regeln für den Einsatz von Atemschutzgeräten (BGR 190, previously ZH 1/701), Carl Heymanns Verlag
- [8] Verband der chemischen Industrie: Sicher Entschichten mit dichlormethanhaltigen Abbeizmitteln. VCI-Merkblatt, 2000
- [9] European Commission, Brussels, Effectiveness of vapor retardants in reducing risks to human health from paint strippers containing dichloromethane, Final Report, April 01, 2004, ETVAREAD
- [10] ATV-Arbeitsblatt A 115 »Hinweise für das Einleiten von Abwasser in eine öffentliche Abwasseranlage«. Arbeitsgemeinschaft der kommunalen Abwassereinleiter, Hennef 1994
- [11] ATV-DVWK Merkblatt 370 » Abwässer und Abfälle aus der Reinigung und Entschichtung von Fassaden«. Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall, September 2001

Appendix

1 Technical, organizational and personal protective measures when using paint strippers in the trades sector

(1) The order of priority of the protective measures should be observed:

1. Substitution
2. Technical and organizational measures
3. Personal protective measures

(2) Protective measures are specified in the safety data sheets for paint strippers. Detailed technical, organizational and personal protective measures for working with methylene chloride-free paint strippers can be found in WINGIS, the hazardous substance software from the Employers' Liability Insurance Association for the Construction Industry (Berufsgenossenschaft der Bauwirtschaft), or by visiting www.gisbau.de.

(3) If the occurrence of high solvent concentrations in the air at the workplace cannot be excluded, then in interior workspaces – particularly when stripping large areas – a good flow of air must be ensured. If no other local means is possible then this should be achieved by mechanical ventilation. When carrying out stripping work in rooms and tanks, it is also important to observe the provisions in Appendix III Nos 1 and 3 of the German Hazardous Substance Regulations (GefStoffV) and in TRGS 507 "Surface treatment in rooms and tanks".

(4) Work areas in which stripping work is being carried out should be clearly demarcated from other areas and only made accessible to those employees who have to enter it to undertake stripping work. The entry of unauthorized persons should be prevented by prohibitory signs. Reference should be made to German Employers' Liability Insurance Association Regulation BGV A8.

(5) Employers should regularly check the operation and effectiveness of the technical protective measures and ensure that the personal protective measures are used and the organizational measures observed.

(6) In temporary workplaces in the trades sector, such as construction sites, technical or organizational measures on their own are often not sufficient to protect employees. For this reason, additional individual protective measures are required. In Appendices 1.1 and 1.2 to TRGS 612, therefore, the most important personal protective measures when working with paint strippers are listed. Employers must bear in mind, however, that wearing cumbersome personal protective equipment, such as respirators that provide breathing air from a source independent of the surrounding atmosphere, should not be a permanent measure if technical or organizational measures, such as the use of less hazardous paint strippers, are feasible. Respirators with filters and breathing hoods with AX filters are unsuitable for stripping work with methylene chloride-based strippers. Reference should be made to the wearing time limits specified in the "Regulations for the use of respirators" in Employers' Liability Insurance Association standard BGR 190 [7].

(7) Employers should provide employees with a sufficient number of protective gloves and respirators.

(8) The risks posed by the thermal decomposition of methylene chloride or flammability of solvent-based paint strippers require the exclusion of heating coils and infrared heaters from the work area. Smoking, naked flames, sparks and hot surfaces are also prohibited in all areas in which penetration of solvent vapors is possible. Attention should be drawn to the prohibition by the use of prohibitory sign P02 in accordance with the accident prevention regulation on "Safety and health protection labeling in the workplace" (BGV A8) published by the German Employers' Liability Insurance Association.

(9) The solvent vapors emitted by paint strippers are much heavier than air. The tendency of the solvent vapors to sink makes it necessary when carrying out stripping work on staircases, for example, to work from bottom to top.

(10) In carrying out stripping work, employers must observe the relevant environmental legislation. The wastewaters and paint residues generated in the paint stripping process must be collected and pretreated to comply with the existing discharge limits of the individual local authorities (wastewater by-laws). Further information on this can be found in Worksheet A 115 (ATV-Arbeitsblatt A 115) (Notes on the discharge of wastewater into a public sewerage system) [10] and Data sheet M 370 (ATV-Merkblatt M 370) (Wastewater and solid waste from façade cleaning) [11] published by the German Association for Water Management, Wastewater and Solid Waste (Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V., previously known as the Abwassertechnische Vereinigung or ATV). Sludge and paint residues that are filtered from the wastewater should generally be disposed of as hazardous waste.

(11) When using paint strippers in large open areas such as is usual on construction sites, it should be borne in mind that even methylene chloride concentrations as low as 690 mg/m³ have been observed to cause neurobehavioral changes in humans [6]. This applies particularly to children, since they are more sensitive to methylene chloride exposure because of their faster inhalation rate. In addition, the concentration of methylene chloride is higher at floor level than in the breathing zone of adults [6]. On construction sites, there is consequently a risk to employees in other trades. It is therefore particularly important when using methylene chloride-based strippers to prevent risk to persons not working at the construction site.

(12) When using paint strippers containing high-boiling organic components on a porous substrate, there may be considerably delayed emission into the room air, which can result in occupants being subjected to long-term exposure, e.g. in living areas. This should be taken into account in the risk assessment when using such strippers.

1.1 Additional personal protective measures when using methylene chloride-free paint strippers

(1) Alkaline paint strippers (caustic stripping agents) (labeled with Xi or C)

Eye protection:

For spray/splash risk: Face shield and closed goggles

Hand protection: Protective gloves made from latex, polychloroprene, nitrile or butyl rubber; specific glove brands are listed in WINGIS*.

When wearing protective gloves, cotton undergloves are recommended.

Skin protection: Barrier cream

Respiratory protection:

For spray methods: P2 or FFP2 particle filter (white); in manual application, no respiratory protection is required

Body protection:

For spray methods: Liquid-tight chemical protection suit (type 3)

The spray process may not be used for alkaline strippers labeled as “corrosive” because of the high risk of chemical burns.

(2) Solvent-based paint strippers (unlabeled or labeled with Xi or Xn)

Eye protection:

For spray/splash risk: Frame or closed goggles

Hand protection: Protective gloves made from butyl rubber; specific glove brands are listed in WINGIS

When wearing protective gloves, cotton undergloves are recommended.

Respiratory protection: If required after risk assessment, A1 gas filter (up to 1000 ppm) or A2 gas filter (up to 5000 ppm) (brown), depending on atmospheric concentration at the workplace.

In spray processes, suitable combined filters, i.e. A1-P2 or A2-P2, should be used instead of gas filters.

*) WINGIS hazardous substances software from the Employers' Liability Insurance Association of the Construction Industry (Berufsgenossenschaft der Bauwirtschaft); www.gisbau.de

Body protection:

For spray methods: Liquid-tight chemical protection suit (type 3)

1.2 Additional personal protective measures when using methylene chloride-based paint strippers [8]

Eye protection:

For spray/splash risk: Frame or closed goggles

Hand protection:

Protective gloves made from fluororubber (Viton), maximum wearing time 150 min

When wearing protective gloves, cotton undergloves are recommended.

Respiratory protection:

Respirators that provides breathing air from a source independent of the surrounding atmosphere should be used (e.g. fresh-air or compressed-air equipment). Respirators with a filter and breathing hoods with AX filters are generally unsuitable.

Body protection:

For spray processes: Liquid-tight chemical protection suit (type 3)