Chapter 31

Thiourea Dioxide

Thiourea dioxide, or formamidine sulfinic acid (UN 3341, Class 4.2), is a white to pale yellow, crystalline powder used as a reductive agent in the paper industry and a bleaching agent in the textile industry. It is produced by oxidation of thiourea with hydrogen peroxide.

During 1996–97, there were several incidents related to the decomposition of thiourea dioxide. In one incident in the Far East, 400 workers were evacuated from a marine terminal and several workers required hospitalisation. At that time, the chemical was not included in the IMDG Code.

When exposed to heat above 50°C and moisture, it is likely to decompose visibly and rapidly, a reaction that may be catalysed by metal salts. This decomposition is accompanied by the release of toxic and corrosive gases, including sulphur oxides, ammonia, carbon monoxide, nitrogen oxides, hydrogen sulphide, etc. Sulphur oxides can further react with moisture to form acidic conditions and the acid may then attack neighbouring cargo, leaving solid residue and causing contamination.

The IMDG Code (Reference 19) requires this cargo to be packed in hermetically-sealed drums. Stowage should be in cool dry areas at ambient temperatures. Stowage should be away from heat sources, such as steam pipes, heating coils, heated bunker tanks and main engine bulkheads.
Under-deck stowage is not recommended (IMDG Stowage and Segregation, Category D) because ships’ holds may reach 65°C in certain tropical zones. However, temperatures in containers carried on deck and exposed to sunlight at the edge of a container stow may also reach 65°C. Containers within the centre of a stow are protected from these high temperatures to some extent.

This cargo should not be accepted in bags.

31.1 Decomposition

Product information varies between manufacturers, with some stating that the material decomposes at 100°C, but will also decompose on lengthy heating above 50°C. Another indicates that the thermal stability is 80°C for two hours although the fate of the material after two hours under these conditions is not revealed. Some manufacturers have shipped this cargo under the names ‘Thiourea D’ or ‘Thiourea De’, claiming that it is less hazardous than thiourea dioxide, although this is not the case.

Ships’ crew should be made fully aware of the possible hazards of the carriage of thiourea dioxide. Shipowners must ensure that, if any such cargo is offered for shipment, the relevant personnel are able to make qualified decisions, even if this requires them to reject the shipment.
Chapter 32

Expandable Polymeric Beads

Expandable polymeric beads, also known as expandable polystyrene (EPS) (UN 2211 Polymeric Beads, Expandable), are used to produce a moulding material in the form of granules or beads of approximately 3 mm in diameter. The beads or granules may contain 5 to 8% of a volatile hydrocarbon, chiefly pentane. During the moulding process, the beads are heated, causing expansion and fusion, forming the familiar polymeric packaging material. During storage or transport, the material will release a portion of the pentane. The rate of this release increases with a rise in temperature. Pentane vapours are heavier than air, so higher concentrations can be found closer to the deck level. To add more complexity, pentane is liable to ignition at relatively low concentrations, eg 1.3% by volume in the air, with the rate of gas release increasing with a rise in temperature.

The beads have been found to generate flammable concentrations of gas in enclosed spaces and have been involved in several major explosions, one incident causing severe damage to a container ship.

Expandable beads are included in the IMDG Code (Reference 19), under Class 9 (miscellaneous dangerous substances and articles). Packaging
recommended in the IMDG Code includes outer drums and inner plastic packages. Intermediate bulk containers include composite fireboard or plastic materials. Under-deck stowage is permitted, but good ventilation must be ensured so that any ignitable concentrations can be avoided. Use of ventilation containers must be considered with caution as the level of ventilation provided may not necessarily be sufficient to rid any build-up of pentane. When ventilated containers are used, the ‘Criteria for the Selection of Ventilated Containers’ provided by the Expandable Polystyrene (EPS) Transport Group of PlasticsEurope in Guidelines for Transport and Storage of Expandable Polystyrene Raw Beads (Reference 55) must be complied with in addition to complying with other requirements of the IMDG Code for labelling, packaging and segregation. This requirement must include additional labelling for closed containers such as ‘keep away from all sources of ignition’, ‘no smoking or use of fire/naked lights’ and other cautions.

Transportation on ships in closed, non-ventilated containers is permitted, but the consignees must be advised about the risks associated with any accumulated pentane in high concentrations, including additional requirements for making an entry into the container, which should be treated as an enclosed space. This may require use of supplementary labels to warn workers of the hazards.

The Code of Federal Regulations 49 CFR, Chapter 1, Part 173 (Reference 56) describes various packaging materials but states that, except for transportation by highway and rail, the packaging must be capable of containing any evolving gases from the contents during normal conditions of transport.

The IMDG Code (Reference 19) states that storage and segregation is category ‘A’, on deck or under deck, but mechanical ventilation should be provided for under-deck stowage to prevent the formation of a flammable atmosphere. The Code advises that, during storage, a small proportion of the pentane may be released to the atmosphere and that this proportion is increased at elevated temperatures. There is also a cautionary note relating to the opening of doors if the material is carried in containers.

Reputable manufacturers of polymeric beads are well aware of the hazards of storage and transportation of the beads and provide detailed lists of precautions to be observed. They provide detailed warning labels to be fixed to drums and freight containers, labels in several different languages and graphic symbols.

The recommended storage is in a well-ventilated space and preferably below 20°C. Warehouse storage below 20°C may be a relatively simple operation. However, stowage in the holds of an ocean vessel may be more difficult and should, at least, be away from heated bunker tanks or engine room bulkheads. Temperatures in ships’ holds might be of the order of 65°C in some tropical areas. Adequate hold ventilation with ‘suitable equipment’ should be stressed.
because the arcing of an electric fan motor may readily ignite a flammable concentration of pentane in air.

Deck temperatures in tropical climates can also exceed the recommended limits for safe stowage of the beads. However, if the cargo is containerised, the containers can be placed in a central area of the stow where they will be insulated from the effects of direct sunlight. This arrangement will create extra movement during loading and discharge, but can assist toward safe carriage. Pentane released from containers in deck stowage will be dispersed by wind and movement of the vessel and should not create flammable or explosive conditions outside the containers.

Manufacturers are well aware of the problems of release of pentane, which is heavier than air, into freight containers. Recommended ventilation periods are suggested prior to entry and unpacking the container. If opened in a container yard, containers should be sited away from drains so that pentane released when the doors are opened does not enter them, creating a potential fire hazard at some nearby location.