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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

Amendments to CALCIUM HYPOCHLORITE entries of UN 1748, 2208 and 2880 of class 5.1

Transmitted by the expert from Germany

Background

On the 18th session of the Sub-Committee of Experts a proposal of Japan for an entry for calcium hypochlorite hydrated with more than 10 % water (see document ST/SG/AC.10/C.3/2000/22) was adopted. In Paragraph 40 of the report of this session (see ST/SG/AC.10/C.3/36 page 9) the Expert from Germany informed the Sub-Committee that the stability of calcium hypochorite, hydrated with more than 10% water depends on the impurities it contained, the water content and manufacturing processes. Furthermore he stated that a full study of the hazard characteristics of these products was in progress in his country. The experts from Japan and Germany agreed to carry out round robin tests of various calcium hypochlorite preparations. These round robin tests are finished by this time. The test results including proposals on amendments for the entries of the above mentioned calcium hypochlorite entries of UN 1748, 2208 and 2880 are listed in this document as follows. The tests were carried out with products from the USA, Japan and China. The products Pittclor (USA), HTH (USA), NJE-30 (Japan), Hypochlorite (Japan) und Chemochlor CH (China) are related to the UN 1748 and the products HI-Chlon 65 NJG-05 (Japan), HI Chlon 65 NJF-30 (Japan) and HI Chlon 70 NJH-05 (Japan) to the UN 2880. The properties of the calcium hypochlorite of UN 2208 have not been tested, since the hazard potential of this substance is far beyond that of UN 1748 and 2880.

On the part of the expert from Germany there are no objections for safety reasons against the upgrading of the water content from 10% to 16% for UN 2880 due to the test results.

Testing method

The heat storage tests for the determination of the SADT on various calcium hypochlorite samples were carried out according to the definitions in the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, third revised edition 1999, section 28.4.4. 500 ml-Dewar vessels were used, filled with 400 ml substance. The „Heat loss"-values for the Dewar vessels were between 76,8 and 62 mW/kg.K, when filled with 400 ml water. A Heat loss L= 73 mW/kg.K (500 ml Dewar with 400 ml Wasser) corresponds to a Heat loss L = 21 mW/kg.K when filled with 450 g calcium hypochlorite (NJE-30, Japan), at a c_p-value of 1088 J/kg.K, and is, therefore, representative for about 50 to 100 kg calcium hypochlorite in packagings of type 1G and 4G. According to section 28.4.4.2.8 the Heat loss L for the Dewar vessels is supposed to be 80 to 100 mW/kg.K (water), if they shall be representative for 50 kg-packagings. People can work on the principle that the used Dewar vessels were normally only representative for drums of 50 to 100 kg. Solids with comparable packagings show lesser Heat loss-values (e.g. packaging type 1G, filled with 85 kg Dicyclohexyl phthalate (solid), L= 22 mW/kg.K).

Test results and conclusions

From the results follows that,

- All tested samples at a storage temperature of 60 °C were not stable.
- According to the UN-criteria (max. admissible temperature increase ≥ 6 K above storage temperature during 7 days, timing from 2 K below storage temperature in the Dewar) at 55 °C storage temperature 7 of 8 samples „run away", where the samples wetted with water (12,7 to 13,5 %) reacted more violently (higher maximum temperature).
- At 50 °C storage temperature all samples survived the test (formally for „Chemoclor CH-Granulat“ a temperature increase around 6 K was measured; the analysis on available chlorine, however, showed only a lower decrease).
- From the UN-prescriptions for the SADT, table 28.2 in section 28, Tests and Criteria, results, therefore, for „single packagings“ from 50 to 100 kg a SADT of 55 °C and a control temperature of 45 °C as well as an emergency temperature of 50 °C. For packagings with ≥ 200 kg calcium hypochlorite according to the experiences a SADT of 45 °C has to be assumed, which leads to a control temperature of 35 °C and an emergency temperature of 40 °C (see as well DSC 5/INF of 4.11.1999 and B. F. Gray und B. Halliburton, Fire Safety Journal 35(2000)223-239).(Information material will be distributed separately).
- For a safe transport it is as well decisive, at which substance temperature the substances will be offered for transport: the lower the initial transport temperature, the longer the time is likely to be until the substance temperature raises to hazardous values. Therefore, the substances should be offered for transport at the least possible temperatures (<< 20 °C). The transport period is as well of decisive importance: the longer the transport takes the higher is the risk of a temperature increase in the substance and the lower the initial transport temperature should be.
- If a dry calcium hypochlorite gets moist during transport or comes into contact with water all the more violent the exothermic decomposition reaction will be.

The obtained test results are shown in table 1. Table 2 gives the analytical data of the samples.

Table 1

Sample name	**Pittclor USA**	**HTH USA**	**NJE-30 Japan**	**Hypo-chlorite Japan**	**Chemo-clor CH China**	**HI-Chlon 65 NJG-05 Japan**	**HI-Chlon 65 NJF-30 Japan**	**HI-Chlon 70 NJH-05 Japan**
Available Chlorine (BAM)	61,7%	67,2%	67,2%	72,9%	67,9%	70,4%	68,4%	74,1%
Heat accumulation storage test (UN test H.4) at 60 °C								
Dewar vessel	500 ml	500 ml	500 ml	500 ml	500 ml	500 ml	500 ml	500 ml
Dewar heat loss (400 ml water; mW/kg.K)	76,8	62	73	70,1	64,5	73	67	70,1
Sample mass (g)	456	410	450	480	520	450	450	450
Exothermic decomposition	yes	yes	yes	yes	yes	yes	yes	yes
Temperature (max.)	171 °C	71 °C	140 °C	163 °C	>200 °C	141 °C	139 °C	140 °C
Time to exothermic reaction (hours)	35	56	61,5	72,5	25,5	80,5	46	61
Available Chlorine after test	1,4%	44,1%	1,2%	0,9%	0,5%	0,4%	0,8%	0,6%
Heat accumulation storage test (UN test H.4) at 55 °C								
Dewar vessel	500 ml	500 ml	500 ml	500 ml	500 ml	500 ml	500 ml	500 ml
Dewar heat loss (400 ml water; mW/kg.K)	67	67	62	73	73	64,5	67	70,1
Sample mass (g)	456	410	450	480	520	450	450	450
Exothermic decomposition	yes (1)	no	yes	yes (1)	yes	yes	yes	yes
Temperature (max.)	61 °C (1)	58 °C	66,5 °C	61,5 °C (1)	67 °C	80 °C	136 °C	137 °C
Time to exothermic reaction (hours)			174		64	170	155	162,5
Available Chlorine after test	46,9%	56,5%	41,1%	53,3%	51,6%	16,8%	0,4%	0,9%
Heat accumulation storage test (UN test H.4) at 50 °C								
Dewar vessel	500 ml		500 ml	500 ml	500 ml	500 ml	500 ml	500 ml
Dewar heat loss (400 ml water; mW/kg.K)	62		64,5	67	62	64,5	67	73
Sample mass (g)	456		450	480	520	450	450	450
Exothermic decomposition	no		no	no	yes (1)	no	no	no
Temperature (max.)	55 °C		51 °C	52,5 °C	56 °C (1)	50 °C	49,5 °C	49 °C
Available Chlorine after test	50,6%		62,4%	66,2%	63,2%	66,7%	65,6%	68,1%

(1) borderline case

Table 1 Heat accumulation test results

Table 2

Sample name		**Pittclor USA**	**HTH USA**	**NJE-30 Japan**	**Hypo-chlorite Japan**	**Chemo-clor CH China**	**HI-Chlon 65 NJG-05 Japan**	**HI-Chlon 65 NJF-30 Japan**	**HI-Chlon 70 NJH-05 Japan**
Available Chlorine	[%]	63,2	67,6	67,3	74,2	69,0	66,7	67,6	73,9
Calcium chlorate $Ca(ClO3)_2$	[%]	4,3	3,1	0,6	1,9	2,5	1,4	1,4	1,7
Calcium chloride $CaCl_2$	[%]	3,33	1,0	1,5	0,8	4,9	2,0	2,0	0,1
Calcium hydroxide $Ca(OH)_2$	[%]	2,00	2,15	1,63	1,11	5,03	1,5	1,2	1,80
Calcium carbonate $CaCO_3$	[%]	2,00	3,50	1,60	1,40	2,40	1,0	1,0	1,40
Sodium	[%]	8,1	7,3	5,6	5,0	4,2			
Moisture (water)	[%]	0,2	0,1	0,1	0,1	0,1	13,5	12,7	13,3
Mg	[%]	0,18	0,13	0,14	0,05	0,14	0,1	0,1	0,10
Sodium chloride NaCl	[%]						14,8	14,9	7,60
pH value		11,66	11,45	11,68	11,19	11,54			

Table 2: Analytical data submitted by companies/determined by an institute in Germany

Class 8 subsidiary risk

Calcium hypochlorite is a corrosive substance asking for a subsidiary risk Label of class 8. This classification is in line with the directive 67/548/EEC, where calcium hypochlorite is marked with the indications O (oxidizing),C (corrosive) and N (dangerous for the environment) supplemented by the indications R8, R31 and R34. Hypochlorite forms corrosive hypochloric acid with the humidity of the tissue of the skin. The corrosive destruction of the skin is on one hand a direct oxidation (bleach) and on the other hand a damage to the tissue of the skin as specific for acids.

"Marine Pollutant" mark for sea transport

According to the evaluation and rating for the fish toxicity in column B = "4" of the GESAMP HAZARD PROFILE calcium hypochlorite meets the criteria of being a "**Marine Pollutant**" **(P)**.
This evaluation is based on data on fish toxicity:
$96^{h}LC_{50}$(fish) = 0,049 - 0,16 mg/L (Lepomis macrochirus)
$96^{h}LC_{50}$(fish) = 0,13 - 0,2 mg/L (Salmo gairdneri)

The containments for sea transport should, therefore, bear a **Marine Pollutant** mark.

Packagings for the transport of calcium hypochlorite

Basing on the safety aspects drums, jerricans and boxes made of steel, aluminium or rigid plastics should be used, provided that the packing material is not reacting with calcium hypochlorite and its decomposition products (for metal receptacles a liner, plastic bags or coating may be used).
The maximum net mass per package should not exceed 200 kg. For packagings with ≥ 200 kg net mass calcium hypochlorite according to the experiences a SADT of 45°C has to be assumed, which leads to a control temperature of 35 °C and an emergency temperature of 40 °C. Flexible packagings made of plastics, woven plastics, plastics film or paper should not be used, because the heat developed by decomposition could not be conducted away rapidly enough to the surroundings and therefore spontaneous combustion could occur when the rate of heat production exceeds the rate of heat loss.
All packagings should be provided with venting devices.

On the fifth session of the Sub-Committee on Dangerous Goods, Solid cargoes and Containers it was decided that the transport of calcium hypochlorite in flexible packagings (bags), IBC and large packagings should not be allowed for safety reasons. Furthermore the transport of calcium hypochlorite in bulk has been forbidden (see German proposal DSC 5/3/27). These consideration have been taken into account by implementation of a new special packing provision PP78 for packing instruction P002. PP78 reads as follows:
"for UN 1748, UN 2208 and UN 2880, bags are not allowed". Additionally the packing instruction IBC 08 including special provisions B2 and B4 for UN 1748, 2208 and 2880 has been deleted. (see Amdt. 30, IMDG Code).

General safety measurements

The general safety prescription as **"Packages containing calcium hypochlorite should be protected from direct sunshine and stowed in a cool, well-ventilated place. Packages should be securely stored so as to allow for adequate air circulation throughout the cargo"** should be complied with.

Proposals

Amendments for UN 1748, UN 2208 and UN 2880 to chapter 3.2 - Dangerous Goods List -

1. In column (4) the subsidiary risk 8 should be added.

2. In column (6) the following new special provision "XXX" should be added:

   "XXX a) Substances are liable to exothermic decomposition at elevated temperatures. Decomposition can be initiated by heat or by impurities (e.g. powdered metals (iron, manganese, cobalt, mangnesium)) and their compounds

   b) Cargo transport units shall be shaded from direct sun light and all sources of heat. Packages in cargo transport units shall be placed in adequately ventilated areas."

3. For packagings and IBCs in column (8) and (9) the following amendments should be carried out:

   a) Delete in column (8) packing instruction IBC 08 and in column (9) special packing provisions B2 and B4

   a) Implement the following new special packing provision "PPXX" which should read as follows:

   "PPXX For UN 1748, UN 2208 and UN 2880 bags are not allowed. Quantities shall not increase 200 kg net mass per package. Transport under temperature control only; for packagings up to 100 kg net mass control temperature of 45 °C and for packagings up to 200 kg net mass 35 °C".
