Article: The Formation & Testing of Sludge in Bunker Fuels

By Dr Sunil Kumar

Laboratory Manager - VPS Fujairah

15th January 2018

Introduction

Sludge formation in bunker fuel is the source of major operational problems for the ship-owner. This paper explains the processes by which sludge may be formed and how testing the bunker fuel can help to prevent these problems.

Sludge can be a combination of hydrocarbons, asphaltenes, resins, paraffin's, water, sediments and bio-mass produced by bacteria and oxidized or polymerized material. It may arise as a result of various causes such as:

1. Blending with non-compatible fuels of the same matrix or different matrix
2. Decrease in the aromaticity of the fuel by blending with paraffin rich oil, which can lead to the formation of unstable asphaltenes, which fall from the fuel solution.
3. Addition of incompatible waste oils
4. Agglomeration of inherent organic compounds in the fuel due to physical or chemical grounds
5. Presence of high concentration of asphaltenes and high molecular weight waxes
6. Formation of insoluble compounds during the production of the fuel
7. Presence of significant concentrations of oxygen based compounds to promote oxidation
8. High concentration of unsaturated hydrocarbons to promote the formation of long chain polymers
9. Microbial Contamination

The sludge formation mechanism is very complex in nature, with the affected stability of a fuel creating numerous operational problems, such as blockage of filters, centrifuges, pipes, service tanks, damage to pistons, rings, liners and combustion difficulties etc. Compared to many petroleum products, fuel oil has a relatively complex chemistry and yet only a general compositional study has been done so far to understand these issues in detail, especially with respect to high boiling fractions.

Incompatibility between fuels arises as a result on the aromatic (asphaltenes/resins) and paraffinic nature of the fuel. The chemistry of asphaltenes is highly complex and this plays a major role in maintaining the stability of a fuel. The stability or instability depends upon the asphaltene to resin equilibrium which may become disturbed due to the presence of a considerable concentration of paraffins. Inappropriate blending can create problems with the stability of the fuel by disturbing the asphaltene to resin equilibrium, resulting in the aggregation of colloidally dispersed asphaltenes forming sludge.

Sludge formation in fuel can also arise from the presence of compounds which are capable of undergoing oxidation or polymerization. These compounds may not be the naturally occurring compounds present in the fuel but can result from the fuels used for blending (eg.cutter stocks, used lube oils, biofuels etc.). When fuel is stored for a longer period, various factor like heat, oxygen and water can also influence the formation of unstable molecules which may react with certain compounds present in a stable fuel.

Preventative Fuel Testing

There are various test methods which predict the tendency of the fuel to form sludge. Although some of these are detailed in the ISO8217 standard (Specification of Marine Fuels), many are not. It is important to distinguish between fuel stability, which is the potential for the fuel to change condition in certain circumstances depending on its resistance to breakdown, as compared to fuel compatibility, which is the tendency for the fuel to produce deposits when mixed either prior to bunkering or on board ship. A summary of fuel tests that may be applied to determine the tendency to form sludge are given below.

Compatibility

Compatibility test identifies the incompatible nature of fuels or blends that could lead to sludge formation resulting from excessive centrifuge loading, plugging etc.

Total Sediment Existent

Existent sediments are the total organic and inorganic matter which are not soluble in the fuel oil matrix. These insoluble sediments can accumulate in storage tanks, filter screens, burner parts, etc.

Total Sediment Potential (Thermal Ageing)

Thermal ageing can determine whether sediments can precipitate from the fuel oil matrix during storage and handling.

Total Sediment Accelerated (Chemical Ageing)

Chemical ageing determines the equilibrium between the aromaticity of the asphaltenes and available aromaticity of the oil phase by introducing a paraffinic solvent which in turn gives the probability of asphaltene precipitation from the fuel.

Separability Number

Separability number (SN), also referred to as reserve stability number (RSN), indicates the resistance of a residual fuel oil to form sludge. Separability number determines the extent an oil phase separates from the colloidally aggregated asphaltenes upon the addition of a paraffinic solvent. High separability number is an indication of asphaltene aggregation resulting a poor stability reserve of the oil.

Separability number is an excellent accompaniment to the routinely hot filtration methods. It can identify potentially troublesome fuels (unstable) even when the HFT method is indicating a low sediment content. Conversely, it may indicate that a high sediment fuel is in fact quite stable and unlikely to form sludge. This information in combination, is extremely useful from an operational perspective, as it will indicate in advance if and what mitigation steps are appropriate.

Asphaltene Content

High asphaltene content fuels have the greater tendency to form sludge especially when blended with incompatible hydrocarbons. If the paraffinic nature of the hydrocarbon medium increases then the asphaltene separation may occur.

Wax Content

When substantial concentration of waxes are present in the fuel especially high molecular weight waxes, there may be a tendency to form sludge. Wax separation can occur when the aromaticity of the hydrocarbon medium increases.

Vacuum Distillate and Bromine Number

Bromine number is useful as a measure of aliphatic unsaturation in petroleum samples. The indication of high concentration of olefins in the vacuum distillate of the heavy fuel oil may give an indication of the possibility of the polymer forming tendency in the fuel.

Toluene/Xylene Equivalents

Toluene and Xylene equivalents are used to determine the stability of heavy fuel oils. It is the lowest added aromatic solvent concentration of the solution where asphaltenes are not precipitated.

Microbial Contamination

Bacterial growth can lead to the production of sludgy biomass and acids. Biomass clog the filters and acids cause corrosion.

Biofuel (FAME)

The presence of significant concentration of biofuel and water in the fuel can facilitate microbial growth which can lead to sludging and thereby filter clogging.

Gas Chromatography and Mass Spectrometry (GCMS)

VPS has identified various unusual chemical contaminants in fuel oils which can promote sludging especially the presence of unsaturated compounds that can lead to the formation of polymers if present in significant concentration. These chemical contaminants are present individually or in combination with different functional groups that can have an impact on the sludge formation. The presence of such type of unusual chemical contaminants identified by GCMS method is then correlated with ship experienced operational problems.

VPS has extensive knowledge in the identification of unusual chemical contaminants present in the fuel oil and various GCMS processes like screening head space method, extended head space method and comprehensive method are involved in the identification of such type of chemical contaminants.

Solid Contaminant

This test is for the determination solid contaminants in the fuel oil like polypropylene, polystyrene, polyethylene or other synthetic fiber particles, beads and fibers as well as high melting wax.

Fourier Transform Infrared Spectrometry (FTIR)

FTIR may give information on the presence of oxygen based organic groups which may promote oxidation if present in considerable concentration.

Problem-Solving After Sludge Formation

When fuel has not been tested for stability prior to the use and forms a sludge which then requires characterization to determine the cause a number of tests can be useful. The ISO8217 standard (Specification of Marine Fuels) is not designed to address such circumstances and accordingly does not contain these test methods. VPS uses a various in-house procedures and investigations based on experience in order to identify the nature of the sludge formed as detailed below:

Physical nature of the sludge

Evaluate the solid, semi-solid, emulsified or partially emulsified appearance of the sludge

Solubility Characteristics

Solubility properties of a sludge may also indicate if its of organic or inorganic in nature. The sludge can either be dissolved in the hydrocarbon medium or separated from the organic medium.

Insoluble material separation

Treating the sludge with a suitable solvent then separating the insoluble material by centrifuging/filtration or other means for further characterization

Organic and Inorganic nature of the sludge

Ash and elements determination may give identify the organic and inorganic nature of the sludge.

Asphaltenes and Waxes

Presence of asphaltenes and waxes may provide valuable information on the cause of the sludge

Microscopic evaluation on the sludge separated from the oil

Microscopic evaluation may give an indication of the physical nature of the solid contaminant such as strands of fibers, wax, inorganic sediments, and carbonaceous material. The following

figures show a few examples of solid contaminants separated by VPS Labs from the sludge and fuel oil.

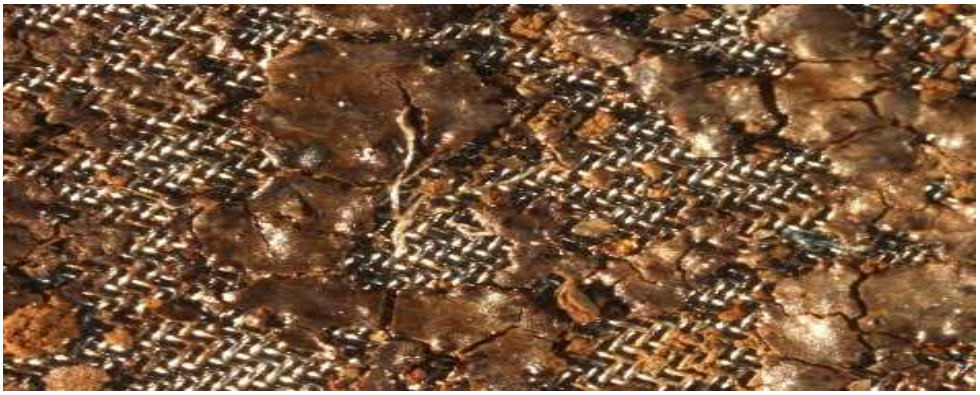

Figure 1: Polyethylene terephthalate separated from a sludge

Figure 2: Scattered mix of light and dark coloured solids with few strands of fibers separated from the fuel oil

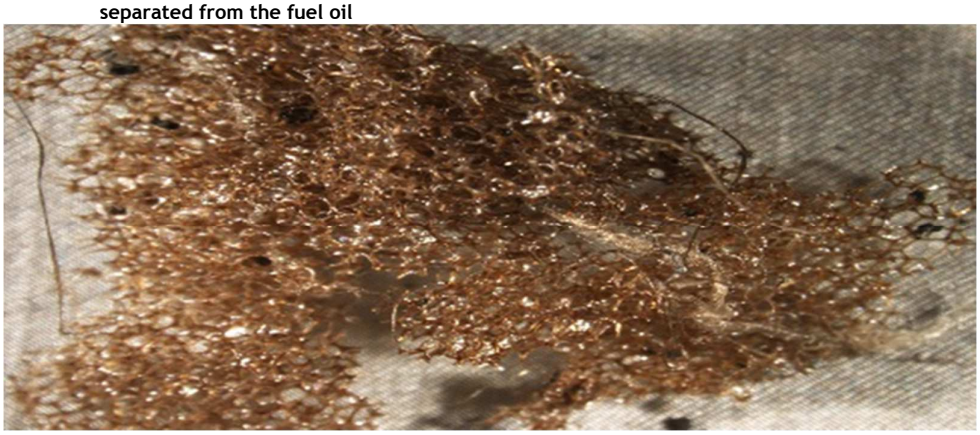

Figure 3: Golden yellow fiber like spongy material separated from a sludge

Figure 4: Poly methyl methacrylate and dispersed mix of dark coloured solid masses and inorganic matter separated from a fuel oil

FTIR on the sludge separated from the oil

FTIR analysis on the sludge separated from the oil may also give information on the organic/polymeric/waxy nature of the sludge.

Melt test to differentiate Polyethylene polymer and wax

Since both petroleum wax and polyethylene polymer have similar structural characteristics (polymethylene groups), a combination of FTIR and melt test may help to identify whether the separated solid is a polyethylene or wax.

Conclusion

In order to prevent fuel stability problems, it is always recommended to analyze the fuel prior to use. This will help to determine potential incompatible behavior of the fuel and the possible tendency of the fuel to form a sludge. By knowing such possibilities, major ship engine break down may be prevented. Also it is important to characterize the sludge already formed to know the cause so that decision may be made what to be done to the fuel for further use.

Dr. Sunil Kumar
Laboratory Manager
VPS – Fujairah
Sunil.kumar@v-p-s.com

VPS also offers additional tests beyond the standard ISO8217 scope that can help ship owners and managers remove even more risk from their operations. Contact your local VPS office or http://www.v-p-s.com/contact-us/ *to explore what more can be done to manage your risks.*