



KISH P & I LOSS PREVENTION CIRCULAR KPI-LP-19-2012 ***(Prevention of Chemical Products Contamination)***

Carriage of chemical products involves various problems due to their complex molecular structure & properties. The shipboard operations carried out by the concerned staff on board should consider numerous incident & especially contamination prevention measures.

Once a chemical product has been contaminated by a foreign substance, the whole liquid is referred to as damaged. Irrespective of the concentration of its contaminant, the loss incurred by such an accident tends to be a large amount. Notable accidents are to mono Ethylene Glycol (“MEG”) and Methyl Alcohol (“Methanol”) which are said to be the most sensitive of all chemicals for contamination during transit. In this circular, the details about how these specific products come to be damaged and in what way such damages could be prevented have been explained.

A) Properties and applicable standards:

“Mono Ethylene Glycol” (MEG):

Clear, colourless, syrupy liquid; infinitely soluble in water. Hygroscopic but of little solvent power; unlike other chemicals, odorless and odor-absorptive.

Uses are mainly for polyester fibers and antifreezes.

Trade specifications are determined depending on its uses and the most important items for use of polyester fiber are (1) ultraviolet transmission and (2) odor.

Especially, a test is carried out to identify the color (unidentifiable by visual inspection) by means of transmission of ultraviolet rays of certain wave length and put the result into numerical value (hereinafter called “UV test”).

Though its dissolving power is low, if the product happens to be contaminated by the slightest amount of foreign substance, the fact can be detected by odor and further by UV test, whereon cargo claims will be made to the carrier immediately. Even though utmost care is exercised by the carrier, contaminations may occur to the cargo on board due to the presence of previous cargo(es) remaining in the tanks, for which the carrier would be held responsible.

It is true that the number of such accidents in carriage of chemical cargo seems to be reduced gradually as a result of remarkable improvements in tank cleaning, washing machines and detergents, modernized construction of chemical tankers including the use of stainless steel for tanks and efficient pump/piping systems, but we still see a large number of accidents occurring to these products.

This loss prevention guide tries to introduce very interesting data regarding the tests of odor and ultraviolet transmission. The “table A” shows the results of laboratory tests as to what effects are made to the cargo in question by the residues of chemical products the vessel has carried on her previous voyage. The table covers only the result of the tests to which apparent odor and some effects to transmittance of 220nm wave length in ultraviolet rays are given after the sample of MEG has been mingled in 5ppm of various samples of “previous cargo”.

The data indicates that *aromatics (especially Xylene), unsaturated compounds, acrylate, higher alcohol and animal fats are unsuitable as previous cargoes.*

Specifically, Alkyl Benzene and Phenol which have boiling points comparatively close to MEG are difficult to distill for reconditioning when contamination occurred and may result in a heavy loss.



TABLE A

Previous Cargo Product	Test Solution (ppm)	Odor	UV Test			
			220nm	260nm	275nm	350nm
Mix Xylene	5	○	XX	○	○	○
	10	X	XX	○	○	○
	20	X	XX	X	○	○
	50	X	XX	X	X	○
	100	X	XX	XX	X	○
Meta Xylene	5	○	XX	○	○	○
	10	○	XX	○	○	○
	20	X	XX	X	○	○
	50	X	XX	X	X	○
	100	X	XX	XX	X	○
Ortho Xylene	5	○	XX	○	○	○
	10	○	XX	○	○	○
	20	X	XX	X	○	○
	50	X	XX	X	○	○
	100	X	XX	XX	○	○
Para Xylene	5	X	XX	○	○	○
	10	X	XX	X	X	○
	20	X	XX	X	X	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
Cumene	5	X	○	○	○	○
	10	X	X	○	○	○
	20	X	X	X	○	○
	50	X	XX	X	○	○
	100	X	XX	XX	○	○
Alpha-Methylstyrene (AMS)	5	○	XX	XX	○	○
	10	○	XX	XX	○	○
	20	X	XX	XX	X	○
	50	X	XX	XX	X	○
	100	X	XX	XX	XX	○
Styrene Monomer (SM)	5	X	XX	XX	X	○
	10	X	XX	XX	X	○
	20	X	XX	XX	XX	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
Phenol	5	X	XX	XX	X	X
	10	X	XX	XX	XX	X
	20	X	XX	XX	XX	X
	50	X	XX	XX	XX	XX
	100	X	XX	XX	XX	XX



TABLE A continued

Previous Cargo Product	Test Solution (ppm)	Odor	UV Test			
			220nm	260nm	275nm	350nm
Ortho-Cresol	5	○	XX	X	XX	○
	10	○	XX	X	XX	○
	20	X	XX	XX	XX	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
Para-Cresol	5	○	XX	X	X	○
	10	X	XX	X	XX	○
	20	X	XX	X	XX	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
Alkyl Benzene	5	○	X	○	○	○
	10	○	X	○	○	○
	20	○	X	○	○	○
	50	○	XX	○	○	○
	100	○	XX	X	○	○
Dimethyl Phthalate	5	X	XX	X	X	○
	10	X	XX	X	XX	○
	20	X	XX	XX	XX	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
Dibutyl Phthalate	5	○	XX	○	X	○
	10	○	XX	X	X	○
	20	○	XX	X	X	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
Diocetyl Phthalate (DOP)	5	○	X	○	○	○
	10	○	XX	X	X	○
	20	○	XX	X	X	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
n-Hexanol	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○
Furfural	5	○	X	XX	XX	○
	10	○	XX	XX	XX	○
	20	○	XX	XX	XX	○
	50	X	XX	XX	XX	X
	100	X	XX	XX	XX	X
Propionic Acid	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○
Ethyl Ether	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○



Previous Cargo Product	Test Solution (ppm)	Odor	UV Test			
			220nm	260nm	275nm	350nm
Iso Propyl Ether	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○
Ethyl Acetate	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○
Cellosolve Acetate	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○
Butyl Acetate	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○
Vinyl Acetate Monomer (VAM)	5	X	X	○	○	○
	10	X	X	○	○	○
	20	X	XX	○	○	○
	50	X	XX	○	○	○
	100	X	XX	○	○	○
Methyl Acrylate	5	X	○	○	○	○
	10	X	X	○	○	○
	20	X	X	○	○	○
	50	X	XX	○	○	○
	100	X	XX	X	○	○
Methyl Methacrylate (MMA)	5	X	XX	○	○	○
	10	X	XX	○	○	○
	20	X	XX	○	○	○
	50	X	XX	○	○	○
	100	X	XX	X	○	○
Ethyl Acrylate	5	X	○	○	○	○
	10	X	X	○	○	○
	20	X	X	○	○	○
	50	X	XX	○	○	○
	100	X	XX	X	○	○
2-Ethyl Hexyl Acrylate	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	X	○	○	○
	50	X	XX	○	○	○
	100	X	XX	○	○	○
Trichloroethylene	5	○	XX	○	○	○
	10	○	XX	○	○	○
	20	○	XX	○	○	○
	50	X	XX	○	○	○
	100	X	XX	○	○	○

TABLE A continued

Previous Cargo Product	Test Solution (ppm)	Odor	UV Test			
			220nm	260nm	275nm	350nm
Perchloroethylene	5	○	XX	○	○	○
	10	○	XX	○	○	○
	20	○	XX	○	○	○
	50	X	XX	○	○	○
	100	X	XX	X	○	○
Ortho Nitro Chloro Benzene (ONCB)	5	○	XX	X	X	○
	10	○	XX	X	XX	○
	20	X	XX	XX	XX	○
	50	X	XX	XX	XX	○
	100	X	XX	XX	XX	○
Tallow	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	X
	50	X	X	X	X	X
	100	X	X	X	X	X
Fish Oil	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	X	X	X	X
	50	X	X	X	X	X
	100	X	XX	XX	X	X
n-Decane	5	X	○	○	○	○
	10	X	○	○	○	○
	20	X	○	○	○	○
	50	X	○	○	○	○
	100	X	○	○	○	○

*Odor : Result of smelling test by five persons.

Mark "X" denotes that one or more persons smelt any foreign odor.

*UV Test	220nm	260nm	275nm	350nm	Judgment	Mark
Over 70%	Over 89%	Over 90%	Over 98%	Acceptable	○	
50~70%	69~89%	70~90%	70~98%	Bad	X	
Under 50%	Under 69%	Under 70%	Under 70%	Unacceptable	XX	



Methanol (Methyl Alcohol):

Clear, colorless, mobile liquid ; miscible with water and almost all kind of organic solvents. The use of cargo is mainly the material for production of “Formalin” , “Acetic Acid” , “Methyl Acrylate” and other secondary chemical products. However, its specifications cover a wide range of items including the very severe one of chlorine whose content is sometimes set at 0.1ppm max (the situation is same with the fiber grade MEG).

It is also important to note the potassium permanganate test (PPT) done to Methanol (and also Acetone but rarely to other chemicals).

The test is to detect the presence of reductive substances by measuring the length of time for fading of purple color of the sample by the addition of potassium permanganate solution. It is also called “chameleon test” as measuring the change of color. If for instance, iron, unsaturated compound, olefin, acrylate or aldehyde is contained in the test samples, the purple color of the samples disappears. Some examples of the tests carried out by a reliable Japanese laboratory are shown in the “Table B”.

TABLE B

Name of sample	Conc. of sample in MeOH (ppm)			Remarks
	100	50	10	
Acrylonitrile (AN)	X	X	X	Discoloration in 30 minutes.
Cresylic Acid	X	X	X	Discoloration in 30 minutes.
Styrene Monomer (SM)	X	X	X	Discoloration in 30 minutes.
Methyl Methacrylate (MMA)	X	X	X	Discoloration in 30 minutes.
Propylene Tetramer (PT)	X	○	○	
Sanflower Oil	X	X	X	Discoloration in 30 minutes.
Cotton Seed Oil	X	X	○	Discoloration in 30 minutes.
Soy Bean Oil	X	X	○	
Tallow	X	X	X	Discoloration in 30 minutes.
Palm Oil	X	X	X	Discoloration in 30 minutes.
Linseed Oil	X	X	X	Discoloration in 30 minutes.
Sperm Oil	X	○	○	
Phenol	X	○	○	
Cresol	X	X	X	Discoloration in 30 minutes.



B) Examples / types of accidents:

With regard to both cargoes, the most reported accidents are incurred by *contamination with the previous cargo, the second largest cases by ingress of sea water through the manholes and the less frequent are the cases incurred by deficiencies to the tank construction* (cracks, holes etc.).

Such cases occur most to MEG, where the contamination is detected by means of UV test to prove insufficiency of tank cleaning. The above-mentioned Table A shows many of the cases where the cargo fails to pass both odor test and UV test, but it happens that some cargo passes odor test and fails to pass UV test. This is caused by the usual method of tank cleaning where the cleanliness of tanks is checked and approved by smelling. In the case of most chemicals (solution) the surveyor approves the tank so far as it is free of odor, without remains of cleaning water and sufficiently dried.

However, for loading MEG or Methanol which requires UV test or PPT, the tank cleanliness survey is more severely done, where in addition to the surveyor's visual inspection, "Wall Wash Test" is sometimes carried out as physicochemical analysis to spray samples of Methanol to all tank walls, then recover the liquid and detect whether or not it contains any residue of "previous cargo".

Further, it is a general practice to test the tank condition by "One Foot Loading" in which such residues as unidentifiable through visual inspection in the pipelines can be detected. In spite of "Wall Wash Test" and "One Foot Loading Test" done at loading port, the cargo may sometimes fail to meet the specifications on discharging, which in most cases is caused by contamination with previous cargo remaining in the tanks and pipelines. Special care should be paid to the tank cleaning done at the ports of cold climate because some chemicals are apt to freeze in the pipelines.

Methanol is now mostly carried in large lots by "Methanol Tanker" devoted to the trade, therefore the cases of contamination with previous cargo have been remarkably reduced, but the smaller lot of cargo is still carried by normal chemical tankers where the risks of contamination exists. Furthermore, even when Methanol is carried by the "Methanol Tanker", the ingress of small amount of seawater into tanks through manholes or butter-worth holes may cause troubles because chloride content of the cargo is one of the critical items of the trade specification.

C) Preventive measures for contamination:

In addition to the performance of sufficient and adequate tank cleaning before loading MEG and Methanol, one will have to be aware of many problems in order to meet their specification different from and severer than those of ordinary chemicals. It is important for carriage of chemicals to choose the method of tank cleaning most suitable for the cargo, depending on the nature of previous cargo loaded in the tank. Thorough investigations into its property and compatibility with the cargo to be loaded will be essential. In case of heating required, careful checks should be made to the adjacent tanks in order to avoid any damage occurring.

1-Tanks to be loaded : Such products as shown by the abovementioned tables are not compatible with MEG or Methanol and should not be co-loaded. The use of stainless steel tanks is preferable to facilitate tank cleaning operations except for carriage by "Methanol Tanker".

2-Structures in tanks : The function of tank washing machines has been greatly improved, and they are capable of spraying cleaning water on all surfaces of tank walls, but are sometimes unable to cover the back side of pipelines, joint part of flanges, valves, etc. Therefore, it is necessary to check the final



conditions at these structures. Special attention shall also be paid to submerged pumps which may leak oil on rare occasions.

3-Structures outside tanks :The foreign odor of previous cargo may sometimes remain in packing of manhole or butter-worth holes, so they must be replaced by new ones. It is also necessary to check closure of manholes and butter-worth holes after loading to prevent seawater ingress (due to severe chloride content on specification). After closure, it is recommended to cork them with Teflon and cover with canvas. In case of any bad weather foreseen, it may further be necessary to cover the top of vent line.

4-Requirements at the final stage of tank cleaning :As strictly required by the specification for suspended matter, it should be avoided to use any material causing remains of waste thread in tanks. For removal of dust on the tank top, adhesive tapes should be used.

5-Chloride contained in cleaning water :The chloride content of the fresh water used for tank cleaning varies according to the place and season. In case the fresh water of comparatively high chloride content is used, the cargo may not pass the tests. It is recommended that the crew should carry out steaming of the tanks whenever high chloride content of water is suspected as it is useful to remove chloride and odor (steam itself seldom contains chloride).

6-Wall Wash Test :As previously stated, absence of odor in the tank does not necessarily mean that the tank is suitable for loading. "Wall Wash Test" will be most effective to eliminate the risks of contamination or, at least "Water Solubility Test" will be useful to check remains of previous cargo. If the tank fails to pass this test, there may also be possibilities of failing in other items of specification, necessitating re-cleaning of the tank.

The following is a brief introduction of the method of Wall Wash Test and its standard.

Wall Wash Test:

Tank wall area to be washed by Methanol : $0.25M^2 * 4$ walls / tank

Methanol volume to be used for washing : 1 liter in total for 4 walls

Acceptable limit – chlorine increased : 2 ppm max

Appearance : Clear and free of suspended matter

Water miscibility test : Pass sales specification

Permanganate time test : Pass sales specification

