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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

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Issues relating to GHS and labelling of chemicals: corrosivity criteria

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals
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Co-operation with other bodies or international organizations: corrosivity criteria

Contribution to the work of the joint informal correspondence group on corrosivity classification – approaches to classifying corrosive mixtures under Class 8

Transmitted by the expert from the United Kingdom

Purpose of document

1. This document contributes to work stream (b) of the joint informal correspondence group on corrosivity criteria, set out in document UN/SCEGHS/21/INF.6 – UN/SCETDG/39/INF.14:

"Identify and analyse the discrepancies between assignment to subcategories 1A, 1B and 1C, based on in vitro and in vivo testing and alternative approaches (bridging principles, mixtures calculations, pH…)."

2. One issue that arises in relation to this work stream is that while the GHS sets out detailed rules and principles for classifying mixtures as corrosive, the UN Model Regulations do not currently give such detailed rules. Nevertheless, mixtures are routinely classified for corrosivity under the UN Model Regulations (or the modes that harmonise their provisions with the Model Regulations) and assigned to generic or N.O.S. entries in the Dangerous Goods List. Therefore, to better understand the potential sources for discrepancies between the GHS and the Model Regulations, it is useful to understand how in practice mixtures are classified as corrosive under the Model Regulations.

3. To gain a better understanding of this the expert from the UK asked three experienced practitioners of transport classification to outline the approaches they use to classify mixtures as corrosive for transport under Chapter 2.8 of the UN Model Regulations. The responses are collected in **Annex 1**.

4. The responses in Annex I are the views of three practitioners and may not necessarily represent practice across UK industry. The expert from the UK welcomes feedback from other experts together with information on the approaches taken in other countries or regions.

Annex I

Feedback from three UK expert practitioners on approach taken to classifying mixtures for corrosivity under Chapter 2.8 of the UN Model Regulations

Contribution 1

Substances

1. In my business (detergents, disinfectants etc) we very rarely if ever innovated new substances. We did use commercially available substances not in the DGL and accepted the manufacturers' classifications. Sometimes of course these could be different when we would err on the side of caution - if we were just selling on the substance. Looking at the DGL there are very few recent additions which are Class 8 so I expect "new" substances have been classified by manufacturers as n.o.s. One recent one, which may therefore have readily searchable supporting data is Iodine, UN 3495. However as it is PGIII it may have been classified on the basis of its metal corrosion properties, which I'm sure it has.

Mixtures

2. Mixtures can be considered as two types: dilutions and mixtures. For dilutions of acids and bases we generally went along with the EU Dangerous Substances Directive (Directive 67/548/EEC or 'DSD') limits: PGII if it corresponded to R35 ("Causes severe burns") and PGIII if it corresponded with R34 ("Causes burns"). Our industry did not/ does not use the real nasties that are PGI (e.g. red fuming nitric acid). Below the cut off for R34 we would test for metal corrosion. The DSD %s for Irritant often aligned with metal corrosion e.g. phosphoric acid UN 1805, irritant from 10 - 25% and metal corrosive in this range. From 25% it is corrosive to both metal and skin. Sodium hydroxide solution is particularly aggressive to aluminium - from 0.5% in our tests, lower than the Irritant cut off of 1%.

3. Mixtures of two or more corrosives, with or without non-DGL-listed substances: in some cases these would be straightforward e.g. mixtures of sodium hydroxide and EDTA (manufacturers' classification 8, III.) The caustic (at any useful concentration) "wins" so 8, II.

4. More complex mixtures we have been using OECD 435 which seems pretty well suited to our types of formulation, and ties up with earlier evidence. For example, Young et al. noted that mixtures of silicate (PGIII) and carbonate (not listed) - common in commercial laundry detergents - are more corrosive than might be expected. OECD 435 bears this out and many such are found to be PGII. The Young titration is a good guide - if it comes out corrosive we'd accept that: if it doesn't we'd do metal corrosion testing which more often than not gives a corrosive result.

(Not skin tested but we have also found that mixtures of e.g. citric & sulphamic acids or citric & lactic acids are remarkably corrosive to metal and so are 8,III.)

5. So the approach is rather pragmatic, with much use of experience, various tests and, dare I say it, common sense. This is probably not ideal but it's worked pretty well in our industry in practice.

Contribution 2

Classification of class 8 corrosives for transport purposes

6. In the first instance classification as a skin corrosive is carried out based on assessing results of in vivo or in vitro tests against the criteria.

7. In the absence of these data, account is taken of information provided in safety data sheets and reference publications including catalogues of suppliers of chemicals, especially laboratory chemicals. This information is then assessed using specialist judgement based on experience as a chemist and knowledge of dangerous goods rules and particularly the dangerous goods list.

8. For solutions and mixtures sometimes the lower case text associated with a name or description of a substance will determine whether the substance is to be regarded as dangerous for transport and if so, the appropriate packing group. In assigning the appropriate entry, it is important to use the most specific proper shipping name applicable in the case of generic or n.o.s. entries as indicated in Appendix A of the UN Model Regulations.

Contribution 3

Introduction

9. This paper describes how in practice a European Union based classifier of hazardous and dangerous preparations/mixtures may be expected to approach the classification of such mixtures for supply and transport purposes.

10. The 1999/45/EC Dangerous Preparations Directive (known in short as DPD), as enacted by national legislation of EU Member States, and Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures, amending and repealing [in June 2015] Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (known in short as “CLP”), provide methods for the classification of preparations/mixtures for skin corrosion by calculation methods. These methods rely on the substances in the mixture having first being classified for their corrosive effect on the skin.

11. The UN Model Regulations in Chapter 2.8, and the modes which harmonise their provisions with the UN's transport provisions, however do not currently provide any method for the calculation of the corrosiveness to skin of a preparation. Currently classification is thus technically required based on the results of animal testing of the specific preparation for skin corrosion. In 2.8.2.4 there is a mention of account being taken of human experience, but this would rarely be available for a mixture being classified.

12. Since testing on animals is both extremely expensive and generally not permitted in practice most classifiers must in practice for transport use some form of estimation of the corrosiveness to skin of a preparation.

This paper describes how this approach may be taken in practice.

Practical classification of preparation for transport

13. The first step would be the collection of information about the constituents of the preparation and any known data. This will include the physical state and the result of any classification for skin corrosion that has been made for the purpose of supply under the DPD or CLP, covering both the constituent substances and the preparation as a whole.

14. This approach would apply whether or not the preparation is a simple solution, for instance a reasonably dilute solution of sodium hydroxide in water, or is a more complex preparation containing several known corrosive components. A request will also be made as to whether or not any metal corrosion information has been obtained on the preparation (Note: if classified as dangerous on the basis of metal corrosion this means that the preparation must at least be considered a Class 8 Packing Groups III material, regardless of whether or not any skin corrosion is likely to occur).

15. If a DPD classification has been carried out, and is available. This will indicate that the preparation is either classified with R34 “Causes burns”, or R35 “Causes severe burns”.

16. In the absence of any direct correlation with transport Packing Group allocation, classification with R 35 would normally result in the assumption that classification for transport as at least Class 8 PG II. Consideration would then be given as to whether or not classification as Class 8 PG I was warranted. This consideration would take into account the corrosiveness of the individual constituents, as far as is known, and particularly whether any of the constituents are listed in the transport dangerous goods list at a PG I level, and the percentage thereof in the preparation. If there was compelling evidence from such examination then classification at PGI level would be given.

17. Classification with R34 would normally result in the assumption that classification for transport as at least Class 8 PGIII. Consideration would then be given as to whether or not classification as Class 8 PGII was warranted. This consideration would take into account the corrosiveness of the individual constituents, as far as is known, and particularly whether any of the constituents are listed in the transport dangerous goods list at a PGI or PGII level, and the percentage thereof. If there was compelling evidence from such examination then classification at PGII, rather than PGIII level would be given.

18. Currently in Europe the DPD classification would be used in preference to a CLP classification, especially where the CLP classifications of the constituent substance(s), or the preparation, have been obtained by using the default CLP Annex V translation chart. This since this is known to default to a higher level of hazard than might be given by classification from basic data.

19. For instance sodium hydroxide is classified as R35 under the 67/548/EEC Dangerous Substances Directive (known in short as DSD), which would mean a simple solution of sodium hydroxide in water at equal to or greater than 2% would get R34, and thus be clearly classified as Class 8 PG III (which it would anyway because of its known corrosive to aluminium). At above 5% the classification would be R35, and allocation to PG II level would increasingly be appropriate. However as for transport sodium hydroxide pure is allocated to PG II there would seem to the classifier to be absolutely no basis for possible classification to PG I level.

20. Translation of the classification of the > 5% mixture to CLP system would however have indicate skin corrosive category 1A, and thus possibly a PG I allocation, but clearly, given the maximum Packing Group allocation of "II" in the transport dangerous goods list for such a solution, this would currently be considered as excessive for transport (given the many implications that a PG I rather than a PG II classification would involve – e.g. inability to ship in IBCs, absence of any Excepted and Limited Quantity package provisions for very and small receptacle/package quantities) be ignored.