FILM FORMING AMINES AND THEIR APPLICATIONS IN THE POWER PLANT INDUSTRY

Introduction

Use of Film Forming Amines (FFA) or Film Forming Amine Product (FFAP) is a growing trend in the power industry for maintenance of boiler systems. Case study literature suggests FFAPs offer protection from corrosion, reduce corrosion product transport, provide smooth heat transfer surfaces, and protect equipment during shutdown or layups. FFAPs can be used with or replace conventional corrosion inhibitor treatment regimes. FFAPs are used in various kinds of steam-generating power plants including conventional fossil, combined cycle, nuclear, and biomass power plants. They are also applied to different components of the steam cycle including the boiler feedwater, generator, and condensate return lines. As water treatment chemical vendors continue to expand their product offerings, FFAP formulations are being customized to suit the individual power plant's operational conditions.

FFAP Properties

FFAPs have a strong surface affinity for metals, forming an impermeable layer which prevents corrosive agents from contacting the surface. This binding behavior can be attributed to the chemical structures of FFAs, which are long carbon chains with an amine at one end. The amine "head" attaches to a metallic surface while the "tail" forms a protective hydrophobic film layer.

Octadecylamine (ODA) is an example of the simplest FFA molecule and is constructed from a straight chain of 18 carbons. ODA was the primary FFA in use over 40 years ago when it was first introduced. More complex FFAPs were introduced to the marketplace as ODA operational challenges began to be better understood. These newer FFA compounds contain various functional groups such as primary or secondary amines which branch off from the FFA backbone. They may be referred to as polyamines or fatty amines. As use of FFAs has grown, many chemical vendors have created their own proprietary FFAPs which are formulated with other amines as well as neutralizing and emulsifier agents.

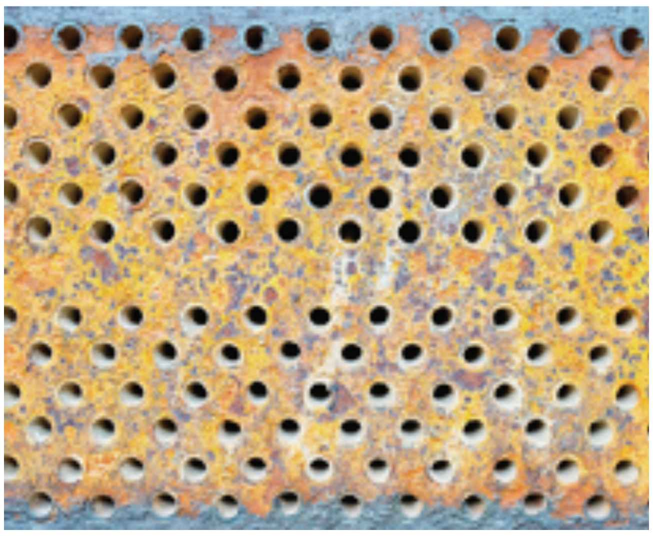
FFA Benefits

FFA technology has been shown to offer better heat transfer rates across steel tube surfaces than traditional phosphate-based corrosion inhibitor programs. Case studies in the literature also document improved bubble evaporation and the formation of smooth and homogeneous magnetite layers. FFAs will adsorb to the protective metal oxide layer and provide an extra barrier between it and the water or steam. Additionally, it has been shown that FFAPs remove loosely bound deposits within the boiler system resulting in cleaner surfaces overall. Together, these performance improvements can lead to reductions in operating costs.

FFAPs are usually touted as a greener alternative than conventional boiler treatment chemicals such as hydrazine. Since FFAs are relatively non-toxic, extensive personal protective equipment (PPE) is not required when working with these products.

FFA Pitfalls

While FFA treatment programs offer many benefits, some drawbacks are possible. A primary concern is the formation of FFA degradation products which are largely carbon dioxide and organic acids that form after extended exposure to high heat. These degradation products can lower the pH of condensed steam and increase Conductivity After Cation Exchange (CACE) unless compensated for by other water treatment methods. Another major concern is optimizing for the appropriate dosage. Overdosing offers no additional protection and runs the risk of creating micelles or "gunk balls" that can clog pipes and reduce efficiency. Supplier product and site-specific dosage rate recommendations should be followed.

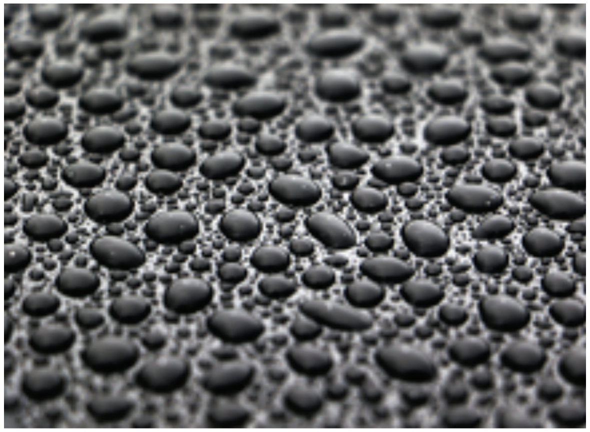


Preparations Before Switching to an FFA Program

It is important to establish baseline readings of key steam cycle performance indices before changing the treatment regimen. Without these reference points, plant personnel will not have the ability to validate quantitatively whether the addition of an FFA/FFAP has provided any benefit. Some of these key parameters include total iron and/or copper, feedwater pH, oxygen, and CACE. Also, inspecting interior surfaces for loose deposits and sludge on high pressure (HP) evaporators or conventional boiler waterwalls is recommended before starting a course of FFA/FFAP. If the deposits are not removed, under deposit corrosion may occur.

FFA Dosing

Once the decision has been made to begin using FFA, the primary focus shifts to establishing the optimal dosage. Usually FFAs are fed undiluted into feedwater through an automatic pump. When introducing FFA for the first time, it is recommended to start at a low dosage and gradually increase to the target dosage, which typically takes a minimum of 3 to 4 weeks. FFA/FFAP exert a moderate cleaning effect that can lift particulate deposits of iron and/or copper oxides within the system. These deposits should be monitored to assess the FFA cleaning period duration. The effect of the FFA dosage on the iron and copper must be compared to corrosion product control guidance published in the applicable boiler technical manual. Determining dosage levels should occur in conjunction with the chemical supplier to ensure that the product is compatible with the conditions and materials within the system. It is commonly found that no FFA will be detected in the condensate phase initially as the FFA will bond to the metal surfaces and not be freely circulating.



FFA Sampling

Testing for FFA offers unique challenges as well. Since FFAs adhere to metallic, glass, and plastic surfaces, surface contact must be kept to a minimum when obtaining water samples. This means limiting sample transfer to a single container if possible; samples should be cooled to prevent flashing; sample lines should be flushed thoroughly before sampling; and sampling points should be representative of the system.

FFA Analysis

The two most common test methods for FFAs are methyl orange extraction and xanthene dye reaction. The methyl orange extraction method makes use of an organic solvent to extract the FFA to form a colored complex with the methyl orange. The xanthene reaction method utilizes a class of dyes (represented by Rose Bengal) that form a water-soluble colored complex with FFA. The FFA concentration is proportional to color intensity in both test methods. Commercially available test kits often express results in terms of common FFAs like ODA. For best accuracy, it is recommended that analysts determine a correction factor to express results in terms of the product specific FFA. Test kits that tolerate interference from ammonia or short chain amines and offer a wide measurement range to avoid dilution steps are preferable. Dilution can lead to a loss of FFA during sample transfer from one vessel to another which may affect test results.

CHEMetrics offers a Methyl Orange Filming Amine visual test kit, Cat. No K-1001, that can be used to verify residual FFA in a system in 3 minutes. This kit utilizes a unique extraction technique which eliminates several steps required in other procedures and provides increased sensitivity while limiting the extraction to a single extraction tube preventing FFA loss. If necessary, the measurement range can be extended by performing a dilution in the extraction tube provided in the test kit. Test results are expressed in ppm ODA. The color comparator increments are: 0, 0.05, 0.10, 0.15, 0.25, 0.50,1.0 ppm. Technical Support is available for customers who require assistance establishing a FFA correction factor.

For more information, refer to the CHEMetrics K-1001 Product webpage at: https://www.chemetrics.com/product/filming- amine-aliphatic-amine-visual-test-kits/

References

1. Hater, Wolfgang; Film_Forming Amines: An Innovative Technology for Boiler Water Treatment; The Analyst (Volume 22 Number 4)
2. The International Association for the Properties of Water and Steam; Technical Guidance Document: Application of Film Forming Amines in Fossil, Combined Cycle, and Biomass Power Plants; Sept. 2016.
3. Odar, Suat; Use of film forming amines (FFA) in nuclear power plants for lay-up and power operation; Advanced Nuclear Technology International, Sweden, Dec. 2017.
4. CHEMetrics Inc.; Version 4, Jun 2013, Film Amine (aliphatic amine) Methyl Orange Method Technical Data Sheet, Midland VA.
5. ASTM International, 1980, ASTM D 2327- 80, Mono- and Dioctadecylamines in Water, West Conshohocken, PA.

Author Contact Details

CHEMetrics Inc. • 4295 Catlett Road, Midland, VA 22728, USA • Tel+800 356 3072 • Email: technical@chemetrics.com • **Web: www.chemetrics.com**