

## Hazardous substances in personal protective equipment: how "healthy" must PPE be?

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Personal protective equipment (PPE) comprises modern industrial products that are frequently manufactured from or with the use of dozens of different substances. The manufacturers must nevertheless ensure that the products that they place on the market do not give rise to hazards. In view of the myriad substances and materials used during the manufacture of PPE, this undoubtedly presents a considerable challenge – and not only for the manufacturers, but also for the test bodies that inspect PPE to determine whether it satisfies the statutory provisions (and in the future, the new EU PPE Regulation).

The new EU regulation requires specifically in Annex II, Section 1.2 that PPE must not create inherent risks or other nuisance factors. In particular, the materials of which the PPE is made, including any of their possible decomposition products, must not adversely affect the health or safety of users. Manufacturers and test bodies can draw upon harmonized standards in order to satisfy these and other requirements and to test them. For protective gloves, the first such standard is EN 420:2010, Protective gloves – General requirements and test methods.

This standard is currently being revised – and at international rather than European level. It will therefore be published under a new number, possibly EN ISO 21420. In all probability it will also contain a more comprehensive chapter concerning the innocuousness of protective gloves. The present version of EN 420 already specifies the pH value that protective gloves must have, the chromium (VI) content that must not be exceeded in gloves containing leather, and that protective gloves manufactured from natural rubber must satisfy the requirements of EN 455-3 with regard to their extractable protein content.

Additional provisions are to be added in the future concerning the release of nickel, and the concentration of carcinogenic amines derived from azodyes and of N,N-dimethylformamide (DMF). The growing relevance in standardization of the topic of "innocuousness" and the associated efforts to lend greater weight to the complexity of the issue should be regarded favourably.

In order for a high level of user safety and health to be assured, as required in the regulation, exposure of wearers for example of protective gloves to substances harmful to health should be prevented wherever possible. In other words, materials that at some stage release substances that could be toxic, carcinogenic, mutagenic, allergenic or teratogenic should be avoided even in the manufacturing process of PPE. In satisfying this requirement, manufacturers must not merely consider technical and economic aspects: the state of the art and good practice at the time of design and manufacture are crucial<sup>1</sup>.

### *Assessment criteria with reference to the example of N,N-dimethylformamide (DMF)*

One substance that has been the subject of heated discussion in this context for a number of years is N,N-dimethylformamide (DMF), which is used as a solvent for the coating of protective gloves with polyurethane (PU) in an immersion process. Polyurethane-coated gloves are used in very large quantities; a large plant may use as many as 100,000 pairs per year. Polyurethane-coated gloves have major advantages for the user, particularly for use with oil-based materials, and are also being used again in areas in which efforts had been made to replace them, for example with nitrile-coated gloves.

DMF is however hepatotoxic and is absorbed very rapidly through the skin. It is also classified throughout the EU as a teratogenic substance. Furthermore, it was recently classified by the International Agency for Research on Cancer (IARC) as a Group 2A substance, i.e. as being probably carcinogenic in humans<sup>2</sup>.

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<sup>1</sup> New EU PPE Regulation, Annex II, Preliminary Remark 3; concerning this aspect of the new regulation, refer also to the article by Dr M. Thierbach, p. 187-190, concerning the preliminary remarks to the essential requirements.

<sup>2</sup> Grosse et al., 23 February 2016, <http://www.sciencedirect.com/science/article/pii/S1470204516001376>

For these reasons, the German TRGS 401 Technical Rules for Hazardous Substances<sup>3</sup> specify not only that polyurethane-coated gloves may contain no more than 10 milligrams of DMF per kilogramme of glove material (i.e. 0.001% by weight), but also that they must not release any DMF. It is however currently being discussed whether the future EN ISO 21420 should contain a limit for DMF that would not only lie substantially above the detection limit of the usual test methods, but at 0.1% by weight would also exceed the limit specified by the TRGS 401 by a factor of 100.

Those arguing that this limit or other limits several times higher for DMF should be formulated in the product standard for protective gloves base their arguments on either atmospheric occupational exposure limits (OELs<sup>4</sup>) or the European REACH Chemical Regulation<sup>5</sup>. For a number of reasons, these approaches could easily be misleading and could lead to results that are unacceptable from the perspective of workplace safety and health.

The European Single Market not only assures fair market conditions, but also has the objective of assuring protection against workplace health hazards by preventing them at source. For that reason, a differentiated view is required, both in the particular case of DMF under consideration here, and with suitable adaptation also for other hazardous substances in PPE.

*Arguments against the use of occupational exposure limits for the assessment of products:*

- Irrespective of the hazardous substance to which it applies, an occupational exposure limit is intended for workplaces at which contact with the hazardous substance cannot be avoided because it is required for the production process concerned. If this is applied to the example under consideration here, it follows that the occupational exposure limit would be a relevant variable only if, for example, the intention was to assess the value for the average concentration of DMF in the atmosphere at workplaces in glove production. In Germany, the occupational exposure limit is the limit for the time-weighted average concentration of a substance in the atmosphere in accordance with the Ordinance on hazardous substances (GefStoffV). DMF released from PPE is however particularly absorbed by the user through the skin.
- In addition, the teratogenic effect is explicitly not covered by the occupational exposure limit for DMF. Owing to its teratogenic properties, Section 5 of the German Ordinance governing the protection of pregnant and nursing women at the workplace (MuSchRiV) prohibits the exposure of pregnant women to DMF. From a prevention perspective, it must be assumed in this context that:
  - Pregnant women are often not immediately aware that they are pregnant and consequently are not able to inform their employers of the fact in time for the latter to take the necessary measures.
  - Many users of PU-coated protective gloves are smaller businesses or companies without adequate in-house expertise in hazardous substances, and are consequently not even aware that protective gloves may contain teratogenic substances that they are obliged to protect their pregnant employees against.
- Gloves exhibiting avoidable DMF concentrations, for example because they have not been washed adequately during the manufacturing process, may also contain higher concentrations of other water-soluble production residues, such as phenols, that present additional hazards and may also lead to combined exposure. A combined exposure that is difficult to evaluate also arises when workers are exposed simultaneously to DMF and to other chemicals in gloves and in their working environments.

Neither the occupational exposure limit, nor possible alternatives such as derived no-effect levels (DNELs<sup>6</sup>) under the REACH Regulation are therefore variables that can be used to justify avoidable high levels of hazardous substances in personal protective equipment.

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<sup>3</sup> TRGS 401 concerning risks resulting from skin contact

<sup>4</sup> TRGS technical rules for hazardous substances, occupational exposure limits, TRGS 900

<sup>5</sup> Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency

<sup>6</sup> DNELs are "derived no-effect levels" above which human beings should not be subjected to exposure.

*Further limits to the use of REACH in order to determine the state of the art for products:*

- Put very simply, chemicals must be registered under REACH as soon as a certain quantity threshold is exceeded when a substance is manufactured and placed on the market. Substances in articles (such as PPE or electrical equipment) are required to be registered only if they are likely to be released during normal or reasonably foreseeable use. In addition, authorization procedures exist for substances of particular concern.
- Annex XVII of the REACH Regulation governs the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles. One example relevant to PPE is that the chromium (VI) content in leather articles and articles containing leather parts is limited to 3 mg/kg (i.e. 0.0003% by weight) in cases where these parts are able to come into contact with the skin. In addition, azodyes which may release certain amines in detectable concentrations (at present > 30 mg/kg, i.e. 0.003% by weight) by reductive cleavage may not be used in leather or textile articles which may come into direct and prolonged contact with the human skin or oral cavity. Parts of items of clothing that come into direct and prolonged contact with the skin may also not release more than 0.5 µg/cm<sup>2</sup> of nickel per week.
- Where such dangerous substances have already been evaluated, it is generally correct for the limits specified in Annex XVII of the REACH Regulation (and which are frequently based upon the detection limits) also to be adopted in product standards for PPE. Such limits were adopted some time ago in EN 420 for chromium (VI) compounds; this will in all probability be extended to the azodyes and nickel in the coming EN ISO 21420.
- The situation is different for DMF: to date, DMF has been included only on the *list of candidates* for substances of high concern for which authorization under REACH is an objective. During the authorization procedure the availability of suitable alternative substances or technologies is examined for each application. This evaluation, which has not yet been completed, must be considered for requirements in occupational safety and health rules and product manufacturing methods, and is also relevant to product safety standards. This particularly militates against the value of 0.1% by weight that is now being proposed as a threshold for product safety purposes. This value, currently under discussion for DMF in PPE standardization, and as already stated corresponding to 100 times the concentration by weight specified as a limit in the TRGS 401, can at best be regarded as a *threshold for the duty to communicate information* as stipulated in Article 33 of the REACH Regulation.
- Ultimately however, the applicability of REACH to DMF in polyurethane-coated PPE must in any case be examined more closely: in this context, DMF is not released under normal circumstances, but has fulfilled its function after the manufacturing process and strictly speaking has the status of waste. Its status in the glove would therefore have changed, and it would not constitute a substance, mixture or article in the sense of Article 1, Paragraph 2 of the REACH Regulation<sup>7</sup>.

Irrespective of whether a substance is subject to mandatory registration, restriction or authorization under REACH, it is not possible for the *threshold for the duty to communicate information* in REACH to be used to formulate a generically valid concentration of the substance by weight in a product at which the substance can be classified as being innocuous when this product is used – much less used as a yardstick in support of the Single Market legislation governing PPE<sup>8</sup>.

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<sup>7</sup> For more information on this topic, refer for example to p. 21 of the BAuA's REACH-Info 6 brochure, "Articles – Requirements for Producers, Importers and Distributors"; available for download in PDF format at [www.reach-clp-biozid-helpdesk.de/en/Publications/Brochures-en/REACH-Brochures-en.html](http://www.reach-clp-biozid-helpdesk.de/en/Publications/Brochures-en/REACH-Brochures-en.html)

<sup>8</sup> The Ökotex standard permits 0.1% DMF by weight for clothing; in contrast to normal clothing however, PPE is replaced very frequently, in some cases several times a day, which considerably influences the long-term exposure.

*Assessment from the perspective of prevention:*

- Employers have an obligation to take the measures necessary to ensure the safety and health of their employees, and also to protect groups at particular risk. These groups include (for example) young people, persons with allergies, and pregnant women. It follows that when PPE is made available, it must 1) provide protection against the hazards for which it is intended without itself giving rise to a greater risk; 2) be suitable for the conditions at the workplace; and 3) take account of the health requirements of the employees.
- Prevention and product safety legislation impose a requirement for exposure to be reduced to the minimum possible. Where attainable by the state of the art, the release from PPE of substances that could have a harmful effect upon the wearer of the PPE is to be avoided, irrespective of the toxicological rationale of limit value scenarios.
- In order to satisfy the applicable statutory provisions, the manufacturers must therefore ensure that gloves contain no more than 10 mg of DMF per kg of glove material. Measurement methods suitable for standardization and protective gloves in which this value is observed are available<sup>9</sup>.
- In particular, it is not sufficient to assess polyurethane-coated gloves with reference to limits for N,N-dimethylformamide that have been specified for operational workplace exposure or in the context of a duty to communicate information under the REACH Regulation.

The increasingly relevant topic of "innocuousness" and the associated limit values for products must be treated in product standardization in a way that is consistent with the principles of prevention and of Single Market legislation, not only for DMF, but also for other future potentially dangerous substances in PPE.

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<sup>9</sup> KANBrief 3/2015, Method for analysis of DMF in protective gloves, Schripp