DEPARTMENT OF TRANSPORTATION
UNITED STATES COAST GUARD

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NAVIGATION AND VESSEL INSPECTION CIRCULAR NO. 5 - 79

Subj: Inerting and Tank Cleaning Procedures for Alkylene Oxide Containment Systems

1. PURPOSE. This Circular publishes information and procedures for inerting and cleaning cargo tanks that carry alkylene oxides, particularly ethylene oxide and propylene oxide.

2. DISCUSSION. Alkylene oxides are highly reactive and extremely flammable products. Ethylene oxide and propylene oxide are the two most reactive and flammable alkylene oxides and are also the most common alkylene oxides shipped in bulk. Consequently, extreme caution must be exercised whenever a cargo tank on a tank barge or tankship is changed to or from alkylene oxide service. Enclosure (1) discusses the particular reactivity and flammability hazards of ethylene oxide and propylene oxide. Enclosure (1) also lists specific procedures for inerting and washing cargo tanks used to carry alkylene oxides.

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3. ACTION. Cargo containment systems that are either removed from or returned to alkylene oxide service must be cleaned to the satisfaction of a Coast Guard Marine Inspector under 46 CFR 151.50-10 and 46 CFR 153.1011. Coast Guard Marine Inspectors shall ensure that alkylene oxide cargo containment systems on tank barges and tank ships are cleaned in accordance with enclosure (1), or by a procedure specifically approved by the Commandant (G-MHM). Any questions concerning procedures for inerting and cleaning alkylene oxide containment systems should be referred to the Commandant (G-MHM).

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Acting Chief, Office of Merchant Marine Safety

Encl: (1) Inerting and Tank Cleaning Procedures for Ethylene Oxide and Propylene Oxide

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List CG-12

Inerting and Tank Cleaning Procedures for Ethylene Oxide and Propylene Oxide

Characteristics. Ethylene oxide and propylene oxide have four hazardous characteristics:

a. They have extremely flammable vapors. Ethylene oxide's vapor is flammable even by itself, with no oxygen present.
b. Their vapors can decompose violently (detonate) under some circumstances.
c. They are somewhat toxic and may cause long term damage to health at very low concentrations.
d. They are extremely reactive.

For these reasons, ethylene oxide and propylene oxide have special shipping requirements when they are moved in bulk.

Inertion. To stabilize the vapors above the cargo or the vapors remaining in an empty tank, ethylene oxide and propylene oxide tanks are inerted, usually with nitrogen.

Ethylene oxide vapor is flammable at concentrations ranging from 2 through 100% by volume in air. The vapor space of a tank can be inerted by keeping the inert gas pressure in the vapor space rather high. The total tank pressure necessary to inert an ethylene oxide cargo tank with nitrogen when the cargo is at 25°C (77°F) is roughly 520 kPa gauge (about 75 psig). Ethylene oxide may require different inertant pressures if a gas other than nitrogen is used as the inertant.

Since propylene oxide vapor is not flammable at concentrations greater than 39% by volume in air, the vapor space inertant is needed only to prevent oxygen from entering the tank. No minimum pressure is necessary as long as the tank stays above atmospheric pressure and the oxygen content remains below about 5% by volume. To give a margin of safety, the oxygen content of the vapor space is usually kept below 2% by volume.

Effect of relief valve venting on inertion. One important point to remember with any inerted tank is that the inert gas is only in the vapor above the liquid. If the tank vents, the inert gas goes out the vent with the cargo vapor. If the inert gas is not replaced, the vapor in the tank is no longer inerted.

Under normal circumstances, tanks either stay cool and do not vent or vent at a slow rate for a short time. Inertant can then be reintroduced and maintained in the vapor space from an inertant supply connected to the tank. However, if a tank is involved in a fire or loses refrigeration, the vapor relief valves may discharge vapor so quickly that the inertant supply is no longer able to keep the vapor space inerted. The tank then has a vapor space that is essentially pure cargo vapor. With most products this situation is safe if enough inertant remains in the inertant supply to refill the vapor space as the tank cools. However, since pure ethylene oxide vapor can burn without oxygen, an ethylene oxide tank can be dangerous any time its relief valves are venting.

Compatibility. Because ethylene oxide and propylene oxide are very reactive, they can be dangerous if contaminated by chemicals with which they are incompatible. Ethylene oxide must be carried in an isolated containment system under parts 151 and 154, in which case compatibility is not at issue. In loading propylene oxide, one should follow the Guide to Compatibility of Chemicals (NVC 4-75). Propylene oxide is in group 16.

Changing cargoes and tank washing. The rules for alkylene oxides in 46 CFR 151.50-10(c)(1) and 153.1011 describe special procedures that a vessel owner must follow if he wants to carry an alkylene oxide in a tank that carried a cargo other than an alkylene oxide as its previous cargo. Specifically, if any of the previous five loadings of a tank was a cargo that is not compatible with the alkylene oxide, the owner must clean the tank to the satisfaction of a Marine Inspector (or another person authorized by the Commandant (G-MHM)). The same must be done if the owner wants to carry any other cargo after having carried the alkylene oxide. (Note: The restrictions that apply to cleaning ethylene oxide tanks on gas ships in 46 CFR part 154 do not require Coast Guard approval of tankwashing.)

Washing Procedures for Changing from an Alkylene Oxide to Another Cargo

The following points are important to consider when washing an alkylene oxide tank:

a. Alkylene oxide vapors have wide flammable limits.
b. Alkylene oxide vapors ignite easily.
c. Alkylene oxides react with water, producing heat. The reaction rate (and therefore the rate of heat generation) varies among the alkylene oxides with ethylene oxide being the most reactive. When small amounts of an alkylene oxide, such as the residual quantities in an empty tank, are diluted quickly with water, the heat generated by reaction is safely dissipated in the water. The alkylene oxide must be diluted at least 25 to 1 with water and the resulting solution thoroughly mixed to ensure that the heat of reaction is safely dissipated.
d. Alkylene oxides are very soluble in water. The solubility varies among alkylene oxides, with ethylene oxide being the most soluble.
e. Tanks vary greatly in their shape and internal structure, which affects the cleaning procedures one uses. Spherical or cylindrical smoothwall tanks are probably easiest to clean. Internally framed rectangular tanks are the most difficult to clean but are generally not used for the alkylene oxides.

Knowing these characteristics, one can safely wash alkylene oxide tanks using one of the following procedures:

Procedure One

Note: This procedure is suitable for any type of cargo tank.

1. Have self-contained breathing equipment, gas testing equipment to measure both oxygen and alkylene oxide concentration, an adequate water supply to flush away alkylene oxide spillage, safety harness and rope, and protective rubber suit and boots on hand. These items are required for testing the tank vapor during washing and for safety in the event a person must enter a tank after it is cleaned. Under no circumstances should a person enter a tank before the tank has been cleaned.

2. Make sure the nitrogen inertant is still in the tank. Check the oxygen content of the vapor space with the oxygen detector. The vapor space in the tank must be less than 2% oxygen by volume. The tank must also be connected to a nitrogen supply so that the inertant is maintained.

3. Pump the tank down so that as little alkylene oxide is left in the tank as possible. A tank can usually be pumped down to 1 m^3 or less, including the contents of the piping system.

4. Set up the cargo piping system so that wash water can be pumped through the cargo lines, through spray headers, and other places that cargo could collect.

5. Fill the tank with water, displacing nitrogen and alkylene oxide vapor out through the vent stack or into a vapor recovery system.

6. Run the cargo pumps so that the wash water is pumped through the piping system.

7. Slowly discharge the water to a waste treatment facility, being sure that the nitrogen pressure is maintained on the tank.

8. Relieve the tank pressure.

9. Check the tank vapor for alkylene oxide with the alkylene oxide detector. Flush with nitrogen until the alkylene oxide content is less than 5% by volume.

10. Install a tank washing machine.

11. Wash the tank with unrecirculated hot water. Route the hot water through the cargo piping before discharging it.

12. Drain the wash water to a waste treatment facility.

13. Dry tank.

14. Break down the valves and check for alkylene oxide, water, and other chemicals.

Procedure Two

Note: This procedure should be used only when all of the following conditions are met.

(a) The alkylene oxide is not ethylene oxide.
(b) The cargo tank can be sealed up and maintained under at least a 6.9 kPa (1 psig) inertant pressure during washing.
(c) The cargo tank has smooth walls.

1. Have self-contained breathing equipment, gas testing equipment to measure both oxygen and alkylene oxide concentration, an adequate water supply to flush away alkylene oxide spillage, safety harness and rope, and protective rubber suit and boots on hand. These items are required for testing the tank vapor during washing and for safety in the event a person must enter a tank after it is cleaned. Under no circumstances should a person enter a tank before the tank has been cleaned.

2. Make sure the nitrogen inertant is still in the tank. Check the oxygen content of the vapor space with the oxygen detector. The vapor space in the tank must be less than 2% oxygen by volume. The tank must also be connected to a nitrogen supply so that the inertant is maintained.

3. Pump the tank down so that as little of the oxide is left in the tank as possible. A tank can usually be pumped down to less than 1 m^3, including the contents of the piping system.

4. Set up the cargo piping system so that wash water can be run through the cargo lines, through spray headers, and other places that cargo could collect.

5. Relieve the inertant in the tank until the pressure is at atmospheric. (Keep the tank closed as much as possible until the next step is completed. Keeping the tank closed will reduce the loss of inertant and the diffusion of oxygen into the vapor space of the tank.)

6. Install tank washing machines in a way that enables the inertant pressure to be maintained during washing. (This requires that the tank be pressure-tight with the washing machines installed.)

7. Apply inertant to the tank and purge until the oxygen content of the vapor space is less than 2% by volume. This can be checked using the oxygen detector. Then keep the inertant pressure at least at 3.5 kPa (about 0.5 psig) during the next step.

8. Wash the tank with unrecirculated, fresh water, flushing the cargo piping, spray headers, and so forth. Pump the wash water out as soon as enough water is in the tank to operate the pumps. This procedure will remove the last of the undiluted cargo residue. Discharge the wash water to a waste treatment facility.

9. Continue to wash the tanks. If available, hot water is preferable in the later stages of washing.

10. After washing, sample the tank vapor and measure the alkylene oxide content with the alkylene oxide detector. Flush the tank with inertant until the alkylene oxide content is less than 5% by volume.

11. Relieve the tank pressure, and complete tank cleaning as would be done with any other cargo.

12. Break down the cargo valves and check for alkylene oxide.

Changing from Another Cargo to An Alkylene Oxide

Putting a tank back into alkylene oxide service after the tank has carried other cargoes can be hazardous unless the tank is cleaned properly. The tank must be dried and residues of previous cargoes removed from all parts of the containment system, including piping, valves, and other places where cargo may be trapped or isolated from normal washing. If the residue of one of these previous cargoes reacts with the oxide, the heat generated by the reaction may cause the oxide to begin reacting with itself. These self reactions can take place despite the fact that the tank is inerted and may speed up to the point that they become explosive.

1. Follow the normal washing procedure for the cargo in question.

2. Make certain that any cargo lines are flushed during washing.

3. Dry the cargo tank and lines thoroughly, removing heavy rust, that is, rust other than light surface rusting.

4. Break down the cargo valves to be sure they are thoroughly clean and dry.

5. Reassemble the containment system and prepare it for inerting.

6. Purge the tank and cargo lines with nitrogen and measure the oxygen content of the purged gas until it falls below 2% by volume.

Reference: Title 46 CFR 151.50-10, 151.50-12, 151.50-13, 153.530, 153.1010, 153.1011, 154.1725, 154.1730