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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

Sub-Committee of Experts on the
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PROPOSALS OF AMENDMENTS TO THE RECOMMENDATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Supplementary information to STS/SG/AC.10/C.3/2006/11 (Chrolosilanes)

Transmitted by the International Council of Chemical Associations (ICCA)

During the 29th session of the UNSCETDG, in its document ST/SG/AC.10/C.3/2006/11, ICCA proposed to reclassify 2 chlorosilanes and to reconsider the conditions of transport for all chlorosilanes. This proposal was supported by several experts, whereas others wanted more information. It was decided to keep the document on the agenda whereby ICCA would provide additional information to specific requests. These were received from the Netherlands and from UK.

Queries mainly related to the re-classification of UN 1250 and UN 1305 and the classification of chlorosilanes in general. The detailed replies by ICCA to the UK (covering also the general classification issue, raised by the Netherlands) can be found in Annex from which the following main conclusions can be drawn:

- The proposed re-classification from PG I to P II for UN 1250 (Methyltrichlorosilane) and UN 1305 (Vinyltrichlorosilane) is justified based upon their flammable properties (flash point and boiling point), upon the analogy to the whole group of similar chlorosilanes and the knowledge about corrosivity to skin and upon. This puts both entries solidly into Class 3, subrisk 8, PG II.
- A complete revision of the classification criteria for substances which, in contact with water, release toxic/corrosive gases is currently being discussed in a GHS Working Group: therefore the adoption of the ICCA proposal to enhance safety should not be delayed till a decision has been made at GHS.
- There is neither a need for further amendments to the proposed changes in the provisions for packing instructions nor for the portable tank instructions and tank special provisions. Indeed even the proposed change from T11 into T10 for the 2 entries (UN 1250 and UN 1305) will result in a net positive gain of safety because the reduction in minimum test pressure (which is not justified by the vapour pressure of the two substances concerned) is more than offset by the additional safety afforded by the mandatory use of top filling and emptying portable tanks fitted with frangible discs.

Therefore ICCA invites UNSCETDG to adopt the proposals made in ST/SG/AC.10/C.3/2006/11.

If the proposal is adopted, ICCA will provide information on the consequential changes for the Guiding Principles for the Model Regulations, corresponding to the 15th revised edition.

Annex

Details of replies by ICCA (text inside the boxes) to queries raised

a. I think we can be a little critical of ICCA and the three contributing silicone manufacturers from Europe, Japan and USA about their tardiness in bringing this paper forward in the first place.

Better late than never …

b. Some of the substances from the chlorosilane family of chemicals are some of the first substances to appear in the Dangerous Goods Lists. I checked with Herbert before the meeting who assures me that the early UN numbers in the range UN 1162 - UN 1305 are some of the earliest ever allocated by the UNCOETDG, most probably in the second edition of the pink book, the precursor of the orange book in the late 1950s. At that time the criteria for assigning substances to Class 4.3 had not been developed nor the criteria for assigning substances of this division to their packing groups. Indeed it was not until the mid to late 1980s that work was begun at the UNCOETDG in developing the criteria and confirming the test methods for determining the data needed for classification. All along during that period of some 30+ years, the UNCOETDG assigned the class, subsidiary danger and packing group of substances deemed to have Class 4.3 dangerous properties by opinion and judgment ("seat of the pants", as Lance confirmed when I spoke to this paper). It is inevitable with hindsight that some inconsistencies can be found with the classification of this family of substances.

The assignment of chlorosilanes to class 4.3 is not put into question by our requested classification changes for chlorosilanes. The requested tank code changes for class 4.3 chlorosilanes are aimed at higher quality portable tanks (minimum test pressure 6 bar instead of 4 bar). The release of a corrosive and or toxic gas in contact with water is not taken into consideration in the classification criteria for substances of class 4.3

c. That the paper has been tabled in mid-2006 is quite astonishing given that the test methods and grouping criteria were established for Class 4.3 around 15 years ago. Why has it taken these three trade associations under the umbrella of ICCA so long to react? The classification issues should have been raised soon after the test methods and grouping criteria were established.
They should have posed the classification anomalies as they see them firstly for discussion. Only when these have been resolved should the consequentials for containment be dealt with.

Same comment as under b

f. There are relatively few substances in the chlorosilane family with any commercial use. I count 28 specific entries for them (I discount UN 1818). If the three trade associations are so concerned "to further enhance the safe transport of dangerous goods" they would have proven this by providing full and accurate data sheets for all 28. These substances are not particularly new. Several decades have passed when they could have been doing all the testing - here I think of the required flammability and corrosivity testing which has been long established in the Model Regulations - and at least a decade and a half during which the division 4.3 testing could have been done. They could have been determining essential data such as liquid densities and vapour pressures at the required temperatures. They are, for example, asking the UNSCOETDG to take some decisions on tanks on the basis of vapour pressure based on two representative data sheets which show that vapour pressure is low at the relevant temperatures. Why not show us the data for them all? They must have the expertise among them.

Our intention was not to put into question the classification of chlorosilanes in general but to improve the provisions for those entries where we noticed some drawbacks with respect to transport safety (change of bottom discharge to top discharge only) and to adjust the packing group for UN 1250 and UN 1305 in analogy to the whole group of chlorosilanes based on our knowledge about corrosivity to skin.
We suppose that the assignment of packing groups to chlorosilanes with respect to skin corrosivity must have been done earlier without testing. We have never seen test results on skin corrosivity according to OECD Guideline 404 and an inquiry for such data amongst member companies did not provide any results.
However, skin corrosivity of chlorosilanes is not worse than that of concentrated hydrochloric acid and hydrogen chloride gas, by-products formed in presence of humidity. The effects from other by-products such as silicone oil or solid silicic acid can be neglected with respect to skin corrosivity.
The decision on tanks should not be a big problem for UNSCETDG because our proposals are targeted to higher quality portable tanks (no bottom discharge) than the previous ones with the two exceptions UN 1250 and UN 1305 (T10 instead of T11).
The missing three data in the data sheet for Vinyltrichlorosilane (UN 1305) are as follows:
Density (15 °C) = 1,30 g/cm3
Density (50 °C) = 1,24 g/cm3
Vapour pressure (65 °C) = 44,2 kPa
We do not think it is necessary to carry out tests and provide data for all chlorosilanes.
Considering that there is no evidence, that the chlorosilanes Methyltrichlorosilane (UN 1250) and Vinyltrichlorosilane (UN 1305) are more severe corrosive than all other chlorosilanes, the adjustment of the Packing Group from I to II (which is assigned to all other chlorosilanes, excepted the ones in division 4.3) is just consequential.
Further it should be considered, that Dimethyldichlorosilane (UN 1162), which is rather similar to Methyltrichlorosilane (UN 1250) is officially classified by the EU as „F, R 11 Highly flammable“ and „Xi, R 36/37/38 Irritating to eyes, respiratory system and skin“. Due to its published inhalation toxicity data (RTECS: LC_{50} (4h) 930 ppm or 5,35 mg/L and German BG Chemie: LC_{50} (4h) 4,91 mg/l) it cannot be regarded as inhalation toxic. The oral toxicity is reported by RTECS as LD_{50} rat oral 5660 µl/kg or 6056 mg/kg – which means, that Dimethyldichlorosilane is not considered to be orally toxic. RTECS consider Dimethyldichlorosilane to be a moderate skin irritant and severe eye irritant, while in the IUCLID dataset severe burns are reported. Upon contact with water/moisture evolution of hydrogen chloride can be expected triggered by the amount of water involved as an exposure related risk and not as an intrinsic hazard. Hydrogen chloride is not considered „extremely toxic“; RTECS states an LC_{50} (1h) of 3124 ppm or 5,1 mg/l. These facts for Dimethyldichlorosilane can be taken analogous for Methyltrichlorosilane and Vinyltrichlorosilane in principle

g. The two data sheets supplied are incomplete: that for methylchlorosilane in that it shows the rarely stated liquid density and vapour pressure data at the temperatures required to be known for tank transport. The second does not state all the required density and vapour pressure data. The three trade associations should be told to go away and prepare data sheets for all the 28 substances listed including producing missing data for the two provided in this paper. We would prefer that the data sheets are complete, especially with essential data required for portable tank operations.

Same comment as under f.

h. Neither data sheet contains any corrosivity data either for skin exposure at 5.5. With respect to metal corrosion, it is interesting to note that they quote the same corrosion datum in both data sheets. Is this a coincidence, a fudge or are the data genuine measurements?

Test results on skin corrosivity according to OECD Guideline 404 cannot be provided.
The identical metal corrosion rate in the data sheets of UN 1250 and UN 1305 is not a mistake.
The value given is that of a reference substance (3-chloropropyltrichlorosilane). This reference substance combines corrosion effects from a chlorocarbon substituent on silicon as well as the corrosion effects based on Si-Cl bonds.
It can be said that the corrosion effects of UN 1250 and UN 1305 are not worse than the value given.
Beyond this we have more than 30 years experience that chlorosilanes and the tank material carbon steel are compatible (under dry nitrogen) with each other. This has been attested by independent Technical Inspection Companies for storage tanks as well as for rail tank cars and for portable tanks.

i. I think there is a genuine problem with these substances in determining corrosivity. The paper points to inhalation being a problem in that chlorosilanes react readily with water to form corrosive hydrogen chloride gas and hydrochloric acid. This sort of property is mentioned in the Model Regulations at 2.8.2.2 as a justification for allocating a class 8 classification. However there are no criteria given in chapter 2.8 for reaching a decision as to at what level this danger should be taken into account. OECD Guideline 404/1992 is referred to in chapter 2.8. I do not know whether this would provide any criteria for this kind of corrosivity as I do not own a copy and the Guideline is not readily downloadable from the OECD website.

Skin corrosivity test data according to OECD Guideline 404 are not available

j. I looked for any analogies from other substances classified as corrosive "taking into account such additional factors as.....reactivity with water". In gases we have boron trifluoride which is describe in the IMDG Code as reacting violently with water evolving hydrogen fluoride (UN 1008, class 2.3/8), an irritating and corrosive gas. Fluorine (UN 1045, class 2.3/5.1/8) has a similar property as does hydrogen bromide, anhydrous (UN 1048, class 2.3/8), dinotrogen tetraoxide (UN 1067, class 2.3/5.1/8), boron trichloride (UN 1741, class 2.3/8), chlorine trifluoride (UN 1749, class 2.3/5/1/8). At least for gases we have criteria for classification of a gas as corrosive [2.2.3 9 (c)] but these are not extended to liquids and solids, it seems to me. (I did not search the DG List to the end.)

UN Model Regulations do not cover the above mentioned additional properties of liquids in contact with humidity

k. Among solids and liquids, the IMDG Code informs us that the following have this property: Ethyl chloroformate (UN 1182, class 6.1/3/8), Chromium trioxide, anhydrous (UN 1463, class 5.1/8), acetyl bromide (UN 1716, class 8), acetyl chloride (UN 1717, class 3/8), aluminium bromide (UN 1725, class 8), anisoyl chloride (UN 1729, class 8), antimony pentachloride, liquid (UN1730 ,class 8), antimony trichloride (UN 1733, class 8), benzyl chloride (UN 1738, class 6.1/8), , bromine pentafluoride (UN 1745, class 5.1/6/1/8), choroacetyl chloride (UN 1752, class 6.1/8), chlorosulphonic acid (UN 1754, class 8). Again I have not gone through the whole of the DG List.

The findings are correct but not comprehensive

l. I remember a discussion at one of the briefing meetings a couple of years ago when the allocation of a corrosivity subsidiary danger to UN 2014 and 2015 (hydrogen peroxide solutions) was discussed. Alan Brown told us that hydrogen peroxide is not particularly corrosive in itself but that a corrosive mist could form in rapid decomposition.

The decomposition of hydrogen peroxide results into the formation of water and oxygen but both are not corrosive.

m. I dipped into GHS to see if I could find anything which would guide one to a corrosive or irritant classification based on evolution of corrosive or irritant vapour caused by reaction with water but did not see anything obviously relevant.

n. I think the point is made. The UNSCOETDG may well have to devise its own Guiding Principles in assigning a class 8 danger as a result of reacting with water before the classification of the chlorosilane family can be rationalised.

A Working Group of UN SCE GHS is currently working out classification criteria for substances and mixtures, which in contact with water release toxic gases (WAT). AN OECD working group is engaged into studying the problem of hazardous materials which in contact with water release corrosive and or toxic gases. As this may take some time, the adoption of this proposal to enhance safety should not be delayed.

o. Under the revised grouping criteria for Class 6.1, methyltrichlorosilane is borderline for this classification. The three trade associations would do well to review the data (a range of values) they put forward. We do not want to be revisiting all this in a year or two's time for this or any of the other chlorosilanes.

We are of the opinion that our requested changes for chlorosilanes should be implemented as soon as possible in order to improve transport safety. The revisiting of the whole class of chlorosilanes (and many other products with similar properties) in view of transport regulations will become necessary anyhow once new classification criteria have been established for substances and mixtures which in contact with water release corrosive and/or toxic gases.

p. There was some discussion about silicon tetrachloride (UN 1818) and one of the chlorosilanes, propyl trichlorosilane (UN 1816) at the sixteenth session of the UNSCOETDG July 1999 - see paragraphs 47-51 when paper ST/SG/AC.10/C.3/1999/44 was considered. This was a USA paper which I have not retained but according to my records must have included a data sheet for UN 1816 as I have some of the physical properties from it recorded in a little data base I retain. You may care to look at what the report says about the corrosivity of these substances (ST/SG/AC.10/C.3/32) as it is relevant to 2006/11. It may be worthwhile having another look at that data sheet for UN 1816.

At earlier sessions the re-classification of UN 1818 and UN 1816 as class 6.1 substances has not been adopted.
Substances without systemic toxicity (such as chlorosilanes) should not be considered toxic and not assigned to division 6.1 at all. This is prescribed in the Note to subsection 2.6.2.2 of the UN Model Regulations reading, that substances meeting the criteria of class 8 and with an inhalation toxicity of mists leading to packing group I are only accepted for an allocation to division 6.1 if the toxicity through oral or dermal contact is at least in the range of packing group I or II; otherwise an allocation to class 8 is made when appropriate (see subsection 2.8.2.3). This was the reason, why the US proposal to shift Propyltrichlorosilane (UN 1816) and Silicontetrachloride (UN 1818) to class 6.1 had been disapproved

q. Why are composite packagings consisting of a plastics receptacle in a steel drum (61HA1) are acceptable whereas plastics inner packagings of combination packagings and plastics drums and jerricans as single packagings are proposed to be prohibited.

Composite packagings with a plastics receptacle are used for the shipment of high purity (e.g. electronic grade for the semiconductor industry) chlorosilanes for which contamination with metal impurities has to be avoided. The steel drum around the plastics receptacle provides the necessary mechanical stability for transport and handling purposes and prevents puncturing by sharp objects. Using metal drums with a varnish layer or a resin coating is less suitable for the shipment of these high purity chlorosilanes because any bump or dent may damage this inner protective layer resulting into possible contact between the product and the naked metal surface. Stainless steel drums could be an alternative but because of their high cost, they are often returnable packagings causing extra risks and costs of handling and cleaning.

To sum up,

1. Criteria are needed for determining when a corrosivity classification is needed for liquid and solid substances which generate corrosive vapour in contact with water. Until the UNSCOETDG does this we are likely to get similar gripes from this and other sectors of industry.

This will indeed result into a long lasting procedure for introducing new classification criteria for substances releasing corrosive and or toxic gases in contact with water.
In the meantime proposals to improve transport safety should not be delayed.

2. The three trade associations should be told to go away and produce full and accurate data sheets (including the essential data needed for tank transport - liquid densities and vapour pressures at the relevant temperatures

See comments under f

3. Establish the classification of these compounds once and for all on the basis of flammability, toxicity and corrosivity. Then look at the containment issues.

See earlier comments under f, n, o

Addendum on the proposed Tank Codes:

Under the latest Guiding Principles their allocation of substances to T10 or T14 at first take looks reasonable. The vapour pressure data quoted for the two substances for which there are data sheets, if this were a trend for the rest of them, would allow a liberal use of T10 for the specific entries.

No comment required