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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 Transport of Dangerous Goods
(Twentieth session, 3-12 December 2001, agenda item 7 (d))

LISTING AND CLASSIFICATION

Miscellaneous amendment proposals (Parts 2 and 3)

Provision for calcium hypochlorite and trichloroisocyanuric acid, dry in tablet form

Transmitted by the experts from South Africa and Germany

Background

Calcium hypochlorite and trichloroisocyanuric acid are used in large quantities all over the world. The historical demand for these chemicals has mostly been for the granular form for desinfection of water to make it potable and generally for swimming pool applications. However, significant global shifts in use patterns towards calcium hypochlorite and trichloroisocyanuric acid in tablet form are currently taking place which necessitate a review of the current transport regulations.

The shift in demand has increasingly been driven for disaster relief operations, water purification and sanitization, as well as in specialized agricultural applications. Means of chlorination such as liquid chlorine gas are wholly unsuitable for such applications as a result of their inherent danger, or the logistical difficulties associated with transportation and storage. At the same time, new technology for dispensing calcium hypochlorite and trichloroisocyanuric acid in tablet form has made these chemicals much more accessible to specialized users.

South Africa is one of the largest manufacturers of calcium hypochlorite in the world. Several hundred tons of calcium hypochlorite in tablet form are manufactured and transported annually. One of the reasons for the increase in demand for the tablet form is that controlled dosing of chlorine can be achieved by the user.

The bulk of the demand for tablets is for low volume applications where an immediate but short term need has to be filled. A typical example would be a requirement for disaster relief during floods or for refugee camps. Dispensing systems that utilize tablets are ideally suited for such applications.

Hazard profile of calcium hypochlorite and trichloroisocyanuric acid tablets

The subdued hazard characteristics shown by tablets compared to that of granules can be attributed to the following two main factors:

a) Reactive surface

It is an established scientific fact that particle size and surface area are fundamental determinants of the rate of chemical activity. It thus follows that a given amount of calcium hypochlorite and trichloroisocyanuric acid granules will react more vigorously than the same amount of calcium hypochlorite and trichloroisocyanuric acid compressed into tablets.

b) Heat transfer properties

To work effectively and to maintain their integrity during transportation and handling, calcium hypochlorite and trichloroisocyanuric acid tablets are compressed under forces of at least 20 tons per square inch. Thus, the heat transfer properties of a stack of 50 kg drums would be quite different when compared to a stack of the same mass made up of plastic tubes containing ten tablets each.

The higher density of the tablets, combined with the individual packing (small size of each package), and the ratio of air to mass of the stack, effectively negate the hazard of self-heating in a cargo made up of tablets.

Test 0.1 Test for oxidizing solids of the UN Manual of tests and criteria, third revised edition

Oxidizing solids are tested in accordance with Test 0.1 *Test for oxidizing solids* of the UN *Manual of tests and criteria, third revised edition.* As the particle size of the solid has a significant effect on the result, the particle size of the substance tested should be stated in the test report.

The substance in the form in which it will be transported, **should be inspected for any particle less than 500 mm in diameter**. If the powder constitutes **more than 10 % (mass) of the total**, or **if the substance is friable**, then the whole of **the test sample should be ground to a powder before testing** to allow for reduction in particle size during handling and transport.

According to this test the **tablets being friable or the tablets which have particles less than 500 mm in diameter of more than 10 % (mass) of the total** have to be ground and intimately mixed with cellulose.

The physical form of commercial tablets and their packaging

There are several issues to consider when comparing the differences in the physical form between compacted material and granules - particularly during shipping. These are:

- **Commercial/shipping package size.** Due to physical manufacturing as well as commercial limitations, tablets are typically only 40mm to 100mm in diameter and 10mm to 30mm in thickness, and are packed either individually or in plastic tubes not exceeding 2 kilograms each. Granular material is typically packed for shipping in 25kg (for cargo air freight) or 45kg drums (sea freight). Due to use patterns, tablets are generally shipped in the final commercial or consumer

package. Whilst both experts are aware that some tabletted material is shipped loose in larger drums and bags, usually for the purpose of re-packing by the consignee or customer, both experts believe that this represents just a fraction of the total amount currently shipped in compressed form.

- **Spillage.** In the event of spillage, compacted material will result in relatively few, large particles coming into contact with the environment. This may be contrasted to the effect that a similar spillage of granular material would have on the outside environment.

Tablet size and the question of friability

This issue has no doubt been raised by the concern that physical attrition during the distribution or shipping would shatter the compacted material in such a way that it would somehow return to the physical characteristics - and hazard profile - of the granular form. Both experts respectfully submit that this is not realistic. Firstly, it must be understood that calcium hypochlorite is much more soluble in water than other forms of solid chlorine (such as trichloro-iso-cyanuric acid), and also does not compact as easily. Therefore, in order to manufacture a viable commercial product, compression forces of at least 25 - 40 metric tons per square inch need to be applied in order to produce a suitably hard product that will have the desired dissolution characteristics in water. These forces far exceed the hardness required to produce a product that is merely suitable for transportation - if this were to be the sole criterion. Secondly, because of the consumer package sizes generally used for tablets, the product is able to withstand the robust handling envisaged during shipping, without changing its form. Even severe handling would, at most, result in extremely small amounts of material breaking away from the tablet. Such amounts are incapable of the described self-heating properties of larger quantities of granules.

To properly accommodate the significantly lower hazard of compacted material through the provision of a separate classification, both experts submit that it is important that certain physical criteria would have to be met in order to ensure that the reactive properties ascribed to compressed material apply to all material that is declared and shipped as tablets. **The best and least problematic way to achieve this could be via a simple, standardized drop test that confirms the impact strength of a single sample tablet produced by the manufacturer.**

It is also important that tablets declared under the new classification are not so small that particle size once again presents a problem. Comprehensive testing of smaller tablets could provide greater insight into their exact characteristics. Both experts are comfortable with suggesting **an initial limit of between 70 and 350 grams per tablet be set down under a new category.**

In Germany calcium hypochlorite and trichloroisocyanuric acid pure substances or preparations in a granular form or in tablets have been tested. It was found that big tablets - up to ten - being individually wrapped in plastic bags and packed in small fibreboard packagings were often neither friable nor did the individual plastic bags contain particles less than 500 µm in diameter of more than 10 % (mass) of the total. Therefore these tablets should be treated as being non dangerous according to Test 0.1 Test for oxidizing solids of the UN Manual of tests and criteria, third revised edition. Small tablets of the above mentioned substances - normally more than ten - being individually wrapped in plastic bags and packed in small fibreboard packagings were often friable and some did in the individual plastic bags contain particles less than 500 µm in diameter of more than 10 % (mass) of the total. Therefore these tablets should be ground before testing.

Classification

In the opinion of the expert of South Africa and Germany the above mentioned problem cannot be solved by establishing individual UN entries for substances in a powdery, granular or in tablet form. Therefore a new special provision should be added to the UN No. 1748, 2208, 2468 and 2880 to excempt tablets between 70 and 350 grams per tablet which according to the producing process are neither friable nor in the individual packaging do contain particles less than 500 µm in diameter of more than 10 % (mass) of the total from the requirements of the UN recommendations.

Proposals

1. The following new special provision xxx should be added to the UN No. 1748, 2208, 2468 and 2880 and should read as follows:

> Special provision xxx "This entry shall not apply to tablets between 70 and 350 grams per tablet which are packed individually and which are neither friable nor do contain particles less than 500 µm in diameter of more than 10 % (mass) of the total in that packaging."

2. The Sub-Committee is invited to adopt the principle to implement a new drop test for determining the friability of tablets.

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