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**Question 58: In your experience has a non-phosphorous corrosion inhibitor been successfully used to mitigate naphthenic acid corrosion? In what circumstances and under what conditions are non-phosphorous corrosion inhibitors used?**

**Doug Meyne (Champion)**

Phosphorus-based naphthenic acid corrosion inhibitors have been successfully used in the refining industry since the early 1980's. Phosphorus provides its protection to steel by corroding it and forming a passive layer that, under SEM/EDS, proves to be an Iron/Phosphorus/Sulfur blend. With rare exception, the protection comes from high TAN liquid attack of the affected metal, which is a good match for non-volatile filmers in pump-arounds like an HVGO. However, when there are zones being attacked by condensing naphthenic acids, the opportunity for contact, and hence mitigation by the inhibitor, is impaired. The P-S-Fe bond is pretty tenacious, with a bonding energy higher than the activation energy for naphthenic acid corrosion. In addition, this bonding is also effective at dispersing existing FeS in a dirty system which can result in downstream fouling issues and/or pluggage of HDS reactor beds. Naphthenic acid corrosion occurs from ~500F to ~650F. non-phosphorus inhibitors can work, but those in commercial use have temperature limitations. Their bonding energy is much lower than the phosphorus-based products, and at elevated temperatures (> 500F) they are simply inefficient at adsorption. Non-phosphorus inhibitors have been successful at the lower end of the temperature range in atmospheric columns. Products that also have a sulfur component are largely dependent on their sulfidation capability for resistance. The controlled application of a reactive sulfur causing sulfidation can be helpful in the sweeter acidic crudes, such as some of those coming out of western Africa with less than 0.5% sulfur. However, their effectiveness is substantially reduced when the crude already has sufficient H<sub>2</sub>S to create and maintain a thin sulfide layer, and they are ineffective in crudes that produce enough H<sub>2</sub>S to cause sulfidic corrosion.

**Jim Johnson (Marathon Petroleum)**

We use phosphorous based inhibitor at one of our refineries and have phosphorous based inhibitor on hand at another, but not using. We have no experience with a non-phosphorous inhibitor.

**Sam Lordo (Nalco Company)**

Nalco has successfully applied sulfur based high temperature corrosion inhibitors to mitigate naphthenic acid corrosion in all streams affected by naph acid, sidestreams, tower bottoms and in a few cases furnace transfer lines since 1992 using patented chemistries. The protective barrier formed by a sulfur-based inhibitor is not as persistent as the phosphorous based product so the use in these is recommend

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in high shear areas such as vacuum furnace transfer lines.

Nalco routinely uses this product when there is concern, valid or not, of downstream phosphorous impacts if a phosphorous inhibitor is used. The sulfur-based products are also used when the circuit to be protected contains fuels such as diesel or jet.

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