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# CARRIAGE OF SULPHUR

Sulphur is abundant in the earth's crust and comprises a very important feedstock material for the world's chemical industry. Its main source is as a by-product in hydrocarbon processing (oil and gas) and petroleum and natural gas producing countries are major exporters. Its largest single use is for the production of sulphuric acid, which in turn is used extensively in the production of fertilisers. Annually, several tens of millions of tons are carried on board ships.

## Corrosion hazard

Sulphur is loaded in granular or prilled forms but also as crushed lumps or coarsely grained material. IMO, in its IMSBC Code (formerly the BC Code), classifies the solid granular/prilled forms as harmless group C, ref: Sulphur (formed, solid) pp 271-2 of the current 2009 edition of the Code, and crushed lumps/coarse grained sulphur as hazardous class 4.1 under UN1350, pp 273-4. Regardless of form, when sulphur is wet, it has potential to cause serious corrosion damage to steel. IMO therefore requires that sulphur should only be loaded after adequate protection against corrosion is in place.

In the 1970 and 80s, there were numerous incidents of corrosion damage to holds on board ships after loading sulphur. Research confirmed that completely dry sulphur does not react with steel but wet sulphur can cause serious damage. The simple fact is that sulphur plus moisture plus mild steel equals corrosion. The mechanism of oxidation is electrochemical in nature and important characteristics are:

- The reaction is promoted under anaerobic conditions and exhibits autocatalytic behaviour. That is, once started further corrosion is accelerated.

- Corrosion proceeds irrespective of the pH of the medium although its fastest rate is at neutral pH.

- Temperature promotes reaction and corrosion rate roughly doubles for each 10 $^{o}$C rise.

- The presence of the chloride ion promotes corrosion.

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Sulphur contains low residual quantities of acids (mainly sulphuric acid). This presents potential for acid induced corrosion although this is not believed to be significant unless conditions are fairly acidic (pH values of 2 or less), which are uncommon for sulphur cargoes.

Most sulphur cargoes are loaded wet and therefore present risk of corrosion. This is because the product is usually stored in large outdoor piles but additionally, in many ports it is standard practice during loading to spray with fresh water in order to reduce dust formation. On board, water plus fine sulphur dust therefore gradually filter towards the tank top to present a potent corrosive system to steel unless protective measures are in place. The fundamental principle for protection against corrosion relies on the presence of a completely uninterrupted physical barrier between steel and sulphur. This prevents direct contact with steel and hence corrosion.

## Hold preparations prior to loading

Holds should be cleaned to 'grain clean' standard. Not only can presence of previous cargo residues affect the protection coat to be applied, but shippers also guarantee very high purity specification for sulphur and holds should in any event be clean. Therefore:

- Sweep and wash thorough with sea water.
- Rinse thoroughly with fresh water in order to remove chloride salts.
- The paintwork comprises an important component of protection against corrosion and repairs should be made to damaged areas of paint. Loose rust or rust scale should be removed as sulphur can easily gain access to steel in such areas.
- The bilges should be covered with burlap.

## Lime wash

Lime wash is the most common method to protect against corrosion although some other means of providing protective coating also are developed. It acts to mitigate against and slow down corrosion, but does not completely eliminate risk of it occurring. It serves two specific functions:

- It presents a physical barrier between sulphur and hold structures.
- The alkaline nature of the lime acts to neutralise acid present in the sulphur.

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Typical preparations are mixtures of lime (calcium hydroxide) and water in proportions of 60 - 90 kg of lime to 200 litre of water. When the solution is sprayed onto hold structures, this white emulsion should completely cover all areas that can be exposed to sulphur and sulphur dust including paint. As the emulsion dries, the lime (calcium hydroxide) reacts in air (carbon dioxide) to form a layer of opaque white calcium carbonate. This is significantly harder than lime and constitutes the actual coat of protection. A lime wash must therefore always be given ample time to dry. Wet lime does not provide protection against corrosion.

During acid neutralisation, the carbonate will gradually be consumed and the protective action lost. A single layer of protection would be expected to last for at least 30 days but sometimes longer, particularly in cold conditions. It is important that due consideration is given to voyage durations and that undue delays are avoided.

During voyages, bilges should be pumped regularly to prevent risk of water (acidic) accumulating on tank tops. When sulphur has been discharged it is important that all residues of this material are completely removed from cargo spaces including the bilge system.

Flammability:

Crushed or coarsely grained sulphur declared under the UN1350 schedule presents a certain fire and dust explosion risk. We refer in this respect to the IMSBC Code.

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Photo 1: Damage to tank top due to corrosion caused by wet sulphur. Note the steep sided pit formations which are characteristic of such corrosion.

Photo 2: Damage to lower part of a corrugated bulk head. Note severe corrosion in way of areas with damaged paint.