

1/19/2012

## Summary

Finding the right treating solution to remove impurities from hydrocarbon streams is a challenging task for any refiner and one of the chief research scientists from the Merichem Company found the FreshAWL chemistry as an interesting and plausible solution to assist in their processing systems for the removal of Mercaptans from RSH (Mercaptan Laden) Kerosene.

FreshAWL® FUEL-WASH™ is the mercaptan scavenger answer to help restore crude oils and fuels to optimal mercaptan levels. FUEL-WASH would also prove to remove highly concentrated levels of mercaptans from the Merichem samples of RSH Kerosene. FUEL-WASH would also show a separation of the remaining mercaptan free sample into reusable kerosene along with reclaimable sulfur.

By using FreshAWL solutions in hydrocarbon treatment systems there are additional value benefits of:

- Reduction of the mercaptan along with H<sub>2</sub>S and sulfur compounds in RSH kerosene
- Corrosion inhibition
- Improved environmental impact through use of non-toxic treatments
- Safety of non-hazardous chemical usage and storage

## Introduction

The FUEL-WASH chemistry and the treatment methodology for removing mercaptans from kerosene solutions, more specifically, the RSH Kerosene that was provided by Merichem was able to consistently achieve better than 90% mercaptan removal.

Research reveals that currently utilized fuel washing processes are only able to obtain from between 10-20% mercaptan removal.

The FUEL-WASH processing has been refined to prove that variable factors are needed to finalize the successful mercaptan removal and separation results including:

- Contact time
- Agitation time,
- Mixing methodology
- Incorporating air into the FUEL-WASH™/RSH Kerosene mixture

A multifaceted methodology is required to achieve the 90% reduction levels including:

- Wetting
- Activation
- Creation of emulsified chemical
- Solubilizing/De-solubilizing of chemical versus kerosene
- Solubilizing/De-solubilizing of mercaptan from kerosene (to air or water)
- Creation of a rag layer
- Split of the kerosene fraction from the reacted mercaptan
- Optional split of the mercaptan layer from the chemical treatment (third layer sulfur compound)

Although the method is multifaceted it is not complex. In fact, another positive feature of FUEL-WASH is its ease of use.

## Conclusion

FreshAWL has worked into the fuel washing methodology the conclusions that the ratios of the reactants will modify the process effectivity and efficiency.

Also, the period of inactivity after reaction between the mercaptan-laden fuel and FUEL-WASH finishes the mercaptan removal process by forming a polymer that congeals into a separate layer. This occurs through a selective volatilization of the mercaptan that keeps the kerosene layer intact. The addition of water was utilized for activating the surfactant, which reactivates the reaction when it has ceased the initial mercaptan reaction.

One of these processes results in the recovery of a special third layer yielding very promising results. This third layer, which appears congealed and amber in color, develops when the reaction mixture is at the 20/50 addition level to the mercaptan laden fuel (20 parts FUEL-WASH diluted with water at 1:1 and 50 parts mercaptan laden fuel) then subjected to temperatures of 50° F or lower.

The temperature and concentrations of reactants saturate the FUEL-WASH causing a salting out of some of the reacted sulfur polymer-like residue. Independent laboratory analysis of this layer of sulfur yields a concentration of 1,900 ppm (see attached lab report). Considering the weight and contamination rate of the solution, this correlates to between 35-60% of the mercaptan present in the fuel tested.

Odor levels on the reacted FUEL-WASH suggest that any mercaptan that has been reacted continues on to this polymer-like material. This sulfur-gel material can be soluble or less than soluble in the water layer, depending on temperature and concentration. Color in the reacted FUEL-WASH betrays this residues presence (it was darker in color) and had virtually no mercaptan odor. It is the exposure to colder temperatures that was the key for separating this sulfur polymer from the reacted mixture.

The entire matrix here appears to rely on two major issues; solubility and reactivity. Having addressed some of the reactivity issues, here are the solubility issues that need to be considered:

- When more air is made soluble in the matrix, a better reaction and neutralization of mercaptan occurs.
- When the surfactant presence is too low or too high, the contact with the mercaptans and the association with the kerosene and solubility of the kerosene in the water becomes an issue:
  - If the mercaptans are reacted they become less soluble in the kerosene layer and appear to fall to the bottom, or at least into the water/chemical matrix.
  - If the addition of the chemical matrix and surfactant is too large, then the mercaptans remain soluble in both layers and separation does not occur.
  - When the chemical matrix is at one level the mercaptans stay with the chemical layer at which point a third layer is formed.
- When not enough time is allowed for settling, some of the mercaptans will remain in the kerosene layer.



Reaction time is also a key factor:

- When the kerosene layer is immediately centrifuged after 20 minutes of shaking and the kerosene is separated from the chemical matrix, the kerosene achieves a minor level (goal) mercaptan reduction, approximately a 20% reduction.
- When allowed to sit for a 24 hour period, the level of reduction increases 300%, equating to a mercaptan reduction of 60%, and this increase is achieved without further agitation or chemical addition.
- Furthermore, when it was allowed to sit for an additional two days and then three days the mercaptan reduction increases to more than 90%.

During these different time tests the kerosene weight was checked. Although there was no measurable weight differential the foul odor reduced to an immeasurable level on day 3. However, there was a scent. It was cherry almond aroma of the FreshAWL FUEL-WASH, which shows that it is the active ingredient remaining in the kerosene layer continuing to react with the mercaptans.

While Merichem was impressed by the efficacy of FUEL-WASH, they decided that their resource focus would need to continue on the existing technologies of their core process components.