

FIRE HAZARDS OF CALCIUM HYPOCHLORITE

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Summary

“Calcium hypochlorite, 70% available chlorine” is a commercial chemical which is transported in large quantities generally packed in steel drums. It is classified by the I M C O Code as an Oxidising Agent. During the past five years there have been about a dozen serious accidents in ships involving this material. The losses caused have been very large, amounting to many millions of pounds sterling.

A number of the P and I Clubs in London set up a sub-committee to investigate the hazards associated with the substance. The investigations include a research programme carried out at the Royal Armament Research and Development Establishment, Woolwich, England.

It has been found that ignition may occur in some circumstances spontaneously, by mechanical stressing or by admixture with some combustible substances. The commercial material is not a definite chemical compound but a mixture, the nature and properties of which may vary according to the nature of the raw materials and method of manufacture.

Accidental ignition may be followed by explosive effects and the fire evolves large quantities of oxygen, which produce an almost uncontrollable burning of any combustible material nearby. It is apparent that the hazards are far more serious than those ordinarily associated with other oxidising agents.

Introduction

“Calcium hypochlorite, 70% available chlorine” is the commercial description of a substance used for purifying water supplies and, in particular, swimming pools. It is sometimes referred to in shipping documents as “bleaching powder”. This is a misnomer and can be misleading because the hazardous properties of the two substances are quite different.

It is of interest because it has been responsible for a number of fires and explosions in ships. During the last few years there have been some twelve major incidents in ships known to the writer. A list is given in the Appendix. The resultant losses run into many millions of pounds. In addition, there have been many incidents on land about which there are little available data.

Shipping regulations, such as the I.M.C.O. Code and the U.K. Blue Book, divide calcium hypochlorite dry mixtures into two categories: those containing less than 39% available chlorine and mixtures containing more than 39% available chlorine. The former covers conventional “bleaching powder”,

which is considered to be non-hazardous. This communication is concerned with the latter and, in particular, with mixtures containing about 70% available chlorine, which is the mixture commonly transported. Many thousands of tons are shipped annually.

The I.M.C.O. Code places it in Class 5.1, Oxidising Agents. Under "Properties" it is described as reacting violently with acids evolving chlorine; may decompose violently if exposed to heat or direct sunlight; powerful oxidant, may cause fire in contact with organic materials such as wood, cotton, straw or vegetable oils. Stowage is to be on or under deck.

Recent experience has indicated that the hazard is considerably greater than suggested by this classification and that it possesses hazard properties in excess of and of a nature different from those normally associated with oxidising agents.

Because of the costly experiences, particularly during 1972-73, investigations have been undertaken and a research programme carried out at the Royal Armament Research and Development Establishment, Woolwich, London, sponsored by the leading London P. and I. Clubs. The writer has had the benefit of personally investigating a number of the incidents and of acting as one of the scientific advisers to the P. and I. Clubs in planning and supervising the research programme.

Nature of the incidents

The pattern of behaviour when there has been an accident has been fairly uniform, suggesting that the behaviour has been a function of the substance itself rather than of the other cargo with which it has been stowed.

The hypochlorite has generally been packed in steel drums with a protective lining or lacquer to prevent corrosion. On at least one occasion it has been packed in polyethylene bottles inside fibre-board cartons. It has been stowed under deck; sometimes on the tween-deck, sometimes in the lower hold; once in the deep tanks.

Many of the accidents have taken place in tropical latitudes. This may be due to the routes followed in trade between the manufacturing country and the destinations, which mainly cross the tropics. Some accidents have taken place under conditions where high temperatures have not been experienced. Thus there is no evidence that high temperatures are a prerequisite, although it would appear, on other evidence, that high temperatures may contribute.

On some occasions the voyage has been calm. On others the ship has encountered heavy weather. Although there has been no evidence of the cargo shifting, undoubtedly small movements of the drums may have been a contributory factor.

In every incident about which information is available conditions in the stow have been normal. There have been no signs of fire or smoke before the incident. Smoke detectors have failed to give any signal before the event, so there has been no period of smouldering or slow development.

The event in each case as described by crew has been very consistent. The first observation was a sudden burst of flame from ventilators, sometimes described as emerging with some force. After this has happened smoke detectors have given a signal. A short time later, which may be half a minute or a little more, there has been an explosion which has lifted the hatch covers. In some cases McGregors have been bodily lifted, steel beams bent and sometimes thrown overboard. A small amount of other cargo from the hold has been thrown out, sometimes to a considerable distance.

Although this has always been described as an explosion, it should be emphasised that the events have been comparatively weak, involving pressures of perhaps 10–20 ps_i. They are quite different from violent gas explosions, producing much higher and more damaging pressures, and from true explosions of solid explosive substances, which produce great local shattering or damage.

Immediately after the explosion a fire has followed which has been of great intensity. This is consistent with the fact that the hypochlorite is an oxidising agent. It produces large quantities of oxygen in which other cargo burns with temperatures much higher than normal, producing a very damaging fire and one which cannot be controlled, except by very large quantities of water. At the same time poisonous fumes, of chlorine, are produced, which prevent approach to the area.

It has been the damage to ship and cargo by the fire of abnormal intensity which has been largely responsible for the very large losses experienced.

Sources of the hypochlorite

As far as is known, all the hypochlorite carried in ships is made by three firms in the U.S.A. and three firms in Japan. With one or two exceptions, all the accidents have involved Japanese products. Attention has therefore been focussed on the Japanese material vis-à-vis the American. Investigations of accidents and research carried out in the laboratory have shown that there are significant differences between the products.

Composition of the hypochlorite

Calcium hypochlorite is made by a process which consists essentially of reacting chlorine gas with a lime slurry. The process is not simple. It requires several steps and close control of the conditions.

The product is not a single substance. The United Nations list (under No. 1748) and the I.M.C.O. Code give it the chemical formula $\text{Ca}(\text{OCl})_2$. This formula is not correct in respect of the commercial substance, which is a mixture.

In the first place, there is present about 30% of inert substances such as sodium chloride, etc. These vary as between different manufacturers and may, indeed, vary from time to time in the output of a manufacturer.

The designation "70% available chlorine" is itself a misnomer. If the substance were pure $\text{Ca}(\text{OCl})_2$ with a molecular weight of 143 and two atoms of chlorine, weight 70.9, the actual chlorine content would be approximately 50%. The so-called available chlorine is assayed by determining its oxidising power in liberating iodine from potassium iodide. In this reaction each molecule of hypochlorite liberates four atoms of iodine. If this oxidising power is then described as "available chlorine" the "available chlorine" is double the actual amount of chlorine present. Consequently, pure $\text{Ca}(\text{OCl})_2$ with about 50% actual chlorine would be described as having about 100% (accurately 99.2%) available chlorine.

Thus if the available chlorine in the commercial product is derived solely from $\text{Ca}(\text{OCl})_2$ the designation 70% would imply that there was present 70.6% $\text{Ca}(\text{OCl})_2$. That is to say, there is present some 30% of inerts, as is, in fact, the case.

The method used in assaying the product does not distinguish between $\text{Ca}(\text{OCl})_2$ and any other substance capable of releasing iodine. Therefore part of the available chlorine may be due to the presence of other oxidising agents such as chlorates or chlorites. As far as can be ascertained the manufacturers do not determine whether or not any such substances are present or absent. It is known that small variations in the conditions during manufacture may result in the production of chemical species other than true hypochlorite. In addition, the calcium hypochlorite may be in a hydrated form or contain a mixture of anhydrous and hydrated forms.

Possible impurities from raw materials

The raw materials are lime, chlorine and caustic soda. The lime is obtained by burning natural limestone. The chlorine and caustic soda are obtained by the electrolysis of common salt.

Natural limestone contains impurities. One of these is magnesium carbonate. The amount of this and other impurities varies between sources. One U.S. producer takes great care to ensure the satisfactory nature of their supply. Not only is the limestone obtained from a specified quarry but also from a particular stratum of that quarry. After burning to calcium oxide each consignment is sampled and analysed to determine suitability for use.

Magnesium has been mentioned above because it is known that magnesium hypochlorite is particularly unstable and could be present in the final product if magnesium oxide was present in the feed-stock. Other impurities which might be present could conceivably add to the hazardous nature of the product. At present we have little information.

Chlorine produced electrolytically from salt is probably substantially pure. If the salt is sea salt, it seems probable that there may be present some bromine. It is not known whether the possible formation of bromine compounds, such as calcium hypobromite, might affect the hazard properties of the product.

The caustic soda may also contain impurities, especially if it is derived from sea salt. It is known that sea salt is used at least sometimes by the Japanese manufacturers. Of course, magnesium compounds may be present as well as other impurities.

Since caustic soda is used, there seems to be a possibility that some sodium hypochlorite may be formed and be present in the product. It is particularly unstable.

Thus the name "calcium hypochlorite, 70% available" chlorine does not imply a definite identifiable chemical. It is really a generic name for an indefinite mixture of which the hazard properties may differ between the products of different manufacturers or between different batches from the same manufacturer.

Possible causes of fire

Investigations which have been carried out show that there are two ways in which an accident can be produced. In one, ignition follows from a spillage. In the other, ignition occurs inside an intact drum.

Fires caused by spillage

The Code says that it may cause fire in contact with organic materials such as wood, cotton, straw and vegetable oils. This is undoubtedly true, but it may give rise to a belief that it is only materials like those quoted which must be avoided. The ordinary person, who is not a chemist, is liable to take the term "organic materials" to mean natural products (and not to include what the chemist calls organic substances). In addition, he is liable to believe that it is only materials like those quoted which present a danger. Incidentally, the shipper is put in a difficulty by the inclusion of wood since this seems to exclude the use of dunnage.

It is a well-established fact that ignition can occur on contact with a variety of substances. There are, in the literature, accounts of fires starting when unclean scoops were used. It is believed that ignition can follow contact with many easily oxidised chemicals. For example, a drop of glycerine added to a drum causes a fire which propagates through the whole contents. Unsaturated organic compounds or one with a reactive group may act in the same way.

Thus a fire may start immediately from a spillage coming into contact with substances of this kind. An important aspect is that once a fire has been started it will spread throughout the contents. It is to be expected that the risk of ignition will be greater if either the hypochlorite or the other substance is present in a liquid form. Since hypochlorite is soluble in water, moisture increases the hazard by bringing the reactants into better contact.

If, as a result of a spillage, hypochlorite becomes mixed with a substance which can act as a fuel, there may be a risk of fire even though ignition does

not take place spontaneously. Such mixtures may be sensitive to friction and ignitable thereby. For example, one sample was found to be readily ignited by a frictional blow if it was spread on a wooden surface.

Thus spillages in a ship's hold may well become ignited either by contact with other matter or by contamination coupled with frictional forces such as those of a cargo in heavy weather. If a fire is started in this way it may well locally heat the contents of a nearby drum to the point where the contents of the drum become involved, leading ultimately to the involvement of the whole stow

Spontaneous ignition, by self-heating

Investigations have shown that in several of the accidents one is led to the conclusion that ignitions occurred within intact drums. Two mechanisms for this can be postulated. The mixture as manufactured was itself unstable so as eventually to go on fire, or it may have become contaminated with some reactive substance prior to packing.

The evidence that spontaneous ignition within a drum has occurred in this way is extremely strong in several incidents. The two processes are differentiated because one implies the production of an inherently unstable mixture, the other involves contamination by discrete particles of some reactive substance after manufacture but before the drum was closed.

In the former case it is envisaged that the contents of the drum are substantially uniform. This may be due to it being itself an unstable product or to the presence throughout the mass of a small quantity of an unstable species.

In either case, decomposition occurs producing heating. If this evolution of heat is faster than the heat can escape, the mass will begin to warm up. Heating will be fastest at the centre. As the temperature rises the rate of decomposition will increase. So the heating will accelerate. Eventually a critical point will be reached when the centre of the mass attains a temperature at which ignition or explosion occurs.

This process, referred to as self-heating, is well known with unstable substances. Given certain fundamental data about the thermodynamics of the decomposition, it is possible to calculate whether it is liable to happen if the drum is initially at a certain temperature. The process takes place more readily in a big drum than in a small drum because the rate at which the heat can escape is relatively smaller for a big drum. In practice, it is usual to calculate the "safe size" of drum for a given ambient temperature, taking for example the temperature to be expected in a ship's hold.

It is generally stated in the literature that the decomposition temperature of hypochlorite is about 180 °C. Even in the absence of foreign, more reactive, species, the safe temperature will be far below this. At ordinary temperatures hypochlorite decomposes slowly. On storage it loses about 2% of its chlorine per year. This involves an evolution of heat but it is so slow that it escapes

and there is no appreciable rise in temperature. At some higher temperatures the heat production will exceed the escape rate so the self-heating process begins. The important thing is whether this can occur from such temperature as may exist in a ship's hold.

A feature of the process is that there is an induction period, *i.e.* an appreciable time elapses between the onset of the process and the final ignition. The induction period may be long—hours, days or weeks. Consequently, the contents of a drum may spontaneously ignite after a very long time.

Spontaneous ignition due to contamination

The other process of spontaneous ignition due to local contamination is similar in some ways but different in others.

In the first place, it requires that a contaminant shall be present. Because of the great reactivity of hypochlorite many possible contaminants must be considered. Any substance which can be oxidised easily is potentially dangerous. In addition, there are various substances such as oxides of certain metals which can catalyse the decomposition.

Contamination can occur in a variety of ways, such as filling into unclean drums or adventitious mixing with foreign matter during handling or filling drums. Mention has been made of the effect of adding a single drop of glycerine. Other substances could be as dangerous. For this reason the greatest care is necessary in inspecting drums and in good housekeeping. Even with the greatest care there is always a chance of contamination in the factory, so the occurrence of an occasional rogue drum cannot be eliminated.

A gross case of contamination has been reported. A drum at the quayside was found to have partially spilled as a result of the lid coming off. Someone swept up the spillage, together with any dirt there was around, put the sweepings into the drum and replaced the lid. The drum then went forward to be stowed. It is clear that those concerned were quite ignorant of the properties of the substance and the dangers involved.

Unlike the risk of self-heating, the effects of contamination cannot be predicted. Each case is unique and depends not only on the properties of the hypochlorite but also on the quantity, position and properties of the contaminant. The effect may be the production of a local hot-spot reaching a temperature high enough for decomposition to spread out through the mass.

The only way to prevent this sort of thing happening is by great care. The carrier must be able to rely on the manufacturer. In practice, it may mean that he should demand from the manufacturer some guarantee, together, perhaps, with a certificate that the packed material has been stored for more than some minimum time.

More hazardous than a simple oxidising agent

Substances of Class 5.1 possess the property of giving off oxygen when involved in a fire, thus increasing its intensity. Of many of them it is said that mixtures with certain other substances may be readily ignited and burn fiercely. In a few cases mixtures may be explosive.

The emphasis is on the dangers from the substance in conjunction with something else. Stowage segregation required is based upon these considerations. The hazards of most of the members of the Class are those which can arise from mixing or by supplying oxygen to a fire in some other cargo. By themselves they do not constitute a hazard.

Calcium hypochlorite, on the other hand, is one of the very few substances in this Class which is not only an oxidising agent but also is hazardous in itself. It can, by itself, decompose with the evolution of heat and toxic gases and this may occur with explosive violence.

If a drum of, say, potassium nitrate (a typical oxidising agent) is heated at one spot, oxygen is produced from the heated material. On removing the source of heat the decomposition ceases. In the case of hypochlorite, however, not only is oxygen produced from the hot area but it spreads, even if the source of heat is removed. Once decomposition has been initiated it spreads as a violent "fire" which involves the whole contents of the drum. The heat produced thereby will set off other adjacent drums until the whole cargo may be involved.

This would appear to be the explanation of the observations recorded in the several accidents. Initiation, by one of the mechanisms indicated, takes place locally. A whole drum or a few adjacent drums become involved and produce the burst of flame first seen. The heat produced raises the temperature of other adjacent drums until almost simultaneously their contents decompose almost instantly giving the "explosion". Ignition of combustible material, such as dunnage and other cargo, occurs. It appears that the total stow of hypochlorite is not involved in the "explosion". There is clear evidence that the contents of a large number of the drums are not consumed at once. This material, exposed to the continuing fire, evolves large quantities of oxygen, which makes the fire in the combustible matter very intense and the heat of decomposition of the hypochlorite adds further to the severity of the fire.

It is quite clear that the connotations of Class 5.1 and the meaning of the Class label as understood by dockside and other handlers do not convey the proper information. Further, the stowage requirements for the Class are insufficient.

Research programme

The research programme sponsored by the leading London P and I Clubs was placed with the laboratory at Woolwich because of the considerable

experience there in investigating hazards and classifying hazardous substances. The contract specified certain limited objectives of an immediate and practical nature.

It was apparent from the accidents that the greatest risk was with material of Japanese origin. The product of the major U.S. manufacturer appeared to be relatively trouble-free

The first task was to determine whether there were chemical differences between samples from the several sources. Conventional chemical analysis was not appropriate for detecting the presence of certain species because changes were to be expected as soon as the samples were brought into solution. X-ray diffraction was therefore used.

Diffraction patterns revealed that there were, in addition to the calcium hypochlorite, sodium chloride and at least four other components. Some were present in some samples and absent in others. When present, the quantities varied. So far the nature of these components has not been identified. It is clear, however, that the several samples are significantly different.

Physical differences were found in particle size and in bulk density. These differences may well affect sensitivity and reactivity. Experimental evidence was obtained, for example, that impact sensitivity of one sample was greater for large particles than for small particles. Differences in reactivity were indicated by determining the heats of solution. In all these properties it was found that the Japanese products were more variable than the U.S. product.

Of particular interest in the present context is the behaviour of the sample at an elevated temperature. Here again, a marked difference was observed between the behaviour of the U.S. product and the Japanese product.

When held at a steady elevated temperature the U.S. product decomposed at a steady rate. Under the same conditions the Japanese product decomposed initially at a somewhat faster rate, then, after a short time, decomposition accelerated to a run-away rate. This may be interpreted as indicating the possibility of self heating to ignition. Further studies are continuing to obtain the data necessary to relate this to the conditions in drums in ships.

Although this work is not yet complete, it is already clear that the hazard status of commercial samples is different as between the products of different manufacturers. Further differences exist between the materials in different drums from the same maker and, perhaps, between material from different parts of the same drum.

It would be premature to discuss these results now in detail. It is intended to publish the results in full when the work has been completed.

Interim recommendations

A fatal accident occurred in September 1973 at Yokohama whilst hypochlorite was being loaded into a ship. As a consequence, all movement of the material was stopped and an official investigation was started. The

Japanese official and labour organisations considered new regulations under which the substance might be handled. Meanwhile, large quantities accumulated awaiting transport.

Prior to this, the sub-committee set up by the London P. and I. Clubs had been considering under what conditions the product might be transported with a smaller risk of serious damage. As a result of the investigations of previous accidents, the currently available results of the Woolwich research and the advice of the several technical experts serving the sub-committee, an interim recommendation was prepared so that movement of the material could recommence.

The main point in these recommendations was that stowage should be on deck only, either in containers or not in containers. In the latter case only drums were acceptable. Consignments in plastic bottles should be in containers. Further details referred to secure stowage, protection from weather (if not in containers), inspection for soundness, avoidance and clearance of spillages, etc.

The Japanese authorities had apparently been influenced by erroneous statements that exposure to sunshine and water was dangerous. This, and other considerations, led them to advocate stowage under deck.

A mission was sent by the sub-committee to Japan to discuss the matter. As a result of discussions with Ministry, dock authorities, ship interests, labour organisations and manufacturers, on-deck stowage was agreed.

It was recognised that on-deck stowage involves some commercial difficulties. Further, in order to provide adequate protection on deck, the use of containers is desirable and this may cause difficulties in a situation where there may not be an adequate feed-back of empty containers.

However, it seemed quite unrealistic to permit stowage under deck when there was a real risk of spontaneous ignition. Nevertheless, there must continue to be pressures for further understanding of the problems.

Future action

The steps taken so far are purely of an interim nature designed to prevent a hold-up of commerce. The Clubs have taken steps which it is believed will lessen the risks but will not eliminate them. So long as calcium hypochlorite of the present quality is shipped there will be a hazard. On-deck stowage is expected to lessen the consequences of an ignition but cannot eliminate them.

The recommendations place ships which conform to them at a commercial disadvantage in competition with ships which do not. Therefore the latter may carry an increasing proportion of the trade. They presumably would abide by the I.M.C.O. and relevant National Codes.

Experience has shown that, as they stand, the Codes do not provide sufficient safeguards. In some of the accidents when full investigation has been possible it has been quite clear that there has been no infringement of the Codes. For example, in one case the ship was on her maiden voyage and the

drums of hypochlorite were the sole cargo on the tween-deck of one hold. The stow was away from any source of heat, the ship was patently clean and free from any materials with which a spillage might have reacted, the stow was secure, the weather was calm and cold

Action should also involve the manufacturers. It is already clear that the hazard status of different products varies significantly. The major U S manufacturer has been most cooperative. Their technical expert has freely provided much information and attended discussions in the U.S A and England. Members of the sub-committee were invited to see the manufacturing process and given all details except those which are commercial secrets. On the other hand, very little has been disclosed by the Japanese makers

What is required, in the first instance, is a more detailed study to determine the source of unacceptable instability in the commercial mixtures. Second, to establish methods of control during manufacture to eliminate or reduce the instability and ensure a uniform product. Third, to devise some form of test or assurance that dangerously unstable material is not offered for shipment. Fourth, to amend the Codes to take account of the hazard properties which are now known not to be adequately implied in the present classification. Fifth, to ensure that those handling the material have access to full information

These requirements are matters of some urgency. In the present climate, particularly that produced by the Yokohama accident and the enquiry arising therefrom, there may well be a lull in incidents, but it is feared that this may only be temporary.

Future action, along these lines, is beyond the scope of the P and I Clubs. It must rest with the competent national and international authorities

Appendix

Known incidents in ships, 1967—1973

- 1 *M V Thorstream*, 2 6.67. Explosion at Buffalo N.Y. while loading; four killed.
- 2 *M V Dynamic Venture* Fire in hold, explosion of drum on quay during subsequent discharge.
- 3 *Unnamed ship* at Sydney, 1969. Incident while unloading; reported by Government of Australia to I.M.C.O.
- 4 *Unnamed ship* at Brisbane, 1969. Fire and explosion while unloading, reported to I.M.C.O. by Government of Australia.
- 5 *M V Griqualand*, 1970. Fire and explosion.
- 6 *M V Indura*, 1970. Fire and explosion at Durban
- 7 *M V Chevron Transporter*, 1970. Fire whilst on passage Panama to Vancouver.
- 8 *M V Nicolaos DL*, 1970 at Savannah S G. Fire and explosion during loading

- 9 *M V Straat Talbot*, 1971. Fire and explosion whilst on passage.
- 10 *M V Catharina Wards*, 1972. Fire and explosion whilst on passage.
- 11 *M V Opatya*, 1973. Fire and explosion whilst on passage.
- 12 *M V Manolo Everett*, 1973. Explosion whilst loading; six killed.