Successful 'Green' Applications of Polyamine Emulsions in Industrial Water Systems

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Abstract

In 2006, *Odyssee Environment* was founded to develop and market innovative polyamine emulsion technologies for the prevention of corrosion, scale and deposition in industrial steam boiler, closed recirculating cooling water, and open evaporative cooling tower systems. A broad range of product formulations was developed and successfully evaluated in field studies under typical industrial water treatment conditions.

This paper summarizes *Odyssee's* experiences over the past nine years developing and successfully applying *Odyssee* industrial water treatments as alternative, viable and economically efficient water management approaches. Several documented case studies and program control procedures will be illustrated. Emphasis on the 'Green Technology' of this unique water treatment approach, improved heat transfer and energy efficiencies, and simplicity in applying and monitoring Polyamine Emulsion water management programs will be discussed.

Steam Boiler Water Treatment Applications

Odyssee's ODYVAP Boiler Water Treatments are based on unique polyamine emulsion technology that are both biodegradable and phosphate-free. Case Studies have demonstrated that *Odyssee's* product applications reduce steam generation costs, minimize the adverse consequences of carbon dioxide emissions into steam / condensate systems, save energy, and reduce makeup water consumption.

Many industrial steam boilers are currently being treated using antiquated technologies utilizing one or more of the following sub-treatment approaches:

- Inorganic phosphates as anti-scaling and/or alkalinity control agents.
- Inorganic sulfites to eliminate boiler and feedwater dissolved oxygen residuals, a dominant cause of pre- and post-steam plant corrosion.
- Hydrazine for oxygen control, accepting its associated health (carcinogenic) risks.
- Alkalinity control agents to maintain optimum boiler waterside pH's and minimize boiler metal corrosion.
- Neutralizing amine steam/condensate line treatments to control the corrosive effects of carbonic acid in post-boiler steam plant areas.

In larger steam plant applications, such broad and complex boiler treatment programs often require the use of multiple treatment additives with individual mix tanks and chemical dosing feed pumps and systems. Varying plant makeup water qualities and unique boiler operational characteristics often require precise application of feed equipment settings for accurate chemical control.

Odyvap Steam Plant Polyamine Emulsions

Odyssee's unique product line is based on proprietary blends of components containing:

- Long chain filming amines.
- Antiscalent and dispersing polymers to control and eliminate waterside sludges from accumulating and depositing on heat transfer surfaces.
- Neutralizing amines to aid in the establishment of boiler water alkalinities and to neutralize carbonic acid condensate systems and other post-boiler areas.

The selection and concentration of each additive is formulated into a stable polyamine emulsion for even the most technically demanding steam plant operation such as in high pressure boilers driving turbines.

For example, a single *Odyssee Odyvap* Boiler Water Treatment can be formulated to successfully treat a complete steam plant, from the feed water tank to the condensate return system. Such a multi-purposed product offers the following technical advantages.

- A single liquid product to address: Boiler waterside scaling; Boiler and steam/ condensate system corrosion; Boiler scale-free waterside conditions.
- A single liquid product application, requiring only dosing system.
- A single liquid product that is easy to control.
- A single liquid product that, when applied, avoids boiler water carryover caused by boiler water concentrations and dissolved solids accumulations.
- A single liquid product dosed directly into the make-up water versus the boiler feedwater, thus reducing the quantity of chemical required to treat a boiler and, hence, significant operating cost reductions based on reduced chemical costs environment impact costs).
- A single liquid product that neither contributes to, nor has any influences on, the mineral solids concentration effects within the operating boiler. This reduction of boiler water dissolved solids results in a decrease in the volume of waste boiler blowdown contributing to even a greater operating cost reduction through both water and energy reductions and reduced environmental impact.
- A single liquid product that improves boiler waterside heat transfer thus contributing to significant operating cost reductions in both energy environmental areas.

The use of *Odyvap* Organic Boiler Water Treatments have been demonstrated to significantly increase the heat transfer coefficients of boiler waterside metallic surfaces resulting in the creation of energy savings through improved overall boiler efficiency. These savings are established in:

- Improved waterside surfaces treated with organic chemistries;
- Increased overall heat transfer coefficients;
- Improved magnetite layer on the tubes;
- Minimized surface irregularities and roughness.

Three Beneficial Advantages of Long Chain Filming Amines

Scale Prevention – Long chain polyamines interfere with crystal growth at the first stages of crystal scale formation. The polyamines are absorbed on the micro crystalline surfaces during their earliest stages of growth, distorting the crystal matrix and rendering them incapable of further growth. The particulates that are formed exist as fluid sludges that are non-adherent to waterside surfaces and rendering them as easily dispersed sludge readily removed in boiler blow down.

Corrosion Prevention – Organic filming amines are chemical compounds that are capable of adsorbing on internal waterside surfaces forming a film that are very effective corrosion inhibitors. One such inhibitor can be represented by the generalized formula $R[NH(CH_2)_3]_nNH_2$. Where *R* represents a hydrocarbonated fatty chain with at least 12 atoms of carbon, but more often 18, the octadecyl- radical. *N* can represent values greater than or equal to zero, but generally less than seven. Although these amines are quite water soluble, they are generally applied as an emulsion. Any dilution must be avoided. A molecular model of a complex filming amine is illustrated in Fig. 1.

When applied to the makeup water, these filming amines will protect all metallic parts through the formation of monomolecular films in feedwater tank, the boiler and steam/condensate systems. They are applied independently of feedwater oxygen concentrations and temperatures, and percentages of condensate returns. The application of film-forming amines also controls carbonic acid corrosion issues in steam and condensate systems. Continued corrosion protection will continue even in the event treatment applications, often for several days. The careful selection of the filming amine can be used to predict the longevity of this protection period.

Formula : $R\text{-}(\text{-}NH\text{-}(CH_2)_3\text{-})_n\text{-}NH_2$

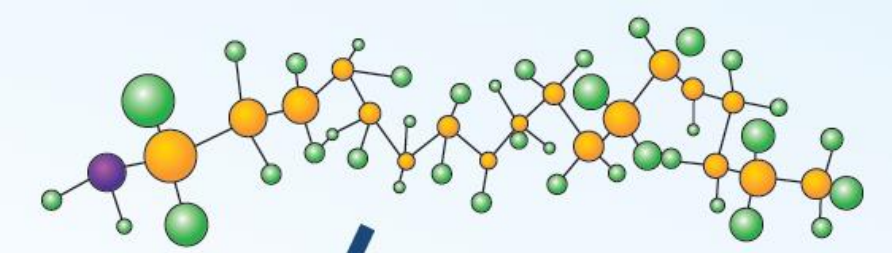

Fig. 1. A complex organic filming amine.

Two mechanisms are involved in the adsorption of filming amines are waterside surfaces.

Electrostatic adsorption – Is the relatively quick adsorption of the polyamines' cationic charge to the negative charges of the metallic surfaces. This attraction is independent of water temperatures.

Chemisorption – The filming amine makes metal surfaces hydrophobic, by moving the water molecules in contact with the surface. Then there is a charge transfer between the nitrogen atom and the atoms of the metal surface: pseudo-complex formation between nitrogen and iron atoms. This reaction depends on the temperature and is slower than the first reaction. Figure 2 illustrates simple electrostatic and chemisorption inhibition mechanisms.

Improved Heat Exchange – The strong metal affinity of filming amines enables the gradual removal of waterside deposits coming, optimizing heat exchange. All deposits, scales and weakly-adhering magnetite, especially when boilers have been previously treated with conventional inorganic based water treatment additives, are generally progressively removed. In addition, the hydrophobic effect of the film makes metal surfaces impenetrable to water films, improving steam condensation and energy transfer.

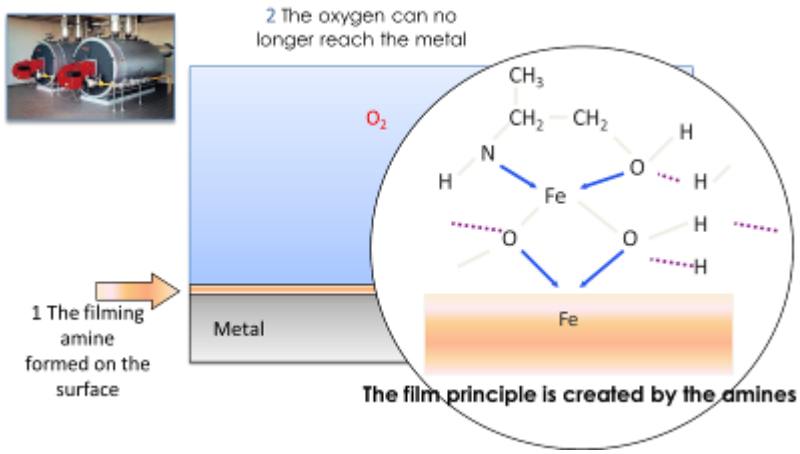

Fig. 2. Illustrations of simple filming amine corrosion inhibitory mechanisms.

Case Study Tredi Salsise France – In 2010 *Odyssee* implemented a boiler water treatment program at an industrial incinerator based in south of Lyon with several high pressure steam boilers, one of the largest plants of its type in France.

Fig. 3. Tredi Salsise France

Incineration of waste completely oxidizes the organic portion destroying all pathogens associated with the waste. The company supplies excess steam generated to local industries in the immediate vicinity of the plant (OSIRIS; Rhodia) or as electrical power generated from a 14.6 MW turbine generator. Any excess electricity is provided back to the ERDF electrical distribution network. Prior to 2010 the water management program for the facility utilized a similar single product approach utilizing older second generation Film Forming Amine (FFA) technology.

Odyssee's water treatment objectives were focused on two specific areas:

- Maintain condensate returns at a pH> 9.0.
- Optimize operating cost savings for energy, water and water treatment products.

Steam Plant Specifics – The plant has four steam boilers, each utilizing demineralized water as boiler makeup. The smaller two boilers provide steam for internal needs and plant distribution (12,000-pph each). The third boiler is rated at 24,000-pph and provides steam for general plant distribution as well

as to replace plant steam losses. The fourth boiler generates 130,000-pph steam @ 638-psi (44 Bars) for electrical power generation.

Steam Plant Objectives: Maintain Condensate Returns at a pH>9.0 – A careful review of alkalizing amine technologies ensured that condensate pH's would conform to customer requirements. The focus on our engineering review was aided, in part, by a thorough survey of the facilities, detailed analyses of the boiler feed water and other associated system water samples, and by *Odyssee Environment's* development work done on the volatility of amines. The length and complexity of the entire condensate system, led to an amine blend that was successfully evaluated within the plant. The results for one period of plant samples is summarized in Fig. 4 (below).

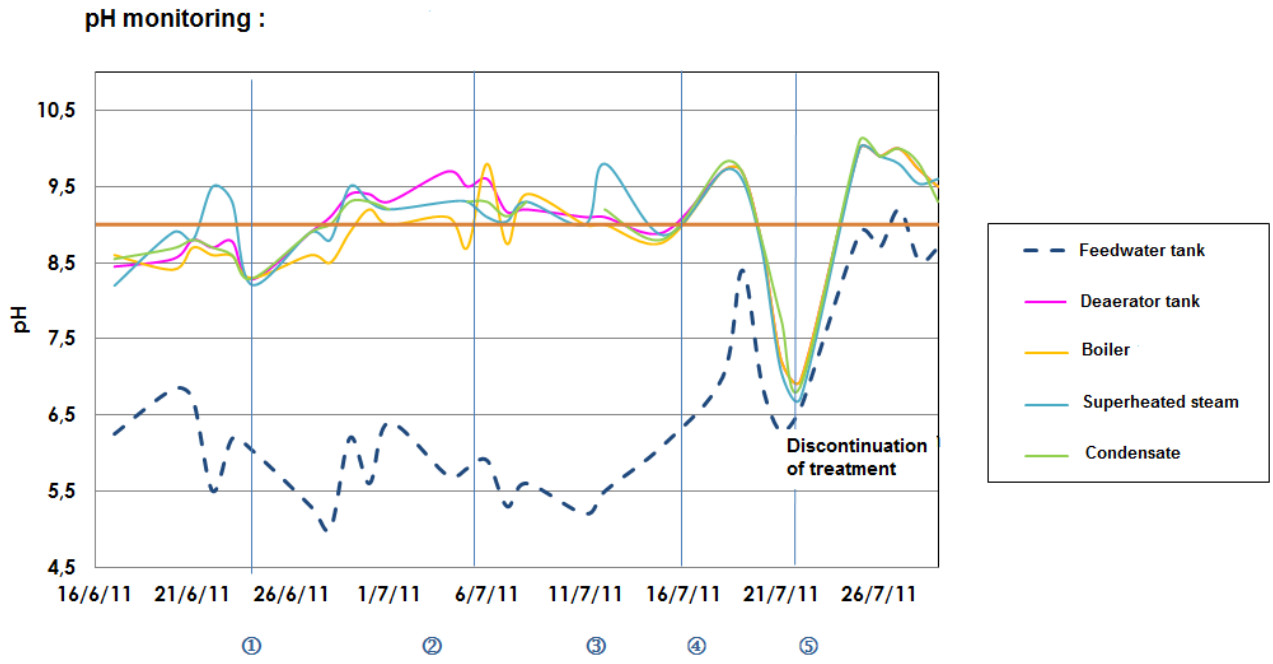

Fig. 4. Condensate pH Trends

Steam Plant Objectives: Optimize Operating Costs – Cost containment was also obtained aided by a through and comprehensive survey of the facility, supported by quality and effective product technologies, and in-depth customer support. Each of these key areas are influential in optimizing the total water treatment program.

TREAMENT OF CLOSED LOOP SYSTEMS

Filming Amine technologies are perfectly adapted for closed loop systems. Filming amines provide possibly the best multi-metal corrosion inhibitor approaches for these systems. The mechanism of corrosion protection for these systems is very similar to that described for steam boilers.

Specifically, polyamine emulsion formulations function in two specific ways:

- Protection through the formation of monomolecular films on all wetted surfaces; and
- Maintaining treated water pH's with the proper selection of alkalizing amines to establish optimum pH ranges depending on the nature of the materials involved in the system.

Filming amine emulsions have demonstrated excellent performance in providing corrosion protection in closed water systems. For example, Fig. 6 depicts a photograph of the internal surfaces of a water recirculation pipe treated for fifteen years from its installation with polyamine emulsion technology. Note the appearance of a perfectly uniform layer of magnetite and remarkable protection of the welding joint.

The cleanliness of the pipe internal surfaces illustrated in Fig. 6 after fifteen years of treatment with filming amines illustrate the natural dispersing effect of the filming amines. This observation can be equated not only to improved system heat transfer efficiencies, but also better performance of system mechanical components such as valves, recirculation pumps, etc.

Microscopic examination of the surface of the pipe depicted in Fig. 6 identified trace quantities of calcium, aluminum, silica, and phosphorus. The absence of any significant accumulation of deposits and/or debris on the pipe's surfaces serve to affirm the dispersancy capabilities of the polyamine emulsions.

In very large, high volume closed loop systems, typically the application dosage is reduced because the filming amine available to coat other areas of the system is readily available to all system surfaces as well. *Odyssee Environment* has developed a broad range of filming amine products for large volume closed loop systems.

Fig. 6. Closed system recirculating water line treated for fifteen years with Polyamine Emulsion technology.

For corrosion prevention in closed recirculating systems, *Odyssee* filming amine technology offers many advantages:

- One drum multifunctional products;
- Easy testing and control;
- Biodegradable;

- Effective performance in multimetal systems;
- Contains bacteriostatic properties;
- Effective dispersant functionality;
- Cost efficient.

Case Study Greenhouse Heating Systems – *Odyssee* treats an approximately 950,000-gl high and low temperature hot water heating system with filming amine technology to prevent corrosion to steel and copper system components. The system also contains a 634,000-gl water storage tank. Raw water provides a source of makeup for the system and filming amine product applications are made by treating makeup additions with 400-ppm of a single-drum treatment (*Oxytherm FS 510*). The facility is depicted in Figure 7.

Case Study Total Headquarters Corporate Offices – The corporate campus complex for Total's headquarters in Courbevoie, France has two closed recirculating circuits for all the buildings in its complex, with a total system volume of 132,000-gl. System makeup water is softened prior to use and system metallurgies are steel and copper. This system is treated with a singular *Odyssee* product @ 1,000-ppm (*Oxytherm FS 510P*).

Fig. 7. Closed recirculating system Case Studies successfully utilizing Polyamine Emulsion technology.

TREAMENT OF COOLING TOWERS

Based on the experiences and expertise of *Odyssee Environment* developing and applying polyamine emulsion technology to industrial water systems, they a broad range of treatments specifically designed for open recirculating cooling towers systems. In cooling water technological applications polyamines offer outstanding results in highly aggressive waters.

Case Study Sugar Cooperative – This French facility converts raw agricultural materials into sugar, alcohol and starch. This progressive manufacturer continuously looks to improve its processes utilizing innovative technologies, and is capable of adapting its industrial facilities, to fulfill new market needs while maximizing the full potential of agricultural raw materials to meet changing demands.

In 2013, the customer sought to produce a more profitable, high viscosity starch. Water quality for this process had to be free of alkaline earth salts, specifically calcium (<0.1-ppm as Ca). A reverse osmosis system was used to produce water which met the required process water specifications. The RO

effluents were also used as makeup to the cooling tower for this production unit, saving added installation costs for a new tower water supply line. This decision would save water and chemical costs, as well as increasing the control of tower legionella contamination. The use of the more aggressive tower makeup water was not ideally suited for the older (twenty years) cooling tower system.

An Odyssee cooling water treatment program (*Odyref A 91*) met all of the client's expectations through:

- Optimal corrosion protection through the application of Film Forming Amines.
- Bacteriostatic benefits attributed to the alkaline surfactants present in the formulation.
- Biodispersants (*Odyzymes*) containing fatty ethoxylated polyamines which exhibit powerful dispersant properties for both biofilm and scale/deposit removal.

Due to the location of the tower in a very dusty manufacturing environment, cycles of concentration have been limited to five-to-seven. During the first production campaign with RO water, system descaling effects have been noted. The cooling tower surfaces have maintained in a significantly cleaner condition, keeping the corrosion rate under control.

Conclusions

Effective 'Green' Industrial Water Treatment products have been developed for steam boilers, closed recirculating heating and cooling water systems, and evaporative recirculating cooling water systems. The products, based on unique polyamine emulsion technologies, have been successfully utilized in large industrial plants for the past ten years. This technology and its products are presently available in US markets.