Carriage of sensitive chemical cargoes

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Wall-wash surveys serve to provide information on tank bulkhead cleanliness, while first-foot surveys provide information on shoreline and vessels' pipeline condition.

Modern-day chemical carriers are capable of safely carrying a wide range of chemical commodities amounting to more than 5,000 different cargoes and grades of material.

While the majority of these commodities are relatively easy to handle and do not demand any special quality requirements, there are certain groups of cargoes that, because of their chemical properties, impose greater handling requirements upon tanker owners, shippers and receivers alike.

Handling requirements – general points to note

Temperature

Certain cargoes demand close control of temperature – heating (e.g. edible oils), cooling (e.g. isoprene monomer) or control of the headspace atmosphere, by either the total exclusion of oxygen (e.g. propylene oxide/hexamethylene diamine-HMD) or partial reduction of oxygen to a proscribed range (as for oxygen-dependent inhibited cargoes such as styrene and isoprene monomers).

Moisture

Exclusion of water might be required, as is necessary for MDI/TDI (methyl and toluene di-isocyanates) and monoethylene glycol (MEG) cargoes, or tank cleanliness may be required to ultra high standards in order to prevent trace contamination by residual organic and inorganic species. Cargoes requiring such high standards include MEG, HMD, methanol, ethanol and products intended for human consumption and end-use in the pharmaceutical industry.

Cleanliness

Generally a high standard of tank cleanliness is required for any chemical commodity and, typically, preloading surveys of the vessel's containment system – tank/pump/heating equipment/lines – include both visual inspection and wall-wash survey prior to the loading of a 'first-foot' trial quantity of cargo. However, for tankers having cargo tanks coated with epoxy-type lining systems, the wall-wash and first-foot survey methods may not necessarily detect previous cargo species that have absorbed into the coating itself. Consideration should therefore be given to cargo sequencing or exclusion of certain tanks, and it is recommended that specialist advice be sought. This consideration does not, of course, apply to tankers with cargo tanks fabricated from marine stainless steels and some of the latest generation of non-epoxy coatings.

Handling requirements – specific cargoes

Monoethylene glycol (MEG)

MEG is a precursor commonly used in the manufacture of polyester and PET resins, with global production for 2015 expected to be in excess of 28m tonnes. The quality parameters critical for the shipment of MEG are water, ultra violet transmission (UVT) and chloride. MEG is hygroscopic, meaning it will readily absorb water from the atmosphere and, as such, an increase in moisture content in the first-foot sample is expected. The unwanted presence of aromatic hydrocarbon species (benzene, toluene, xylene, etc.) has a significant adverse effect upon the UVT parameter, even at parts per million (ppm) concentrations (<5ppm). Such aromatic species can be retained in the vessel's epoxy tank coatings in sufficient concentrations to render

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the cargo's UVT off specification. The carriage of MEG in epoxy-type coated tanks following immediate previous cargoes of aromatic hydrocarbons is therefore not recommended.

Pure MEG has a UV absorption peak at approximately 180nm, and the presence of impurities can increase this wavelength to around 190nm – 250nm. Therefore, when measuring UV transmission, the presence of aromatic or oxygenate impurities causes a reduction in the transmittance measured at 220nm, 275nm and 350nm, with measurements at 220nm being the most affected wavelength and most indicative of contamination. Sabic, the largest exporter of MEG, lists a minimum transmittance of 70% at 220nm, 90% at 275nm and 98% at 350nm, which can be accepted as an industry standard.

However, some deterioration of the UV parameter can occur during the voyage regardless of contamination, primarily caused by contact with oxygen; therefore, a UV transmittance of roughly 75% or more at 220nm before loading is ideal to ensure the cargo remains on specification at the point of discharge. The use of nitrogen blanketing is important in order to reduce oxygen exposure (see following article for further information on nitrogen blanketing). Reducing the number of transshipments between loading and end point delivery can also keep deterioration to a minimum.

The standard used for measuring UV transmittance of MEG is ASTM E2193 – 08. A spectrophotometer is used to measure absorbance at the specified wavelengths, first using water as a reference cell, then using the test sample. The specification % transmittance can then be calculated using the cell absorbance and recorded sample absorbance.

After the initial measurement, the sample may be sparged with nitrogen, by passing nitrogen bubbles through the sample for 15 minutes. Sparging should remove the effect of oxygen complexes on transmittance, which can help indicate the level of other contaminants such as aromatics. Sparging will, however, give a significantly higher transmittance level from the elimination of oxygen, and the bubbling of gas through the sample may release some volatile impurities, such as benzene, giving a high transmittance that may be unrepresentative of the sample. For this reason, it would be prudent to use the unsparged transmittance during loading in order to prevent a false on-specification reading that could lead to later rejection of cargo.

Styrene monomer (SM)
SM falls under a group of cargoes known as 'inhibited monomeric cargoes', which also includes isoprene monomer. Monomeric cargoes require the presence of an inhibitor to avoid polymer formation. Sufficient amounts of inhibitor must be present and cargo cannot be exposed to any heat. Stowage of inhibited cargoes at elevated temperatures will lead to an increased consumption rate of the inhibitor as well as an increased rate of dimer formation. The formation of dimer (the product when two monomers join) is inevitable, but can be minimised by ensuring that the product is carried at the coolest practicable temperature. Attention to the oxygen content of inert atmosphere is critical as the inhibitor is oxygen-dependent for effective inhibition and the charterer's/shipper's instructions to maintain oxygen content of the 'inert' headspace should be followed.

Phenol
Phenol has a propensity to discolour from colourless to a yellow if exposed to high heat and air. Carriage and replenishment of nitrogen overpressure is recommended during carriage and following part discharge operations to avoid oxygen ingress. Care should be taken to avoid overheating the

cargo, and detailed heating and tank atmosphere (pressure/O_2 content) records should be retained. Samples should be carefully stored in cool, dark places out of direct sunlight.

Methanol
Methanol is the highest volume chemical commodity shipped worldwide and is used principally in the manufacture of formaldehyde resins. It is shipped as an ultra high-purity chemical, so the presence of water and trace contaminants, especially inorganic chloride, are unwelcome. As such, particular attention should be given to tank cleaning operations. (Further information on tank cleaning can be found on *page 23*.) An increasing amount of methanol trade is performed using dedicated tankers, eliminating these cross-contamination concerns.

Ethanol
Ethanol can be shipped as either '96% pure' potable grade or '99.8% pure' for fuel blending purposes. The key sensitive quality parameters associated with each differ in that water is most crucial for the 99.8% pure grade, while the presence of organoleptic taint (smell and odour) is crucial for the potable 96% grade. Due to the organoleptic requirement, attention should be given to sequencing and tank cleaning.

Ethylene dichloride (EDC) and acetone
Both grades are water critical and sensitive to the presence of trace contaminants. Tank preparation should be thorough and avoid the inadvertent introduction of condensation or free water via improperly prepared cargo tanks and/or pipelines.