INTERNATIONAL MARITIME ORGANIZATION

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IMO

SUB-COMMITTEE ON DANGEROUS
GOODS, SOLID CARGOES AND
CONTAINERS
5th session
Agenda item 3

DSC 5/3/-
4 November 1999
Original: ENGLISH

AMENDMENTS TO THE IMDG CODE, ITS ANNEXES AND SUPPLEMENTS

Carriage of calcium hypochlorite

Note by the International Group of P & I Clubs (IGP&IC)

SUMMARY

Executive summary:	To describe the hazards of cargoes of calcium hypochlorite and to make recommendations for revisions to the IMDG Code for the marine transportation of calcium hypochlorite and for further research.
Action to be taken:	Paragraph 10
Related documents: (1)	Information paper "A Study of the Thermal Properties of Hydrated Calcium Hypochlorite (UN 2880)" by Professor B F Gray (et al) - November 1999 (Annex 1).

1.0 INTRODUCTION

1.1 There have been several large fires in cargo ships over the past two years which have been attributed to the carriage of calcium hypochlorite. In response to these dangerous and costly losses and because of concern for the safety of life at sea, the International Group of P&I Clubs (IGP&IC), which insures 90% of the world's blue-water tonnage, established a calcium hypochlorite working group which has met to share information and listen to the views of scientific experts. The working group includes consulting scientists, Dr J H Burgoyne & Partners, who commissioned and managed a research programme carried out by Professor B F Gray in Australia to study the thermal decomposition properties of the hydrated form of the material. The research programme was funded by the International Group of P&I Clubs.

1.2 The research led by Professor Gray (Annex 1), (which is continuing) has demonstrated that the hydrated form of high strength calcium hypochlorite is capable of self-heating at relatively low temperatures. For the size of package routinely shipped, a spontaneous runaway reaction is possible at temperatures that could be encountered during a sea voyage.

1.3 Having considered the results of Professor Gray's research, the IGP&IC makes recommendations which are presented in this submission for consideration at the 5th session of the Sub-Committee on Dangerous Goods, Solid Cargoes and Containers Committee (DSC 5) of the International Maritime Organization (IMO).

1.4 The IGP&IC recommendations in section 10 of this paper have been endorsed by the International Union of Marine Insurers (IUMI), the International Underwriting Association (the London Market Joint Hull Committee and the Joint Cargo Committee) and the Salvage Association (SA).

2.0 BACKGROUND

2.1 Calcium hypochlorite is a commodity chemical which is produced and shipped internationally on a large scale. It is used to sanitise drinking water and to chlorinate swimming pools. It also plays an important role in providing potable water, and is particularly valuable for disaster relief. All forms have powerful chemical properties which make this product inherently hazardous. The main forms are the anhydrous and the hydrated high strength forms of calcium hypochlorite, widely known as High test Calcium Hypochlorites (HCH) and the lower strength form commonly known as "bleaching powder".

2.2 In the years 1997-99 there have been at least eight ship fires, involving all three forms of the product, (anhydrous and hydrated HCH and bleaching powder). Total losses, resulting to the industry, are estimated at US$300,000,000.

2.3 Fires started by decomposition of calcium hypochlorite typically occur very fast and the first sign is often an explosion. Decomposition of the product liberates hazardous chlorine gas and also oxygen, which intensifies the resulting fire. After the rapid decomposition of calcium hypochlorite a widespread fire is likely, which will present a severe fire-fighting challenge. Often, boundary cooling is the only practical response.

2.4 Given the scale and intensity of the recent fires it is remarkable that there have been no serious injuries or fatalities. It is clear that steps are urgently required to reduce the risks to seafarers and to others who may have to tackle these dangerous fires.

3.0 PROPERTIES OF CALCIUM HYPOCHLORITE

3.1 Commercial calcium hypochlorite is a mixture of chemical compounds consisting of calcium hypochlorite, sodium chloride, calcium hydroxide, calcium chloride and small amounts of other compounds. The table below indicates the UN number and classification of the most commonly manufactured types of calcium hypochlorite, together with the corresponding IMDG Code references.

Common Name	*IMDG Class*	*UN Number*	*IMDG Page*	*Typical Moisture Content*	*Available Chlorine*	*Packing Group*
Anhydrous calcium hypochlorite	5.1	1748	5137		>39%	II
Hydrated calcium hypochlorite	5.1	2880	5138	>5.5% <10%	N.S.	II
Dry calcium hypochlorite (bleaching powder)	5.1	2208	5138		<39% >10%	III

3.2 It has been reported that calcium hypochlorite products have been improperly declared as UN1479 (oxidising solid N.O.S.) in order to circumvent requirements imposed by concerned shipowners for carriage of UN2880 or UN1748. This misdescription results also in the cargo being subject to less onerous provisions of the IMDG Code. The IMO should be aware of this possibility. All further references in this paper to calcium hypochlorite relate to HCH (UN1748 and 2880) and bleaching powder (UN2208).

3.3 Calcium hypochlorite is a powerful oxidising material. Many organic substances such as oils, greases and solvents burst into flame in contact with the chemical. Even a few drops or a thin film of an organic substance may be sufficient to start a decomposition, which may then spread through the bulk of the product. Poorly informed users have caused many dangerous and even fatal accidents in this way.[1]

3.4 Calcium hypochlorite decomposes without there being any organic materials present, although at temperatures up to 20°C this reaction is normally very slow. At higher temperatures, the decomposition can be violent.

3.5 Heat is produced by the decomposition even at low temperatures and the rate at which it dissipates depends on a number of factors.

These include:

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[1] e.g. R F Cane “Calcium Hypochlorite - A potentially hazardous product” Chem. Aust. 1978; 45(9); pp 313-14

- ambient temperature
- ventilation rate around the package
- bulk density and thermal conductivity of the product
- form and size of the product packaging
- size of the freight container in which the product is shipped (i.e. 20 foot or 40 foot).

3.6 If heat is generated inside a package faster than it can be lost, the temperature of the calcium hypochlorite will rise leading to an accelerating reaction and the possibility of explosion. If the product undergoes thermal runaway while packed in or stowed next to combustible materials, an explosion is likely to be followed by a fire.

4.0 CRITICAL AMBIENT TEMPERATURE

4.1 The ambient temperature at which a substance may start to decompose dangerously is called the Critical Ambient Temperature (CAT). It is the lowest ambient temperature, for a given sample size, above which the normally slow decomposition accelerates to a runaway reaction.

4.2 Professor Gray and his team[2] have shown that the CAT for hydrated HCH when carried in a fully laden 20ft freight container, without efficient ventilation, is likely to be about (a) 37°C when packed in 40 kg[3] plastic kegs, and (b) 30°C when packed in 200 kg[3] fibreboard drums. It can take 2 weeks for the material at the centre of a 200 kg fibreboard drum to reach the ambient external temperature and 3 weeks before the critical condition is reached leading to thermal runaway. Any test on a package performed over a short time scale (i.e. a few hours or days) such as the self accelerating decomposition test (SADT)[4] may suggest a CAT which is too high. Recommendations for carriage of hydrated HCH based on SADT tests may, therefore, be inaccurate.

4.3 It was already known from earlier research[5] that anhydrous HCH is liable to undergo a strong exothermic decomposition when exposed to excessively high transport temperatures or if contaminated. The evidence from recent research is that the same is true of the hydrated form. This self-reactive behaviour

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[2] The research upon which this information is based is subject to legal professional privilege and these conclusions have been authorised for publication by Burgoynes' clients in the interests of safety.

[3] Package weights are net

[4] The self accelerating decomposition tests are defined in the UN Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria.

[5] Uehara Y, Uematsu H and Saito Y - "Thermal ignition of calcium hypochlorite". Combustion and Flame 1978; 32; 85-94

appears to be of critical importance in the ship fires referred to earlier. This suggests that both products should be classified 4.1 in the IMDG Code.

4.4 We note that, on p. 4102 of the IMDG Code item 1.8.2, there is a statement that substances should not be classified 4.1 if they are oxidising substances according to the assignment procedures of Class 5.1. This indicates that the IMDG Code has previously considered oxidising behaviour to be more important in the context of marine transportation than self-reactive behaviour. Industry experience suggests that this position needs to be reviewed.

4.5 Accordingly, it is our recommendation (10.8) that the IMO should review the classification of calcium hypochlorite products with a view to classifying them as Class 4.1 (self-reactive solid) with a subsidiary risk label as IMDG Class 5.1 (oxidising solid).

4.6 Literature search reveals limited information on the thermal stability of calcium hypochlorite products. There is no requirement for manufacturers to provide information on their production materials and methods, but it is known that these can influence thermal stability of the product. In the light of recent explosions and fires, we recommend (10.5) that calcium hypochlorite products offered for marine transportation should be certified to be thermally stable for the intended transport. The certificate should state also the temperature of the product at the time of packaging. It should form part of the IMDG Declaration.

5.0 TEMPERATURE ABOARD SHIPS

5.1 A research report in the Marine Observer[6] assessed the maximum prolonged temperatures within holds of ships in the tropics, relating these maximum temperatures to the maximum air temperatures. It suggested the temperatures in the table below as a basis for assessing dangers from cargo. These temperatures make allowance for the changes in air temperature between day and night, and for the higher temperatures which may be encountered near landmasses (i.e. in port). They are values, which Bowes suggests could be encountered for a period of a few days.

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[6] P C Bowes, “High Mean Temperatures in Ships Holds”, The Marine Observer, 1968, 68, 17

Area	*Maximum air temperature (prolonged)*	*Maximum hold temperature (prolonged)*
Persian Gulf	38°C	48°C
Red Sea	35°C	45°C
West Coast of Africa	29°C	39°C
Caribbean Sea and Panama	32°C	42°C

5.2 In addition to the air temperature and effects of solar heating, sources of localised heating aboard ships should be considered, such as heated bunker tanks. The IMDG Code requirement for limiting time at high temperatures for stowage of hydrated HCH needs to be reviewed in the light of the recent research.

5.3 Deck carriage of HCH products is the best way to avoid exposing freight containers to the high ambient temperatures which can occur in a ship's hold. Placing containers on deck in the shade (understowed) will also help in reducing solar heating. From experience, a fire below deck involving calcium hypochlorite is much more difficult to tackle than one on deck. Accordingly, we recommend (10.1) that these stowage requirements should be incorporated in the IMDG entries for UN1748 and UN2880.

5.4 The current research (see section 4.2) indicates that the CAT of 40 kg kegs of hydrated HCH packed in a 20ft freight container will be of the order of 37°C. The historical information on prolonged air temperatures, (see section 5.1) indicates that on certain voyages the prolonged air temperature may approach or exceed the CAT for such a container. Although in most circumstances the duration of exposure of the cargo to such temperatures should be limited, circumstances can arise in which the vessel and its cargo may be delayed or detained and the cargo exposed for a prolonged period at air temperatures which exceed the CAT of the cargo. This may lead to the cargo being subject to a runaway reaction. Accordingly, we recommend (10.3) that for voyages where air temperatures can be anticipated to reach 35^0 C the total weight of the hydrated HCH carried in a freight container should be limited to 14 tonnes (see section 6.2). Alternatively, a larger size of package (e.g. 45 kg net) should be transported subject to additional measures for limiting temperatures within the freight container, for example by ventilation or mechanical cooling.

5.5 Professor Gray's findings indicate that heat which is generated inside a freight container due to decomposition of calcium hypochlorite can be removed by suitable ventilation. Such ventilation would increase the CAT of the cargo and reduce the risks. The research so far has not examined the detailed effects of ventilation, with or without cooling. We consider that further work on this topic would assist the IMO in devising effective and practical measures to minimise risk. Accordingly, we recommend (10.6) that IMO instigate research to ascertain practical measures to limit temperature rise in containerised cargoes of UN 1748, UN 2208 and UN 2880. Possible measures to examine would include forced ventilation of containers, with or without cooling, or full temperature control of a container.

5.6 We consider that a larger group of 40 kg kegs of hydrated HCH, such as may be stowed in a 40ft freight container, would have a CAT materially lower than 37°C. Accordingly, we recommend (10.4) that hydrated HCH (UN2880) should not be shipped in freight containers larger than 20ft.

5.7 In any event, in the light of Professor Gray's findings, we recommend (10.2) a maximum limit on the size of package used for marine transportation of hydrated HCH (UN 2880) of 45 kg net weight (see also section 6.1).

5.8 We recognise that air temperatures may, over a period of several days or a week, exceed those recorded historically due to exceptional circumstances or climatic conditions. In such circumstances the stowage measures recommended above in 5.3, 5.4 and 5.6 might not, on their own, preclude the possibility of hazardous decomposition of such cargo. The IMO may wish to consider (10.6) whether temperature control measures, such as ventilation with or without cooling, and/or temperature monitoring should be required for all containerised cargoes of calcium hypochlorite.

6.0 PACKAGE SIZE, WEIGHT AND SHAPE

6.1 Professor Gray's research has emphasised the established fact that the size (mass) and package shape of a self-heating material influences the CAT. Simply put, the greater the quantity, the lower the CAT. Therefore, we recommend (10.2) that packages for marine transportation of HCH (UN1748 and UN2880) should never exceed 45 kg net weight. The marine transportation of these products in larger receptacles should be prohibited. (See our comments in sections 7.4 and 9.4 et seq relating to bleaching powder.)

6.2 Not only will the CAT of a freight container, stowed with packages of hydrated HCH, be influenced by the size of the individual packages, the CAT will be influenced also by the number of packages stowed in the container. The CAT of 37°C mentioned in Sections 4.2 and 5.4 was calculated by Professor Gray by reference to 432 x 40 kg kegs stowed inside a freight container. We are aware that shipments of HCH are limited on occasion to 342 x 40 kg kegs and 304 x 45 kg kegs. Professor Gray has calculated the CATs for such shipments to be about 40°C. This forms the basis of our recommendation to impose an overall limit on the weight of calcium hypochlorite stowed in a freight container on a voyage where high air temperatures can be anticipated (see Sections 5.4 and 10.3)

6.3 Dissipation of heat by natural convection from a package of calcium hypochlorite helps to avoid hazardous thermal decomposition. Therefore, packages of calcium hypochlorite should have a shape which promotes air flow around them. Our view is that drums are suitable, but flat sided receptacles (boxes) or bags are not. Accordingly we recommend (10.2) that cargoes of calcium hypochlorite should be packed in drums.

7.0 PACKAGING MATERIAL

7.1 Strictly speaking hydrated HCH is non combustible. Experiments carried out in steel baskets did not result in a fire after the material had become critical. The use of combustible packages greatly increases the risk of a fire occurring after the runaway condition has been reached. Therefore, the use of non-combustible packaging would reduce the risk of conflagration.

7.2 Clean rust free drums would be a non-combustible form of packaging. However, it is known that steel drums can corrode rapidly in contact with calcium hypochlorite. If rust mixes with the product it is possible that the mixture will become less stable, lowering the CAT. Thus, a measure intended to reduce the hazards could actually increase them.

7.3 The advantage to be gained by using non-combustible (steel) drums is, in our view, outweighed by the disadvantages of potentially hazardous contamination of the product. Accordingly, we do not make a recommendation for non-combustible packaging of calcium hypochlorite products.

7.4 Professor Gray’s paper (Annex 1) shows that the majority of the ship fires in the period 1997-99 have involved bleaching powder. At present, the IMDG Code permits the packaging of bleaching powder in bags. As mentioned in section 6.3, and because a split bag may allow bleaching powder to come into contact with organic materials causing a fire, we recommend (10.2) that allowable packaging for marine transportation of bleaching powder (UN2208) should exclude bags, as is already the case for other calcium hypochlorite products.

8. PRODUCTION QUALITY CONTROL

8.1 None of the commercial calcium hypochlorite products is a single pure chemical. There are many manufacturing processes and the stability of the product may vary from batch to batch even from the same manufacturer. Impurities in the raw materials can have an adverse influence on stability. In particular, some metal oxides decrease the stability of the product. If manufacturing methods introduce organic materials into the calcium hypochlorite product, there is a high risk of fire or explosion.

8.2 In the light of recent incidents, we recommend (10.5) that calcium hypochlorite products offered for marine transportation should be certified to be free of dangerous contaminants. Such certificates should form part of the IMDG declaration.

9.0 RECOMMENDATIONS FOR FURTHER RESEARCH UN 1748 AND UN 2208

9.1 Professor Gray's research has clarified the hazards from hydrated HCH, but has not addressed the anhydrous form or bleaching powder.

9.2 The thermal decomposition properties of anhydrous HCH were studied in the 1970s, but apart from the work of Uehara et al[7], full scale tests to determine the CAT have not been carried out or at least the results of any such tests have not been published in scientific literature. Nor are the results of test programmes undertaken by manufacturers available in published literature.

9.3 It would appear that Uehara overestimates the CAT of anhydrous HCH. We recommend (10.7) that a more detailed study of the thermal properties of anhydrous HCH be undertaken. We also recommend that the mode of manufacture of the product is investigated as the manufacturing process can influence the stability of the end product. The CAT's quoted in this paper are for the hydrated HCH, but we feel it is prudent to treat the anhydrous form of HCH, with regard to its marine transportation, in the same manner. We recognise that the CAT for the anhydrous material, for a given sample size, could be greater than for the hydrated HCH. Nevertheless, there is sufficient information available to indicate that the carriage of anhydrous HCH should follow similar rules to those proposed for hydrated HCH, and we so recommend (10.1, 10.2, 10.3, 10.4, 10.5, 10.6, 10.7, 10.8).

9.4 At present the IMDG Code entry suggests that bleaching powder is less hazardous than HCH. The rules for the material are less stringent. For example, there are no current restrictions as to where the material can be stowed with regard to heat sources and the packaging class is "III". This permits shipment in paper sacks or bags and stowage next to a source of heat. This material is far too reactive either to be packed in paper sacks or bags or to be stowed next to a source of heat.

9.5 The thermal decomposition properties of bleaching powder have not been studied in detail, as far as we are aware, and we recommend (10.7) that they should be. When the CATs are determined for packages of bleaching powder, there will be a sound technical basis for IMDG regulations for this material. Meanwhile, we recommend that stowage away from sources of heat and the transportation of the material in small kegs would be prudent. Taking into account the number of incidents in which the material is implicated, the material should also be carried on deck.

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[7] Uehara Y, Uematsu H and Saito Y - "Thermal ignition of calcium hypochlorite" Combustion and Flame 1978; 32; 85-94.

9.6 Accordingly, we recommend that the IMDG Code requirements for marine transportation of bleaching powder (UN2208) should be similar to those for anhydrous and hydrated HCH (10.1, 10.2, 10.4, 10.5, 10.6, 10.7, 10.8).

10.0 RECOMMENDATIONS AND ACTIONS TO BE TAKEN BY THE SUB-COMMITTEE

10.1 Cargoes of calcium hypochlorite classified as UN1748, 2208 and 2880 should be carried on deck, out of direct sunlight and clear of living quarters. (See Section 5.3).

10.2 Cargoes of calcium hypochlorite classified as UN1748, 2208 and 2880 should be packed in clean drums not exceeding 45 kg net weight. (See Sections 5.6, 6.1, 6.2, 7.4).

10.3 On those voyages for which prolonged mean air temperatures can be anticipated to reach 35°C, additional measures for limiting temperatures within freight containers carrying calcium hypochlorite, classified as UN 1748 and UN2880, should be adopted, for example by ventilation or mechanical cooling, alternatively the total weight of calcium hypochlorite should be limited to 14 tonnes per freight container (subject also to sections 10.2, 10.4)(See sections 5.4, 6.1, 6.2)

10.4 Cargoes of calcium hypochlorite classified as UN1748, 2208 and 2880 should not be carried in freight containers larger than 20ft. (See Section 5.5).

10.5 The IMDG Declaration for calcium hypochlorite classified as UN1748, 2208 and 2880 packaged for marine transportation should include:

(a) a certificate from a recognised authority documenting its thermal stability and its freedom from dangerous contaminants including organic materials and metal oxides;
(b) a production certificate showing its date of packaging and its bulk temperature at the time of packaging. (See Sections 4.6, 8.2).

10.6 IMO should instigate research to ascertain practical measures to limit temperature rise in containerised cargoes of UN 1748, UN 2208 and UN 2880. Possible measures to examine would include forced ventilation of containers, with or without cooling, or full temperature control of a container. (See section 5.4, 5.9).

10.7 The IMO should instigate further research to clarify the hazards for marine transportation of anhydrous HCH and bleaching powder. (See Sections 9.3, 9.5).

10.8 The classification of calcium hypochlorite products UN1748, 2208 and 2880 should be reviewed with a view to re-classifying these products as IMDG Class 4.1 (self-reactive solids) with a subsidiary risk label as IMDG Class 5.1 (oxidising solid). (See Section 4.5).

ANNEX 1

A STUDY OF THE THERMAL PROPERTIES OF HYDRATED CALCIUM HYPOCHLORITE (UN2880)

BY

Professor B F Gray[1] , Dr R Holleyhead[2] and Mr B Halliburton[3]

SUMMARY

Executive summary:	The objective of this paper is to explain the thermal decomposition properties of hydrated high strength calcium hypochlorite (UN2880) to enable the DSC to consider a change in the IMDG Code for this material. The scientific research on the material since its introduction in the late 1970's is discussed and an outline of a current research project is included.
Action to be taken:	A review of the IMDG Code entry for hydrated calcium hypochlorite (UN2880 IMDG Code page 5138) to include inter alia changes to the stowage and packaging details.
Related documents:	The paper "Carriage of calcium hypochlorite" prepared and submitted by the International Association of P & I Clubs. This document concludes with suggestions and recommendation for the carriage rules for all three forms of calcium hypochlorite cargoes.

1 BACKGROUND

In the eleven year period between 1967 and 1977 the cause of incidents of fire on board seventeen ships was attributed to the decomposition of high strength anhydrous calcium hypochlorite. One ship, NICHOLAS DL, had two such incidents in 1970. Four stevedores were killed in 1967 as the THORSTREAM was being loaded and six stevedores were killed under similar circumstances on the MANOLO EVERETT. Two other incidents, both in the Indian Ocean (the GRIQUELAND and the CATHERINA WIARDS) were so serious that the vessels were abandoned by their crews.

By the early 1970's marine insurance interests in London became increasingly concerned about the losses and they agreed to fund a research programme into the properties of commercially shipped calcium hypochlorite. A scientific investigation into the properties of the material was carried out and papers submitted to The Inter-

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[1] PO Box 743, Turramurra, NSW 2074, Australia
[2] Burgoyne House, Chantry Drive, Ilkley, LS29 9HU, West Yorkshire, England
[3] Dept of Chemistry, Macquarie University, NSW 2109, Australia

Governmental Maritime Consultative Organisation (IMCO) now called the International Maritime Organisation (IMO).

The material involved in these incidents was the substance known commercially as “Calcium Hypochlorite, 70% available chlorine” (UN1748). It is not a single definite chemical compound, but a mixture of compounds. The main component is calcium hypochlorite, with the chemical formula $Ca(OCl)_2$ but there are present in addition six or more other chemical compounds, produced fortuitously during manufacture.

The amount of calcium hypochlorite present is numerically about equal to the percentage of available chlorine. Thus a nominal 70% available chlorine implies the presence of about 70% calcium hypochlorite, with about 30% of other components. The nature and amounts of the other components depend on the raw materials used and on the precise conditions existing at each stage of the manufacturing processes.

At present there are three products containing calcium hypochlorite shipped around the world and these are included in Table 1. The high strength materials are used for water sanitization and the lower strength material for making bleaching powder a name by which it is often known.

TABLE 1
TYPICAL CALCIUM HYPOCHLORITE MIXTURES

UN NO	**TYPE**	**APPROXIMATE AVAILABLE Cl_2%**	**APPROXIMATE WATER %**
1748	Anhydrous	70	1
2880	Hydrated	65	5 to 8
2208	Anhydrous and hydrated	>10<39	varies

To avoid confusion the name calcium hypochlorite will be used to imply the pure chemical $Ca(OCl)_2$. The abbreviation HCH (high strength calcium hypochlorite) will be used for the commercial high strength mixtures and BP for the lower strength bleaching powder.

HCH is made by several processes one of which involves the treatment of wet lime with chlorine in the presence of caustic soda. These last two substances can be obtained from the electrolysis of common salt and the lime by burning limestone. Thus the end product is not a pure substance and in addition to the calcium, sodium and also chlorine containing substances, magnesium ions (from magnesium carbonate in limestone) may also be present. It is thought that the possible impurities could add to the hazardous nature of the product especially if, for example, magnesium hypochlorite were formed as this substance is particularly unstable. Typical analytical results for the samples of the hydrated materials are given in Table 2.

TABLE 2
THE RESULTS OF THE ANALYSES, EXPRESSED AS PERCENTAGE BY WEIGHT[a]

COUNTRY MANUFACTURER	**JAPAN (TOYA SODA)**	**CHINA (SHANGHAI) CHLORALKALI**	**USA (PPG)**
$Ca(OCl)_2$	73.0%	58.9%	63.4%
$CaCl_2$	4.73%	6.70%	6.83%
$Ca(ClO_3)_2$	1.58%	4.58%	4.29%
NaCl	8.04%	14.8%	14.9%
H_2O	1.28%	5.60%	3.44%
Other calcium salts (as Ca)	3.01%	3.70%	3.05%

Chemistry

The decomposition reaction of calcium hypochlorite is generally thought to be:
$Ca(OCl)_2 \rightarrow CaCl_2 + 0_2 - \Delta H$ - I

It is an exothermic reaction with calcium chloride and oxygen the end products. The smell of chlorine associated with bleaching powder is owing to the reaction with carbon dioxide in the atmosphere
$Ca(OCl)_2 + CaCl_2 + 2CO_2 \rightarrow 2\,CaCO_3 + 2Cl_2$ - II

Chlorine can be produced during the decomposition especially if water is present by the further reaction of calcium chloride with the parent material
$Ca(OCl)_2 + CaCl_2 \rightarrow 2CaO + Cl_2$ - III

At about 170°C the thermal decomposition of calcium hypochlorite becomes explosive and the rate of decomposition increases with an increase in temperature up to this level. However, both HCH and BP are unstable at ordinary temperatures, slowly losing oxidising power during storage. There is also evidence that decomposition may follow paths other than the one in "I". For example chlorate is known to be produced during storage and actual loss of chlorine may occur.

The strength of the material, expressed as “available chlorine”, is determined by the assay of the amount of iodine liberated from potassium iodide when the calcium hypochlorite is reacted with it in acid.

Bleaching powder explosions are not rare events and the first record of such an occurrence appears to have been in 1861 where a bottle filled with “chloride of lime” given to the famous chemist A W Hofmann after the Great Exhibition of

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[a] Analysis carried out by T M Flynn, Unisearch Research Centre for Chemical Analysis, The University of New South Wales, Gate 14 Barker Street, Kennington, NSW 2033

1851, exploded after many years of having been stored on a laboratory shelf [Hofmann AW. 1861].

Not Just an Oxidising Agent

HCH is classed as an oxidising agent (5.1) and indeed it is such a substance. Oxidising agents if involved in a fire, although not necessarily combustible themselves, liberate oxygen, as they are decomposed by heat. This enhanced oxygen supply leads to much higher temperatures being reached than would otherwise have been obtained from a fire of a carbonaceous fuel burning in air. Most oxidising agents do not constitute a hazard (assuming they do not make contact with reducing agents) unless they are involved in a fire but HCH is a notable exception as it can decompose spontaneously by itself with the evolution of heat and toxic gases. An explosion may be the consequence of such a decomposition. Once the decomposition starts it can spread through a store or stow of material and in some instances the entire shipment of material is consumed.

Hydrated HCH material (UN2880) is less reactive, for example with organic materials, than the anhydrous substance. (The hydrated forms cannot be “ignited” by a burning cigarette whereas the anhydrous form can). It has also been found by experiment that the hydrated form of HCH is less energetic when it decomposes than the anhydrous material. In fact if the hydrated material is heated in an open top receptacle until its runaway reaction temperature is reached a violent reaction does not necessarily occur. The hydrated HCH expands out of the top of the receptacle like a soufflé. However, if the material at the runaway condition makes contact with combustible material a fire is likely to occur. Thus if hydrated material packed in combustible receptacles (plastic kegs or fibre board drums) decomposes, involvement of all the combustibles close by is guaranteed. The involvement of a large quantity of HCH will give rise to a rapid increase in temperature and pressure and in a confined space an explosion will result.

Self-heating

Any substance which decomposes spontaneously, with the evolution of heat, is capable of self-heating if the circumstances are such that heat cannot escape from the substance as fast as it is generated. HCH is such a substance. The rate at which decomposition takes place gets faster as the temperature increases. Consequently an exponential reaction rate or a runaway reaction may occur leading to an explosion.

The rate at which heat is generated depends on the chemical properties of the substance. One factor is the amount of heat given out when a unit weight of the substance decomposes. The quantity is known as the heat of reaction (Q). The other factor is the manner in which the rate of decomposition increases as the temperature increases. This is expressed in terms of three quantities known as the gas constant (R), the activation energy (E) and the frequency factor (A).

The rate at which heat is lost to the surroundings also depends on several factors. Heat produced inside the containing package such as a drum has to travel to the walls of this drum. The ease with which heat travels depends upon thermal conductivity (κ)

of the substance and the size of the container package. When the heat reaches the walls of the package the rate at which it can escape depends on the surface area of its walls; on the temperature of the air surrounding it and the efficiency with which the heat leaves its surface.

It is not surprising, therefore, that the size of a package and the characteristics of the material from which it is made (especially its thermal conductivity) are important factors. Heat dissipation from a package will also be affected by the close proximity of other packages of material, which may in turn be self-heating. As the self-heating process can be regarded as a build up of heat within a material, with the rate of heating dependent on the temperature, (the higher the temperature, the faster the rate of reaction and thus the evolution of heat) the onset of spontaneous ignition or runaway reaction will soon follow. To relate this theory to hydrated HCH a 40kg keg of the material which is held at 60°C is likely to experience a runaway reaction after a few days, whereas if a 40kg drum of material had been held at 55°C, the runaway reaction may have taken several weeks to occur. (This comparison assumes that the heat losses for both conditions are similar). Much more is written about this phenomenon in Section 3 of this report.

Safe Storage and Transportation - the Importance of Critical Ambient Temperature

In an attempt to predict the instability of reactive chemicals (in order to take this into account for the conditions under which they are stored and transported) tests are performed to determine their behaviour under set conditions. The critical ambient temperature of a substance is the lowest temperature for a given sample size at which the runaway reaction begins, and it is usually determined by the placing of a known mass of the substance in a container which is placed in an oven preset at constant (ambient) temperature. A small thermocouple buried at the centre of the material under test is used to record its temperature. When the temperature increase becomes very sensitive to the oven (ambient) temperature this indicates that criticality has been reached. A typical example would be for ambient (oven) temperature of 53°C the temperature increase in the body is 10°C ie the centre is at 63°C. However for oven temperature of 54°C the temperature rise is 200°C. In this case the critical ambient temperature would be 53.5 ±0.5°C.

To determine the critical ambient temperature a number of tests are done at different ambient temperatures (using fresh sample each time) until the sensitive region is bracketed.

Related but not identical tests are performed on full sized packages (tests should be carried out on the exact type of package used to transport the material). These are known as Self Accelerating Decomposition Tests (SADT's) and are a recognised United Nations test procedure [UN1995]. Such tests are required to be carried out by the manufacturer of self reactive materials. SADT tests are carried out by placing a sample in its "largest commercial package", in an oven at a maintained constant temperature. *"The sample is heated and the temperature of the sample and test chamber continuously monitored. The time is noted at which the sample temperature reaches a temperature 2°C below the test chamber temperature. The test is then* *continued for a further seven days or until the sample temperature rises to 6°C or more above the test chamber temperature if this occurs sooner. Note the time taken for the sample to rise from the 2°C below the test chamber temperature to its maximum temperature. "The self-accelerating decomposition temperature (SADT) is defined as the lowest oven temperature at which the sample temperature exceeds the oven temperature by 6°C or more".* In the case of HCH this SADT test will probably suggest a critical temperature which is too high for this material.

Tests on large samples are not only expensive to carry out but also may not be such a straightforward exercise in view of the conflagration that may ensue after the runaway reaction occurs. In the case of HCH its problem is compounded by the evolution of chlorine gas. Scientists have, therefore, carried out small scale experiments, (with small sized samples) and using mathematical formulations based on thermal explosion theory have extrapolated from these results to predict the CAT for large commercial package sizes. This theory, developed some sixty years ago by Semenov and Frank-Kamenetskii, incorporates several parameters from reaction kinetics (the study of reaction rates ie how quickly starting materials in a chemical reaction combine to form products) and the factors such as temperature and heat losses. As with many other mathematical treatments of chemical reactions several assumptions have to be made and information is not always to hand to allow the extrapolations be done accurately.

Prior to the new research work reported in this paper surprisingly few studies had been carried out into, (or had been published on) the properties of the hydrated form of HCH. In contrast, as a result of the spate of accidents in the late 1960's and early 1970's mentioned earlier involving the anhydrous form of HCH, that material was studied in some detail [Clancey VJ. 1975/1976, Clancey VJ. 1987, Uehara Y et al 1978].

Early Work on Hydrated HCH

The hydrated form "SENTRY"™ was introduced by "PENWALT", [US PATENT 3,544,267] "OLIN" and "PPG" in the late 1970's. The UK scientists who had carried out the research work on the anhydrous material for the London Maritime Insurers diverted some of their attention to the hydrated form of HCH. This material contained about 65% available chlorine and about 4% to 7% water of hydration. Both these figures varied slightly from batch to batch. The "new" material differed from the anhydrous form in so much as the decomposition of the "new" product was less violent. In the absence of combustible materials the runaway reaction in an open topped container did not cause a fire or explosion.

It is suspected that perhaps the most important difference between the behaviour of the new hydrated form and the original anhydrous form of HCH was that the increased water content may lower the critical ambient temperature ("CAT") of the hydrated HCH.

Uehara Y et al had determined that the CAT for a drum of 38cm diameter (about 50kg) of anhydrous HCH was 75°C. This agreed with the results from some of the work carried out in the UK on the anhydrous material but some of the results of the

UK scientists suggested that the CAT might be lower than this figure. This was certainly thought to be the case with regard to a large number of drums packed closely together. Such an arrangement would in effect increase the mass of the material and, therefore, would lower the critical ambient temperature. P C Bowes [Bowes PC 1984] carried out calculations which were *"sufficient to indicate a possibility of self-heating and thermal explosion in 'high-strength' calcium hypochlorite in warm surroundings, such as the upper holds of ships in tropical waters"*.

Early tests on a sample of hydrated HCH (manufactured by a US manufacturer called at that time OLIN, now called Arch Chemicals) revealed that 45kg of hydrated HCH, packed in a keg of similar dimensions to that used for the earlier tests on the anhydrous material, became subject to a runaway reaction after being held at a constant temperature of 57°C for a period of 3 days [Schroeder 1979] – this was nearly 20°C lower than the CAT that had been determined for the anhydrous material. It was reported some years later [Wojtowicz JA. 1987] that a 45kg keg of OLIN's hydrated HCH survived for 3 weeks at 50°C. At about the same time as this first experiment was being performed (in the late 1970's) tests both in the UK and the USA confirmed that although for the hydrated material the decomposition reaction was indeed less energetic at the runaway temperature than for the anhydrous material the critical ambient temperature (for a given sample size) was lower.

Tests were carried out in the Autumn of 1979 on OLIN's material by Safety Consulting Engineers Inc Illinois [Dahn CJ. 1979]. They tested 10kg and 50kg samples of hydrated HCH and found that a runaway reaction occurred in the former at 64°C after a period of 13 hours and in the latter at the same temperature after 20 minutes. Smaller samples (400g of material in a Dewar flask) were subjected to the "Warmestaulagerung Test" in the UK at the Royal Armament Research and Development Establishment (RARDE) and the results are tabulated below (Table 3).

TABLE 3

WARMESTAULAGERUNG TEST

Sample	Oven Temp	Result	Time after reaching oven temp	Max Temp attained
OLIN (65% Cl_2 6.9% H_2O)	60°C	Runaway	19½ h	170°C
"	60°C	Runaway	21 h	162°C
"	70°C	Runaway	7 h	174°C
"	70°C	Runaway	7 h	185°C
Japanese (70% Cl_2)	60°C	No Runaway	60 h	62°C
"	60°C	No Runaway	60 h	70°C

Anhydrous material from Japan was also tested for comparison. OLIN had supplied the hydrated material and the results were in keeping with the results of the tests carried out by Safety Consulting Engineers Inc of Illinois.

The tests both in the UK and the USA fell well short of what was required to establish guidelines for the storage and transport of hydrated HCH because in none of the tests was the critical temperature determined. Also properly conducted SADT tests were not carried out. For example working with 10kg samples was not a realistic assessment of the size of the packages transported. More importantly a reaction time of 20 minutes for a 50kg package suggests that the material “ran away” as soon as the outermost layer heated up. This indicated a lack of understanding of the phenomenon of self-heating, a property which was in need of elucidation for this material.

Notwithstanding the shortcomings of these tests, the RARDE results illustrated the lower critical temperature of the hydrated material when compared to the anhydrous form. The results prompted the UK scientists to predict that on a long sea voyage where the hydrated material is exposed to high temperatures (in particular when carried through tropical waters) the ambient temperatures would approach the critical temperature of a cargo of hydrated material.

The USA obtained a United Nations number for the hydrated material (UN2880), following representations by several countries to the IMCO sub-committee dealing with HCH at the same time as discussions were taking place relating to an amendment to the IMDG Code for the anhydrous material (UN1748). This may have caused some confusion in the minds of the delegates who were considering the submissions. The entry in the IMDG Code for the hydrated material, which first appeared in 1982, was essentially that as drafted by the USA delegation and included under “stowage”:

> *“Away from, sources of heat where temperatures in excess of 55°C for a period of 24 hours or more will be encountered”.*

This part of the entry was perhaps derived from the few tests that were carried out in Illinois on the hydrated material on behalf of “OLIN” and possibly also because 55°C was deemed to be the highest temperature that would be reached during transport [UNITED NATIONS 1977]. However the entry caused much disappointment within the UK delegation who thought that the critical temperature of hydrated HCH would be much lower than 55°C for a large sample size.

The first entry for UN2880 in the IMDG Code appeared in 1982. The packaging group was “II” and fibre drums with a liner (gross weight 180kg) were allowed also as were metal drums of 250kg gross weight. The form of the IMDG Code book was revised in 1989 after which the packaging details were listed in a large table at the beginning of the section for each class of material. At this time the allowable package size appears to have been increased arbitrarily above the 180kg for fibre drums.

2 THE CURRENT PROBLEM

Towards the end of the 1970’s and indeed throughout the next decade incidents involving the transport of the high strength materials by sea were reduced dramatically. We know of no major incident at sea in the 1980’s where HCH was thought to be the cause of a fire and/or explosion. This may have been a consequence of the heightened awareness generated by the accidents, the widespread use of freight containers to transport the material and perhaps a tightening by the manufacturers of their production procedures.

In this last decade and especially in the last two years there has been a resumption of incidents at sea but this time involving all three forms of the material; the two high strength forms, UN1748 and UN2880 and the lower strength material UN2208 "bleaching powder". Table 4 lists the incidents.

TABLE 4
MORE RECENT CASUALTIES INVOLVING
CALCIUM HYPOCHLORITE

VESSEL	**DATE**	**UN NO**	**ORIGIN**
MV RECIFE	1991	1748	SOUTH AFRICA
TIGER WAVE	1997	2208	INDIA
MAAS	1997	?	
CONTSHIP FRANCE	1997	2880	USA
MAERSK MOMBASA	1998	2208	EGYPT
SEA EXPRESS	1998	2208	CHINA
DG HARMONY	1998	2880	USA
ACONCAGUA	1998	1748	CHINA
CMA DJAKARTA	1999	2208	CHINA

The authors of this INFORMATION PAPER were instructed originally by two P & I Clubs (Liverpool and London, and The Swedish Club) concerned with the casualty "CONTSHIP FRANCE" to investigate the thermal properties of the hydrated form of HCH. The research project was started early in 1998, the practical and mathematical work being carried out by Professor B F Gray and B Halliburton in Australia. By June of 1998 results from the initial experiments indicated that the thermal (self-heating) properties of the material were different to what had been either hitherto known or accepted. In short it appeared that the critical temperature of the material, for the size of samples routinely shipped around the world, was much lower than that on which the IMDG Code apparently was based. In July 1998 a warning based on this research was circulated throughout the maritime community.

The research work was continued and in the Summer of 1999 a further release of information was made to the maritime community, maritime coastguard agencies and some manufacturers of the material. In view of the seriousness of our findings we believe the IMO should be given the opportunity to study them to permit a review of whether the entry in the IMDG Code for this material should be changed. The next section of this paper sets out the description of the main themes of the work carried out by Professor B F Gray et al.

3 A STUDY OF THE THERMAL DECOMPOSITION OF THE HYDRATED FORM OF HIGH STRENGTH CALCIUM HYPOCHLORITE

The main thrust of the work carried out by Professor Gray et al in Australia over the past two years has been to examine the behaviour of hydrated HCH as a material which can undergo a critical transition in the nature of its decomposition caused by the external conditions to which it is subjected, and dependent on the mass of the material examined at any given time.

The ambient temperature at which this transition occurs is called the critical ambient temperature or CAT. It is very important to distinguish between ambient temperature, i.e. the temperature of the surroundings, and the temperature of the reacting HCH. The latter may vary within the sample of HCH - generally being higher at the centre of the sample and cooler towards the edges. However if the sample of HCH has been in place for some time it will always be hotter than the ambient temperature. It should be noted that if the HCH is cold when introduced to the ambient temperature (whether in the laboratory test oven or in a ship's hold) it will take a considerable time for the HCH to 'realise' that it is in a warmer environment than it had been previously. This is because it will take a considerable time for heat to conduct into the HCH from the air outside the HCH in order for the temperature at its centre to rise towards ambient. This process, (which is also present for completely non-reactive materials such as chalk or gypsum) has a time scale approximately proportional to the square of the minimum dimension of the sample. A large part of this physical warming process has to be completed before the self- heating of chemical origin begins to take effect.

Below its critical temperature, the hydrated HCH self heats to a maximum of about 10 – 20° above ambient. Above its critical temperature hydrated HCH self-heats to more than 200° above ambient and the transition is very sharp. (In other materials ignition to flame occurs above the critical temperature, again with only small self -heating below the critical ignition temperature).

The theory dealing with this type of behaviour, normally referred to as ignition theory, has existed for a long time. It is referred to above in the section introducing the concept of self-heating and in its simplest form is closely related to the original formulation given by the Russian scientist Frank-Kamenetskii. This original theory assumed only a single chemical reaction was taking place (or at least was responsible for the self-heating). This assumption is not necessary and later work is able to deal with multiple chemical reactions and other generalisations. We shall see that in the case of hydrated HCH more than one heat producing reaction is involved, albeit that the reactions operate in different temperature ranges. It would appear that two overall reactions dominate the production of heat for hydrated HCH and we shall call them the "high temperature reaction" and the "low temperature reaction". Except in the small range where the two reactions overlap (ambient temperatures of 90°C - 115°C) we can analyse results by using the simple Frank - Kamenetskii theory and make excellent predictions as to critical temperatures for ever larger containers. We should also mention it is possible that, at very low temperatures (40°C - 60°C) a third endothermic reaction may also be playing a role.

Frank-Kamenetskii Theory – Brief Overview

If the simple ideas mentioned above concerning self-heating are quantified on the assumption that a single heat producing chemical reaction is taking place, an equation can be derived relating the critical temperature of a given size and body shape of material to its dimension. For example, if the body is spherical, an equation relating the radius of the sphere to the critical temperature is obtained. If the body is cylindrical a similar equation is derived, but with different numbers because of the difference in the shape. The equation derived is:

$$2\ln\frac{T_a}{r}+\ln d_c=-\frac{E}{RT_a}+\ln\left(\frac{QAE}{kR}\right)$$

where T_a = ambient temperature at criticality, r = radius (smallest dimension) of the body of material, δ_c = a number depending on the shape, (eg for a sphere $\delta_c = 3.32$, for an equicylinder $\delta_c = 2.57$ etc), E is the activation energy for the decomposition reaction, R is the universal gas constant, A is the pre-exponential factor, Q is the heat of reaction and κ is the thermal conductivity of the material. These quantities do not have to be known independently before the theory is applied.

The normal procedure is to measure T_a for a cylindrical container of HCH of a given radius and fixed aspect ratio. This is done simply by filling the container with material at room temperature and putting it into an oven with a preset ambient temperature. Small thermocouples are inserted into the hydrated HCH, always at the centre and sometimes at other points as well. The thermocouple traces record the temperature at the centre of the sample and thus we measure whether it reaches around 20^0 or less above ambient or whether it rises to the vicinity of 200° above the ambient temperature. The material is discarded and replaced with fresh sample. Depending on what happened in the first test, the ambient temperature is either raised or lowered by a suitable amount for the next test. The tests are continued until both a subcritical and a supercritical run have been obtained. At this stage a further test is run with the ambient temperature set at the mean of these two temperatures. If this run is sub-critical the interval is again halved until the required accuracy is obtained. The critical ambient temperature is then quoted as the mean of the last two tests. For example if a 200 kg cylinder of material is observed to reach 200° above ambient at its centre in one test at 44° C and only 2° above ambient at 38° C then we would quote the critical temperature of the 200kg cylinder of material as 41 ± 3° C. Generally we would wish greater accuracy than this so we would start a further run at 41° C. If this were supercritical then the critical temperature would now be quoted as 39.5± 1.5° C.

Normal procedure when testing a material is to use small laboratory samples, e.g. 5cm, 7.5cm, 10cm and 15cm diameter, for the tests and to obtain the critical temperatures for these samples. From the equation quoted above it follows that a plot of $\ln\{T_a/r\}$ versus $1/T_a$ should give a straight line with slope $-E/RT_a$. If indeed the assumptions of the theory are correct then extrapolation of this straight line to larger values of r and correspondingly lower values of T_a should give accurate predictions. However this can be an incautious procedure if the extrapolation is over a large range.

Procedure Used to Test Hydrated HCH

The test procedure described above was carried out by us in order to determine the critical ambient temperature of hydrated HCH in a laboratory oven capable of accommodating up to a 10 kg of sample in an equicylindrical stainless steel gauze basket. The air in the oven was forcibly mixed by fans in order to give an homogeneous ambient temperature. This is the standard procedure in such testing.

Six samples of hydrated HCH manufactured in the USA were tested ranging from radii of 9.25mm up to 105.0mm (which held about 8kg of material). The four smallest sizes of sample appeared to give results which fell on a straight line with a slope similar to that of earlier Japanese work [Uehara et al 1978] using anhydrous material. However the results of tests of the two larger sample sizes deviated significantly from this line. The tests were repeated twice and consistent results were obtained. The whole series of tests were also carried out on two other brands of hydrated HCH (of Chinese and Japanese origin as opposed to American) giving consistent results. The graph plotting the results for the American hydrated HCH is shown in Figure 1 (following).

It can be seen clearly from the graph that the two points furthest to the right (which represent the larger samples with lower critical temperatures) do not lie on the same line of the plot of the smaller samples. A similar graph holds for both the Chinese and Japanese hydrated HCH.

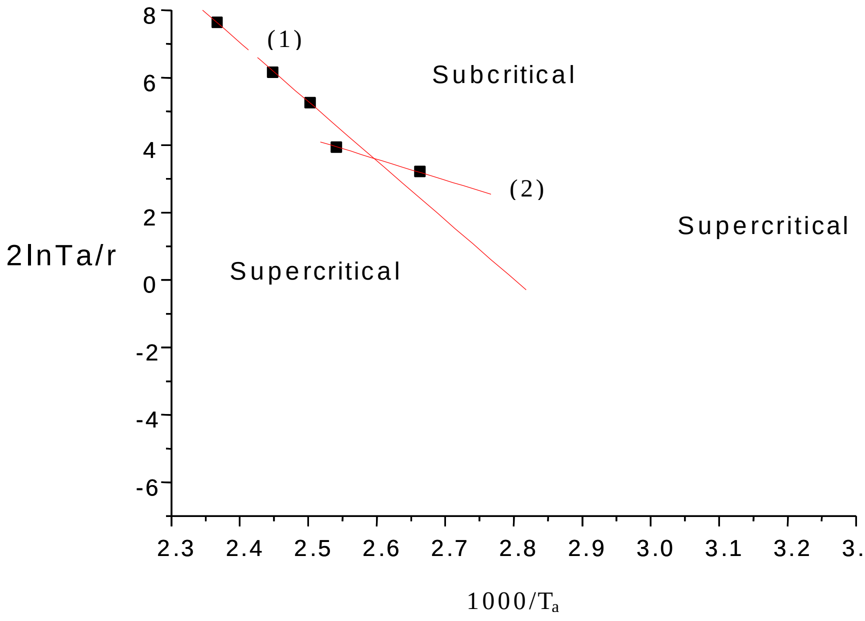

Figure 1 The Laboratory Scale Tests on Hydrated HCH (USA)

Since the region below the lines represents supercritical reaction, or thermal runaway, extrapolation of the high temperature line (1) predicts a much smaller area of runaway temperature of the product than extrapolation of the lower temperature line (2). In particular critical ambient temperatures for larger samples predicted using line (1) will be far too high.

A plot of the work of Uehara et al on anhydrous HCH is shown in Figure 2 below for contrast.

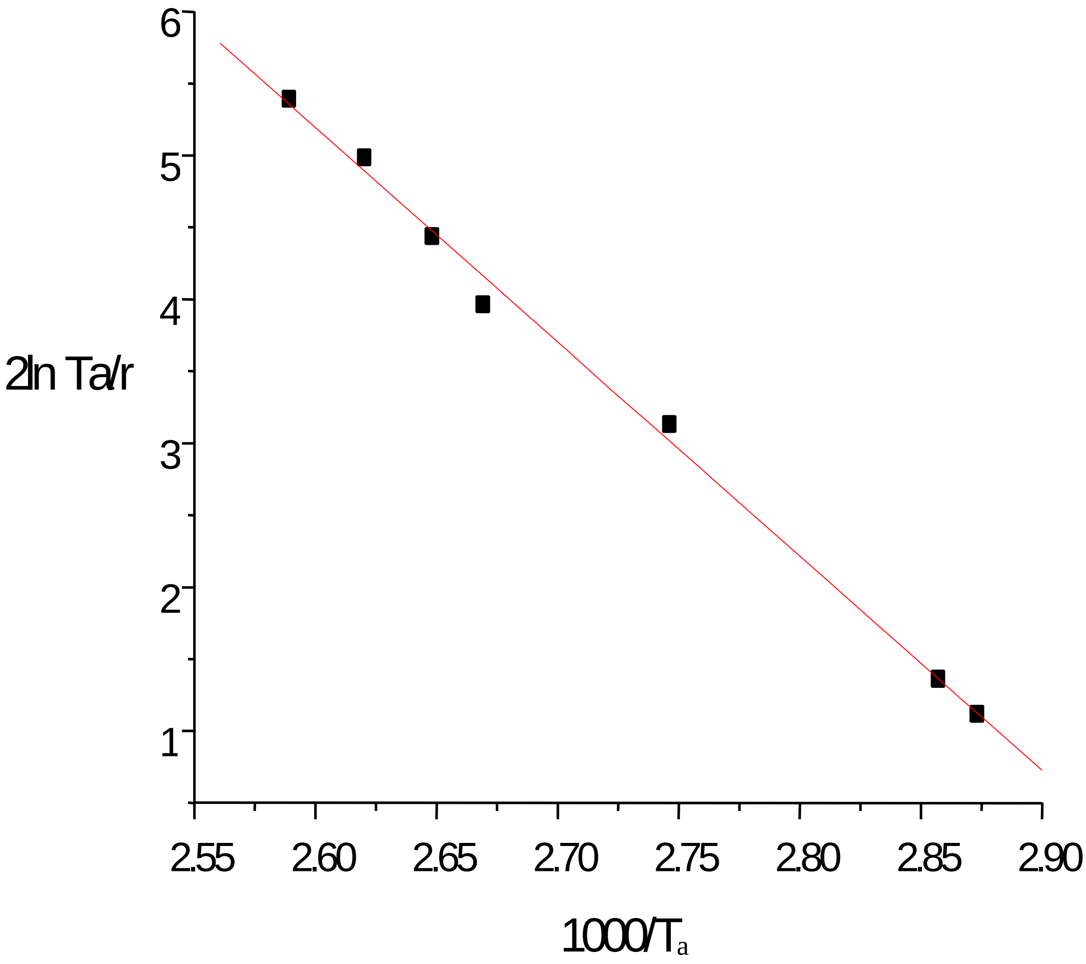

Figure 2 Plot for the work of Uehara et al on Anhydrous HCH

In this plot the two points on the right of the graph represent commercial packages of the material of around 45 kg. They fall very close to the line derived from the smaller samples and represent critical temperatures in the region of 75° C.

However extrapolation of the lower temperature line of our work on hydrated HCH (see Figure 1) predicted much lower critical temperatures for samples of 40 kg or more.

It can be seen that the prediction for a 40 kg sample from our small scale work was a critical ambient temperature of 60° C. Accordingly we constructed a temporary oven large enough to accommodate such a sample and carried out intermediate scale tests using this oven.

At this time we learned of the result of an earlier test carried out by OLIN on a 45kg keg of hydrated HCH which was supercritical at 57° C. Accordingly we added this result to our plot which is shown below in Figure 3.

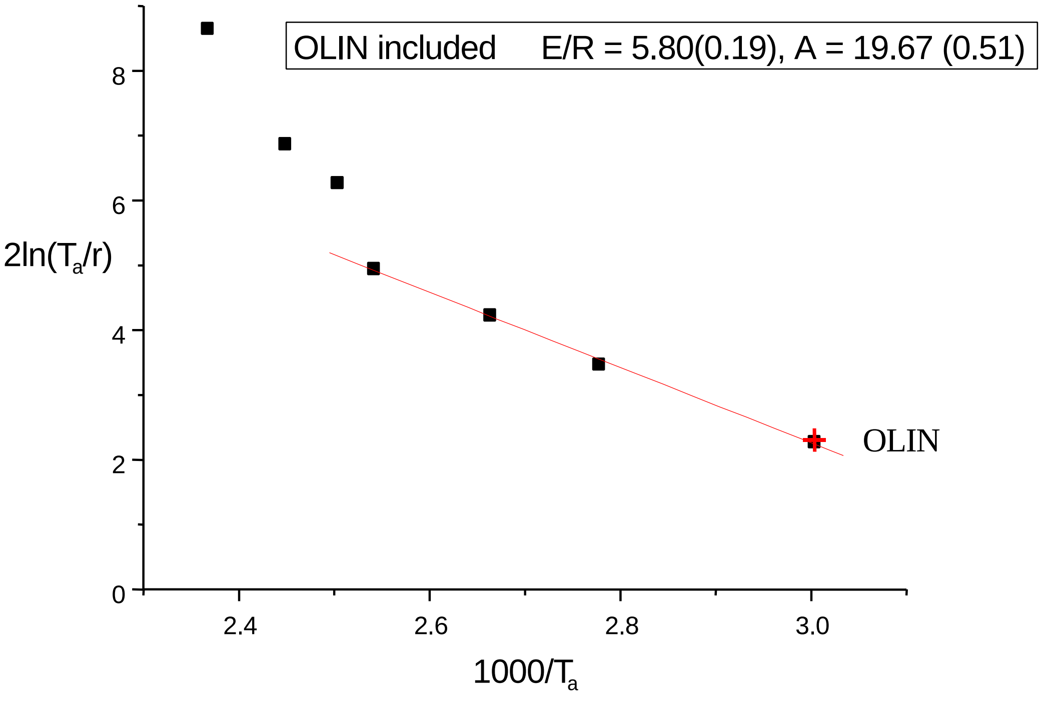

Figure 3 Our graph including earlier OLIN measurement

In view of this rather spectacular agreement (in fact we predicted the result of the OLIN test before we knew it) we decided to construct a large scale and substantial oven which would comfortably hold up to 500 kg of HCH in cylindrical drums. This would enable direct measurement of very substantial amounts of hydrated HCH, which would help us verify as far as possible, the values that we had obtained by extrapolation. This decision was in fact helped because the 60°C run of 40 kg of hydrated HCH, in a high density polyethylene ("HDPE") keg caught fire and destroyed the temporary oven completely.

This result gave a point on the low temperature line close to the "OLIN point".

The Large Scale Tests

A heavy duty oven of volume approximately 8 m^3 was constructed with accurate thermostatting capabilities and also provision for scrubbing (absorbing) the potentially large quantities of chlorine and other noxious gases likely to be emitted in both subcritical and supercritical tests. This will be described in detail elsewhere.

The heating elements used were portable and could be varied according to the shape and size of the kegs or drums to be tested.

At about this time during the tests it was realised that the conditions in laboratory ovens, involving strongly forced turbulent air, did not simulate conditions of HCH kegs inside freight containers transported in a ship's hold. The air inside a freight container will be almost still because, although typical containers are not airtight, the rate of air exchange with their outer environment is very low.

With many materials, which are subjected to tests to determine their critical temperature, the main resistance to dissipation of heat is within the material itself, e.g. sawdust or hay. The thermal conductivity of such materials is around 0.05w/mK and in such cases the dissipation of heat from the outside edge of the container of the material to the surrounding air is not a limiting factor. However Uehara et al quote 0.44w/mK for the thermal conductivity of anhydrous HCH and in this case dissipation to the surrounding air can be expected to be a limiting factor. This will also be true for the hydrated product if the thermal conductivity is of the same order of magnitude. Whether this is correct is easy to test - if it is correct then enclosing the keg or drum of hydrated HCH inside a box which is all placed in turn inside the thermostatted oven, should give a lower critical temperature than running the test without the box. The heat dissipation from the keg or drum of the test material to the still air in the box will be slower than it would be directly to the turbulent air in a normal test oven. Using the large oven we have proved this to be the case - the 40 kg HDPE keg of hydrated HCH which has a critical ambient temperature of 60°C in forced air had a critical temperature of only 55.2± 2°C when tested inside a steel box – a significant drop.

In view of the large amounts of HCH needed for larger scale tests, tests in forced air were discontinued and we performed all subsequent tests with kegs/drums of hydrated HCH inside steel boxes with volume ratios the same as that of cylindrical containers packed inside a 20ft freight container, i.e. about $4/\pi = 1.27$.

Our tests on hydrated HCH contained in 200 kg fibre cylindrical drums heated in an enclosed box have shown the critical ambient temperature to be 43.4 ±1.4°c.

Interaction of Self-Heating Kegs With Each Other

It is obvious that if more than one keg or drum of hydrated HCH is standing inside the same container the air inside the container will get warmer than if only one keg/drum were in the container. In a sense each keg will be "aware of the presence of the other" by virtue of the warmer surroundings. Similarly if three kegs/drums are present the air will be warmer still and so on. In a standard 20ft freight container it is possible to stand 108 cylindrical stacks of 40 kg kegs, four high or 80 x 200 kg drums stacked two high. In either case the critical ambient temperature for the *freight container of hydrated HCH taken as a whole* will be much lower than for the results of the single keg and drum as measured in our oven. It is also clear that the critical ambient temperature of one stack of 4 x 40 kg kegs will be less than that for a single keg. So *two* types of interaction need to be considered :-

1) the lower critical ambient temperature of 4 x 40 kg kegs of hydrated HCH stacked vertically compared with one 40 kg keg on its own (with a critical ambient temperature of 55.2°C). This can reliably be calculated to be 50°C. The lower critical ambient temperature of 2 x 200kg drums stacked vertically compared with one 200kg drum on its own (with a critical temperature of 43.4±1.4°C). This can be reliably calculated to be 41°C.

2) the interaction of 108, or alternatively 80, of these stacks with each other in the confines of a standard 20ft freight container.

Similar comments apply to other size kegs or drums of different weights.

The effect of the interaction at (1) above can be calculated quite reliably using the Frank-Kamenetskii theory and modifying the dimensions of the body from those of a single keg to those of a stack of four. The further effect of the interactions at (2) above can be calculated according to a theory recently formulated in response to this problem [Gray BF. 2000] and soon to be published in the Journal of the Australian Mathematical Society (part 1) and Proceedings of the Royal Society (London), Series A (part 2).

For the 40 kg kegs the CAT for 432 packed 4 high in a freight container is calculated to be 37°C and for 80x200 kg drums packed 2 high in a freight container the CAT is calculated to be 29.5°C. The results of the critical ambient temperature experiments on the individual small kegs and large drums of hydrated HCH together with the extrapolations of the critical ambient temperatures for a 20 ft laden freight container are shown in Table 5 (below).

These calculated numbers are expected to be reasonably accurate and the errors would be such that they would be upper limits to the true figures. In other words these extrapolations overestimate the true value of the critical ambient temperature of hydrated HCH packed and transported in these quantities.

The critical ambient temperatures referred to above are *hold temperatures* outside the container. They are assumed to be constant in time. They are *not* temperatures inside the container. This figure will be much higher at the critical condition.

TABLE 5 CRITICAL AMBIENT TEMPERATURE/SIZE OF A SAMPLE

Size of sample (KG)	Critical Ambient Temp °C
40	55.2 ± 2 (measured)
200	43.4 ± 1.4 (measured)
40 x 432 in container (4 high)	37.0 (calculated)
80 x 200 in container (2 high)	29.5 (calculated)

Consideration of Time Factors

Classical work on ‘times to ignition’ in thermal explosion theory has concentrated on attempting to calculate how much time elapses after setting up an experimental test before a very rapid temperature jump occurs in the test material. These attempts have been based on the assumption that the thermal and self heating properties of the material determine this quantity. This is true only to some extent in some situations and may be misleading in others, such as with our tests of hydrated HCH. An illustration, on a laboratory scale, where it is misleading is when a cold sample (say 15°C) is placed in a test oven at an ambient temperature of 100°C. If the sample turns out to be just supercritical and self-heats slowly for 1 hour after passing through 100°C to say 120°C before igniting, then it will be quoted as having a ‘time to ignition’ of 1 hour.

Such a sample will typically take six or seven hours to reach 100°C from 15°C and this period is determined almost entirely by purely physical heat transfer processes. Thus in a practical situation the real ‘time to ignition’ is very much dependent on the *initial condition (ie temperature) of the sample.* Critical temperatures, critical radii etc. *do not* depend on the initial condition of the sample and this has led to much confusion on the topic of ‘time to ignition’.

Once it is recognised that the (physically and practically) important topic of ‘time to ignition’ is hardly related at all to thermal ignition theory then it becomes possible to focus on which questions really are important in this context. For example, when we realise that heat transfer is crucial we can appreciate that the temperature history of HCH kegs or drums which have been packed inside a steel freight container stowed in a ship’s hold, is very much dependent on the initial temperature of the HCH itself when loaded. If it were loaded cold and not in direct solid-solid contact with the freight container wall, any heat transfer to it would have to overcome two air/metal resistances (the freight container wall) and then another air/solid transfer (to the outside of the keg from the air inside the container). Given the relative thermal capacities of air and HCH it is easy to understand how this process could take a long time. An everyday analogy would be trying to heat your cold bathwater by turning on a space heater to first heat the air in the bathroom. On the other hand if the HCH is loaded warm (say 25°C) and one or more of the kegs/drums is in direct contact with the metal wall of the freight container, then the time to ignition for that keg/drum could be very much shorter than in the previous scenario.

Search for common factors or statistical links with particular ship’s routes (hence average ship’s hold temperatures) is doomed to failure when the initial conditions of the material, (probably the most important factor in determining whether criticality occurs or not), are ignored or unknown.

Consequently we have measured carefully the heat transfer coefficients for the bodies potentially involved in the carriage of hydrated HCH. This practical knowledge would appear to us to be essential for estimating how long HCH in containers on board ship will take to approach the ambient hold temperature. Also this data is essential for calculating the effect of interaction of kegs or drums of HCH with each other in a confined space, such as a freight container, and therefore to calculate the critical ambient temperatures for given numbers of kegs/drums in a freight container as has been reported above. These estimates depend strongly on the values of the relevant heat transfer coefficients and the relative surface areas of the containers themselves and of the kegs or drums stored inside the container.

It does not appear to have been appreciated previously that standard laboratory oven tests in well stirred thermostatted conditions will measure critical ambient temperatures of HCH that are far too high for the real case of drums or kegs inside a freight container, which is itself stowed inside a ship's hold.

Microcalorimetry on Hydrated HCH

Currently we are carrying out an absolute measurement of the heat production rate for hydrated HCH in an isothermal microcalorimeter, capable of measuring the actual rate of production of heat by the hydrated HCH at a fixed temperature of 35°C. A test already carried out at 50°C shows a heat production rate of 400μw/g (microwatts per gm). For comparison we estimate that the high temperature reaction (or anhydrous material) would theoretically produce only 7.4μw/g at this temperature.

A comparable figure for a typical coal would be 40μw/g. The figure at 50°C for hydrated HCH corresponds to a heat production rate of 16w/40kg and approximately 7kw/container at 50°C!

We can calculate with confidence that the absolute heat release rate we will get at 35^0 C will be about 3kw/container at 35°C. This is rather startling considering the folklore which has taken hold in this area that hydrated HCH is totally unreactive below 55°C!

4 GENERAL CONCLUSIONS TO DATE

4.1 – Hydrated HCH behaves in a totally different way at low temperatures (below about 110°C) from its behaviour above this temperature.

4.2 - The low temperature reaction has significantly different kinetic and thermal characteristics from the high temperature reaction.

4.3 – In the low temperature range the reaction which dominates at high temperatures is negligibly slow. An entirely different reaction dominates at low temperatures however, it is swamped at high temperatures. Thus in different temperature ranges different reactions are responsible for the heat production. In a narrow region around 80°C to 110°C they both contribute. The low temperature reaction dominates below 80°C and the high temperature reaction dominates above 110°C.

4.4 - This phenomenon of (at least) two different reactions taking place has the very serious consequence that the standard small scale/high temperature tests carried out on hydrated HCH in laboratories give dangerously erroneous results.

4.5 - The relatively high thermal conductivity of hydrated HCH itself means that a significant resistance to the loss of self generated heat occurs at the keg/air interface and the air/container/air interface.

4.6 - (4.5) above implies that the critical ambient temperatures for such kegs or assemblies of kegs will be sensitive to their large scale situation, i.e. inside a container, where the container is stowed etc.

4.7 - The above comments apply to all versions of hydrated HCH tested up to the present – variations have not been significant for U.S., Japanese or Chinese origin of manufacture of the hydrated HCH.

4.8 - The high temperature behaviour is rather similar to the entire behaviour reported for anhydrous HCH by Uehara et al, the only published work using methods consistent with the ideas of ignition theory (See the appendix for some criticism of this early work).

4.9 – We have proved beyond any doubt, that the critical ambient temperature for a container of hydrated HCH kegs/drums, regardless of their precise size, is in the region of 30°C to 45°C.

4.10 - From (4.9) above it has become clear to us that an important determinant of which HCH cargoes ignite during transport and which do not, is the initial temperature of the HCH itself at the time of loading. It is not impossible that all cargoes are supercritical but do not have time to 'ignite' during most voyages due to a combination of the cargoes initial temperature on loading and the ambient hold temperatures. We add that it appears from our available chlorine analyses that a significant proportion of the hydrated HCH sold in Australia (after relatively long sea voyages) is below the makers minimum guaranteed available chlorine content. These results indicate to us that decomposition of the hydrated HCH had taken place (subcritical) during the voyage. This also means that our critical ambient temperatures are about 2° higher than would be measured for 65% available chlorine as all our tests were done on samples showing only approximately 60% available chlorine.

Appendix - Comments on the paper of Uehara et al (1978)

This paper has the distinction of being the only published work on anhydrous HCH (that we are aware of) that has utilised the basic principles of ignition theory and carried out test experiments which are consistent with these principles. The experiments are therefore capable of giving objective and basic information about the anhydrous material which should enable an advance in understanding and predictions to be made which are soundly based on well understood theory.

Initially our intention was to perform similar tests with a similar rationale but using the hydrated material. During the course of carrying out this program we have noticed some possible criticisms of this work. They may or may not affect the conclusions for the anhydrous material (in other than a quantitative manner) but they are relevant to the extension to hydrated HCH.

1) - The samples were placed in the test oven at the same time as the oven was switched on – normal practice would be to place the sample in a preheated oven providing a constant ambient temperature. This could affect ‘times to ignition’ and critical ambient temperatures to some extent.

2) - The larger samples were heated by steam in a different system. Although these results lie on the same straight line as the others obtained at higher temperatures the consequences for heat transfer from the HDPE to a steam environment at 75°C are difficult to predict. If the main resistance to heat transfer were in the HCH itself (very large Biot number) this would not be a problem, but this is not the case.

3) - For some reason Uehara et al use a critical value $\delta_c = 2.00$ in their work. This is the value for an idealised infinitely long cylinder with very large Biot number. In fact for cylinders of the shape of the commercial kegs referred to in their paper and infinite Biot number one would expect $\delta_c = 2.5$ or 2.6. Correction for finite Biot number reduces this and at most one may hope for a certain degree of error cancellation.

4) - The thermostat chamber was a forced convection type so it is possible (with hindsight) to expect from our results that change of this to still natural convection would reduce the critical ambient temperatures obtained by around 5°C.

How much further the critical ambient temperatures might be reduced taking account of the enhanced heat transfer properties of steam is unknown. Once the body was self-heating, i.e. hotter than the oven wall, it is possible that a reflux mechanism would set in whereby evaporation from the keg surface and condensation on the oven walls may occur. At earlier times, whilst the keg was cooler than the surroundings condensation on the keg would occur with the consequent transfer of latent heat direct to the keg surface. Of course this may be a possible extra mechanism in ultra steamy conditions in a container onboard ship, but it would require a near unlimited supply of external moist air to be supplied. It appears that the use of steam raises a number of questions which hopefully are much less important at 35°C-40°C than they are at 75°C in the tests of Uehara et al. Despite these criticisms we believe this work to date represents a useful contribution to the literature on anhydrous HCH.

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SUMMARY

Results from a research project to study the thermal properties of hydrated calcium hypochlorite (UN2880) are outlined and discussed. The background to early work on this material at around the time the IMDG Code entry appeared in 1982 is included. It is concluded that the critical ambient temperature for a 20ft container load of this material is much lower than that hitherto generally accepted or recognised. The DSC committee are invited to consider a change of the IMDG Code entry for hydrated calcium hypochlorite.