



CHINA SHIPOWNERS MUTUAL ASSURANCE ASSOCIATION

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TO THE MEMBERS

Carriage of Calcium Hypochlorite - Frequently Asked Questions

Dear Sirs,

There have been several large fires in cargo vessels in the 1990's, which have been attributed to the carriage of Calcium Hypochlorite. In response to these casualties, P&I clubs have issued circulars on the recommendations for the carriage of Calcium Hypochlorite, and the International Group established a Calcium Hypochlorite working group which has met to share information and listen to the views of scientific experts.

Based on the submission rendered by the International Group, the International Maritime Organisation had made some amendments to transport requirements for Calcium Hypochlorite in the new version of the IMDG Code, including packaging, stowage and segregation (Please refer to the IMDG Code in amendment 30-00).

The club has prepared the following list of Frequently Asked Questions to clarify some of the issues that have been raised by members in recent years. We hope members can use this for reference on the carriage of Calcium Hypochlorite and keep vigilant attention to avoid any potential risks on the greatest extent.

1 What is calcium hypochlorite?

This chemical is a white or yellowish solid that is soluble in water. There are several products manufactured as water purification and bleaching agents, which contain calcium hypochlorite (CH) as their active ingredient. The three most common products are two high strength types (UN 1748 and UN 2880) and a lower strength type, often referred to as bleaching powder (UN 2208). The entries in the International Maritime Dangerous Goods (IMDG) Code are shown as follows:

Class 5.1 UN 1748 Calcium hypochlorite dry, or calcium hypochlorite mixtures, dry containing more than 39% active chlorine;

Class 5.1 UN 2880 Calcium hypochlorite hydrated, or calcium hypochlorite hydrated mixture containing not less than 5.5% but not more than 16% water;

Class 5.1 UN 2208 Calcium hypochlorite mixture dry containing more than 10%

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active chlorine but not more than 39% active chlorine.

The following are additional to the above and are included in the Amendment 35 to the IMDG Code which is on a voluntary basis from 1 January 2011 and mandatory from 1 January 2012:

Class 5.1/8 UN 3485 Calcium hypochlorite, dry, corrosive or calcium hypochlorite mixture, dry, corrosive with more than 39% available chlorine (8.8% available oxygen);

Class 5.1/8 UN 3486 Calcium hypochlorite mixture, dry corrosive with more than 10% but not more than 39% available chlorine;

Class 5.1/8 UN 3487 Calcium hypochlorite, hydrated, corrosive or calcium hypochlorite, hydrated mixture, corrosive with not less than 5.5% but not more than 16% water.

Calcium hypochlorite or calcium hypochlorite mixtures should be transported in accordance with the requirements set out in the IMDG Code, as appropriate and comply with the advice of the IG.

2 What are the hazardous properties of calcium hypochlorite?

Calcium hypochlorite is an oxidizing agent and is designated a Class 5.1 oxidiser in the IMDG Code. CH and some mixtures thereof also meet the criteria for Class 8 corrosives (see IMDG Code Special Provision 313 and Amendment 35 of the IMDG Code mentioned in FAQ 01).

IMDG Code Special Provision 314 applies to CH and it states: These 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, magnesium} and their compounds).

When involved in a fire the CH decomposes without burning to release oxygen which will intensify the fire. Also, if CH is mixed with organic materials, such as sawdust or oil, it can result in a fire without the need for an external ignition source.

One other important characteristic is that it is unstable and self reactive. At normally encountered temperatures CH decomposes only very slowly and releases heat. However, at higher temperatures the rate of decomposition increases and if the heat is not able to escape from within the material then its temperature increases and the rate of decomposition increases, and so on. As such, the reaction can runaway and result in a violent decomposition of the calcium hypochlorite.

3 What is the Critical Ambient Temperature?

The lowest ambient temperature at which the runaway reaction occurs is the critical ambient temperature (CAT) of the material for the sample size (under test).

The CAT for calcium hypochlorite depends on the size and shape of the package. The CAT will be higher for a small package compared to a larger package of the same material. This is because the smaller package will be able to lose heat to the surroundings much more readily than a larger package. Another factor that affects

stability is the amount of moisture present. For a given package, the anhydrous material will have a higher CAT than the equivalent package of hydrated CH.

Examples in the literature show that Professor Brian Gray determined that the critical ambient temperature for a 40 kg keg of CH containing 8.5% moisture, UN 2880, is about 55°C whereas for a 200 kg drum of the material it is about 44°C. It follows from this that a container load of 200 kg drums will have a CAT lower than 44°C because the drums will thermally interact with each other within the container.

4 What is the Self Accelerating Decomposition Temperature (SADT)?

Testing of a material can be undertaken to determine its SADT. The United Nations Manual of Tests at Section H describes four test methods for determining SADT of a material. The SADT is defined as the lowest ambient temperature at which a 6°C rise in temperature occurs in the material above ambient temperature within a seven day period. The test is conducted on a single package of the size to be shipped, e.g. 45 kg drum.

The SADT test was designed to be used as a guide to a material's sensitivity to heat and to help determine the rules and conditions under which a self reactive material (Class 4.1) is transported. However, calcium hypochlorite is classed as an oxidising agent (Class 5.1), with no self reactive subsidiary risk factor. It is not categorised by the IMO as a self reactive material, even though it behaves as such.

The SADT does not give a reliable guide as to whether or not the material will go into thermal runaway. In some cases the CAT can be well below the SADT temperature. Therefore, the reliable property in assessing the instability of calcium hypochlorite is the CAT.

5 What types of packaging can be used for calcium hypochlorite?

The 2008 IMDG Code defines what packaging can be used for calcium hypochlorite in Volume 1 Page 138 Table P002. It is important to note that bags, sacks, IBCs and Bulk Packaging are not allowed.

6 What other names is calcium hypochlorite shipped under?

Calcium hypochlorite (UN 1748 & UN 2880) may be misdeclared as calcium chloride. Other names encountered in the past have included: BK Powder, CCH, hy-chlor and Chloride of lime or Chlorinated lime.

Calcium hypochlorite is a Proper Shipping Name, as defined in the IMDG Code. As such, it should only be carried under that name and with the appropriate UN Number. UN Nos 2880, 2208, 1748, 3485, 3486 and 3487.

The IG's previous advice was that some shippers were trying to circumvent CH requirements by using improper shipping names such as those above and declaring the material as UN 1479. The IG advised that this was not an approved practice.

7 Is bleaching powder calcium hypochlorite?

Bleaching powder is a lower strength form of calcium hypochlorite identified as UN 2208 and is subject to transport requirements very similar to the higher strength forms, UN 2880 & UN 1748.

Note that UN 2208 has more than 10% active chlorine but not more than 39%. As such, if a product has less than 10% active chlorine it is weaker still and could be shipped as UN 1479 OXIDISING SUBSTANCE N.O.S. (not otherwise specified) which has less onerous carriage conditions.

8 Can I use dry containers?

Yes. You can use 20 ft or 40 ft dry containers provided that the maximum payload of CH does not exceed 14 tonnes. See also FAQ 13.

9 Why is there a limit of 45 kg for cal hypo packages?

Casualties in the mid to late 1990s involved calcium hypochlorite packaged in large drums of up to 180 kg. The bigger the package, the lower the CAT. The CAT of a 20 ft container packed with 45 kg drums is of the order of 40°C. Hence a package limit of 45 kg and a limit on the total mass per container to 14 tonnes.

10 Why has the carriage of calcium hypochlorite been limited to 14 tonnes per dry container?

At present there are insufficient scientific data to confirm that it is safe to carry more than 14 tonnes of calcium hypochlorite in a 40 ft dry container. The IG Working Group considers that ship owners need a simple rule which can be promulgated via the P&I Clubs to advise on the maximum tonnage permitted per 40 ft dry container.

11 Can I use reefers?

Yes. You can ship 14 tonnes in either a 20 ft or 40 ft reefer at a control temperature of 10°C provided you have undertaken a proper risk assessment and have an adequate procedure which requires reefers containing CH to be checked regularly and which identifies what measures are to be taken in the event of malfunction.

12 What are the disadvantages of using reefers to transport calcium hypochlorite?

In the event of a mechanical failure or of an interruption of the power supply, calcium hypochlorite will heat up faster in a reefer than in a dry container. If prompt steps are not taken to restore the power or fix a mechanical failure, an explosion could result. Manufacturers of calcium hypochlorite have not presented scientific data to permit an adequate assessment of the heating rate to be made. Anecdotal evidence suggests that

heating to explosion could result in about 10 to 14 days without intervention.

Another difficulty encountered with reefers has been the corrosive effect of CH on paint and metalwork of the container. This damage has probably resulted from excess CH on the external surfaces of packaging becoming airborne when stirred up by a circulation fan. As such, if reefers are used then appropriate inspections of the cargo are necessary to avoid the problem.

13 Can I put anything else in the dry container?

In practice, CH tends to be shipped on a full container load basis. It is recommended that such shipments should not exceed 14 tonnes for the reasons outlined earlier in this advice. However, it is not recommended that such payloads be consolidated with other cargo because this could detrimentally affect the stability of the CH due to changes in the overall thermal properties of the container contents.

14 Can I ship a few drums of CH in another dry container?

The above FAQs apply to full container loads of CH. If a few drums of CH are being shipped in a container with other cargo then shippers must follow the IMDG Code in respect of the entry for the CH being shipped.

Yours Faithfully

For China Shipowners Mutual Assurance Association