Partnership for Sustainable Textiles

Formaldehyde-releasing substances and auxiliaries

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Content

1. Identification and classification

Formaldehyde (CAS no. 50-00-0) is the simplest aldehyde; in the IUPAC nomenclature it is known as methanal. Formaldehyde is a colourless and highly reactive gas with a characteristic pungent smell. It is readily soluble in water, alcohol and other polar solvents (Römpp, 1995).

Global production of formaldehyde in 2007 was about 21 million tonnes (Wölk 2014). Pure and dissolved formaldehyde is prone to a wide range of accumulation, condensation, redox and polymerisation reactions; after manufacture it is therefore usually chemically converted with phenols to produce phenoplasts or with amines to produce aminoplasts (including urea resins and melamine resins) (Römpp, 1995).

Textile finishing involves the use of substances in which the formaldehyde is firmly bound, as in dispersing agents based on naphthalene sulfonic acid and formaldehyde condensation products for colouring dispersion dyes, vat dyes and sulphur dyes (Peter/Rouette, 1989; Shore, 1990; Fischer et al., 1995), but can also be released, such as from formaldehyde sulfoxylate, which is used as a reducing agent for white and colour discharge printing (Römpp, 1995) or from reactive resins used in crease-resistant and easy-care textile treatments (Peter/Rouette, 1989; Fischer et al., 1995; BfR, 2006). Once applied, these reactive resins cannot be washed out; they are therefore particularly significant, because formaldehyde may be released from them as a residual monomer or during the crosslinking reaction (BfR, 2006). In the context of indoor pollution in private households, furnishing fabrics with an easy-care finish are therefore of particular significance (Kelly et al., 1999).

2. Existing regulations

The use of formaldehyde is regulated by a number of legislative and international processes; only those that are relevant to the textile industry are specified here.

In 2014 the status of formaldehyde under the EU's CLP Regulation was changed from Category 2 (suspected human carcinogen) to Category 1B (carcinogenic in animal experiments). This categorisation came into force at the start of 2016.

As a result of this, the German Committee for Hazardous Materials (AGS 2015) specified an occupational exposure limit (OEL) of 0.37 mg/m^3 (0.3 ml/m^3 or ppm) for the purposes of the Hazardous Substances Ordinance (*Gefahrstoffverordnung*, GefStoffV). The EU classification is in line with the action of the German committee for the determination of occupational exposure limits (the MAK Commission), which in 2000 classed formaldehyde as a Category 4 carcinogen; substances in this category are assumed not to contribute significantly to the risk of cancer in humans provided that the exposure limit (MAK value) is observed.
On account of the irritant and carcinogenic effect of formaldehyde, the German Environment Agency's Committee on Indoor Guide Values has set a Guide Value 1 (RW 1 - Precautionary value) of 0.1 mg formaldehyde per cubic metre of indoor air; this value can be significantly exceeded by furnishing fabrics alone (Kelly et al., 1999).

Under the German Consumer Goods Ordinance (*Bedarfsgegenständeverordnung*, BedGgstV 1992), textiles that contain more than 0.15% free formaldehyde and that are in contact with the skin when used as intended must bear the label 'Contains formaldehyde. For better skin tolerance, it is recommended that this garment is washed before it is worn.'

As part of the REACH programme, formaldehyde is being evaluated by France and the Netherlands under a Community Rolling Action Plan (CoRAP); the grounds for concern are the chemical's CMR properties, the potential risks to workers and the fact that formaldehyde is widely used. The Netherlands is currently evaluating the exposure of consumers, while France has concluded its evaluation of the exposure of workers and has produced the first draft of a Risk Management Option Analysis (RMOA). The deadline for comments on the draft was the end of October 2016; the final results have not yet been published.

This means that formaldehyde has not yet been identified as an SVHC, nor is it on the REACH Restricted Substance List (Annex XVII). Nevertheless, the ECHA has put out a call for evidence on the use of formaldehyde, which is the first step in a restriction process. Registrants have until October 2017 to submit information on the use of formaldehyde.

As a result of the above-mentioned classification of formaldehyde as carcinogenic in animal experiments, the limits on emissions from textile finishing plants are to be altered in the revision of the German Technical Instructions on Air Quality Control (*TA Luft*). Formaldehyde emissions in the waste gas of directly heated thermal aggregates for drying are to be limited to a mass concentration of 5 mg/m^3, while for thermosetting and crimping they will be limited to 15 mg/m^3. For treatment processes, including combustion processes in directly heated thermal aggregates, formaldehyde emissions in the waste gas of easy-care, water-repellent and dirt-repellent treatments and thermosol processes are to be limited to 10 mg/Nm^3; emissions in the waste gas of crease-resistant and flame-retardant treatments, coatings (including laminating) and handle-imparting treatments (hard) will be limited to 20 mg/m^3 (TA Luft-Entwurf, 2016).

3. Use in wet textile production processes

Formaldehyde as such is not used in the textile industry. Instead it is present in products as an impurity or may be released during application. The most obvious example involves the above-mentioned agents used in the easy-care treatment of cellulose-based fabrics (i.e. cotton and viscose textiles). This treatment improves the creasing and wrinkling behaviour of fabrics, making them crease-resistant or crease-free and hence easy-iron or non-iron.

Classically the chemical substances used in these treatments are urea derivatives or melamine derivatives ('old resins' according to GAO 2010). Because they react with the hydroxy groups in the cellulose and with themselves, they are termed reactive crosslinkers.
The best known more modern crosslinker is dimethylol dihydroxy ethylene urea (DMDHEU). As a result of the method of manufacture, this crosslinker still contains formaldehyde at a concentration of over 1,000 ppm. Crosslinkers with a formaldehyde content of less than 1,000 ppm are available but are said to be less effective.

Like melamine-based crosslinkers, DMDHEU is usually applied with a catalyst and other substances by means of a watery solution, using a Foulard process. A reaction is then achieved by drying the fabric at about 170°C in a stentering frame; this releases formaldehyde (Larsen et al., 2000; Bode et al., 2007). The formaldehyde enters the waste gas, but a small amount remains on the textile substrate, from where it is discharged during use into water or the air (Voss 1995; Larsen et al. 2000, BfR, 2006). In the past, the concentration of anti-creasing and anti-wrinkling treatments was up to 8% of the product weight; as a result of the limits that have been introduced, formaldehyde contents are now significantly lower (Platzek 2001). Formaldehyde is also used in adhesives and in pigment printing on T-shirts and bed linen (Friedlipartner 2005).

According to GAO (2010), formaldehyde contamination of textiles has been falling since the 1960s as crosslinkers with a lower formaldehyde content have been developed. This trend has been driven by the following factors:
(1) the identification and classification of formaldehyde as a human carcinogen,
(2) statutory limit values in importing countries,
(3) companies' own policies and
(4) the development of new technologies (GAO 2010).
Various studies have shown that most items of clothing meet the limit values of the most stringent standards (EU 2007, NZ Ministry for Consumer Affairs 2007, GAO 2010). The Ökotex®100 industrial standard also limits the formaldehyde content of textiles.

4. Hazard potential

Acute and chronic human toxicity

The effects of formaldehyde vary depending on the concentration, type of exposure (inhalation, dermal contact, ingestion, eye contact) and the exposure time (UBA 2016).

As a gas, formaldehyde irritates the upper respiratory tract and the eyes at concentrations of less than 0.1 mg/m^3. The European CLP Regulation classes formaldehyde as toxic if swallowed (H301), in contact with skin (H311) or inhaled (H331). It causes severe skin burns and eye damage (H314) and may cause an allergic skin reaction (H317). Allergy thresholds vary from person to person – a general threshold cannot be specified (Friedlipartner 2005).

Chronic exposure to higher concentrations of formaldehyde is suspected of causing genetic defects (H341), and when inhaled formaldehyde may cause cancer (H350). In 2014 it was uprated to CLP carcinogen category 1B (presumed to have carcinogenic potential for humans, classification based on animal evidence) and germ cell mutagen category 2 (may cause mutations in the germ cells of humans that can be transmitted to the progeny). Animal experiments have shown that the exposure/risk relationship is not linear and that formaldehyde becomes carcinogenic only over a certain threshold (UBA 2016).

Conversely, safe application below the threshold is possible. A risk assessment of formaldehyde in textiles worn close to the skin concluded that the amount should not exceed 16 ppm for babies or 75 ppm for adults. Combining the internal exposure estimated using the BfR exposure model with the dermal systemic derived no-effect levels yields sufficiently high safety factors that exclude any risk to textile consumers if the above limits are adhered to (TEGEWA, presentation to the BfR Textiles and Leather Working Group, November 2015).

Of particular concern in relation to textiles is allergic contact dermatitis and irritant contact dermatitis caused by dermal exposure to formaldehyde (GAO 2010). There is no evidence that dermal exposure to formaldehyde can cause cancer.

Environmental toxicity

Formaldehyde does not pose any environmental hazards (H400 series) specified in the CLP Regulation. The derived maximum concentration in food for which it can be assumed that there is no effect on freshwater organisms is 0.44mg/l (PNEC[1]) (Registration Dossier, REACh 2016). The PNEC for soil organisms is 0.2mg/kg soil in dry weight (Registration Dossier, REACh 2016).

5. Environmental behaviour

Small quantities of formaldehyde occur naturally as a metabolic product in mammal cells; formaldehyde is also produced in nature during photooxidation in the atmosphere and as a by-product of incomplete combustion. Because it is highly reactive, formaldehyde breaks down quickly: its half-life in air is about half an hour (WHO 2010). Because it is water-soluble, 99% of the formaldehyde in environmental media is dispersed in water and 1% in the air (Registration Dossier, REACh 2016). Formaldehyde thus has no persistent (P) or bioaccumulative (B) properties.

On account of the use of formaldehyde-releasing substances in textile finishing, there are issues in connection with the exposure of workers to formaldehyde during finishing and the exposure of consumers during the use phase.
The highest levels of volatile formaldehyde are found in indoor air (Kelly et al., 1999; GAO 2010). Analysis of workplace exposure measurements stored in a German database (MEGA) and a French one (COLCHIC) yield mean formaldehyde concentration levels in textile factories of 0.04 mg/m^3 (MEGA) and 0.07 mg/m^3 (COLCHIC) (Clerc, 2015). Formaldehyde exposure in the textile sector is therefore comparable to levels of exposure in the health sector and the timber, furniture, plastics and rubber industries. Because Germany no longer has a major textile industry, Clerc et al. (2015) assume that levels in Asia are likely to be higher.

Of interest to consumers are the formaldehyde emissions of purchased textiles: emissions from shirts were found to be 107 $\mu g/m^2/h$ (unwashed) and 42$\mu g/m^2/h$ after a single washing (Kelly et al. 1999). These figures result in an estimated indoor air concentration of 30 $\mu g/m^3$ for unwashed shirts and 15 $\mu g/m^3$ for washed shirts (Kelly et. al 1999). The emission rates of crease-resistant furnishing fabrics are higher at 215 $\mu g/m^2/h$, and because of the relatively large surfaces involved they yield high estimated indoor air concentrations of between 545 $\mu g/m^3$ and 1635 $\mu g/m^3$, depending on room size (Kelly et al. 1999). These concentrations are comparable to the potential contributions of press boards made with urea-formaldehyde resins (Kelly et al. 1999). Furnishing fabrics can thus add significantly to formaldehyde pollution of indoor air.

[1] Predicted No Effect Concentration

6. Possible substitutes

Technically feasible alternatives are artificial resins based on other aldehydes, such as glyoxal. The chemical properties of glyoxal are similar to those of formaldehyde, which renders it suitable as a shrink-resistant finish for cotton and viscose (BfR 2012). However, glyoxal has similar toxicity to formaldehyde. Like formaldehyde it is mutagenic (GHS Category 2), harmful if inhaled and a skin and eye irritant. It can cause allergic skin reactions but there are no reports of textile-induced allergic reactions (BfR 2012). Crosslinkers based on glyoxal are no longer used (Platzek 2001).

While usable fully formaldehyde-free formulations are available for easy-care treatments, this is not the case for non-iron or easy-iron treatments, and the formaldehyde-free formulations are significantly more expensive (roughly five times dearer), which is an obstacle to competitiveness (TEGEWA, 2016).

7. Summary

Formaldehyde as such is not used in textile manufacture. It is, however, present as an impurity in some textile auxiliaries and is therefore of significance in connection with exposure during the finishing of cellulose fibres (cotton and viscose) and of lesser significance in adhesives and pigment printing.

Acute hazards for humans arise from its potential to irritate the mucous membranes and trigger contact allergies. Chronic exposure to high concentrations of formaldehyde can cause cancer.

When formaldehyde is used in the textile sector, the most significant issue is dermal exposure and hence its effect as a contact allergen. Occupational exposure to formaldehyde is another relevant issue.

Because formaldehyde has a short half-life, it does not pose an environmental hazard.

Glyoxal has been used as a substitute in the past, but because it has similarly toxic properties it is not well suited to this purpose.

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