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Diethylhydroxylamine (DEHA): A Volatile Oxygen Scavenger for Boiler System Treatment

By Frank Kasinecz "MR. GOOD CHEM" INC.

Abstract
Diethylhydroxylamine (DEHA) has been utilized as an oxygen scavenger in boiler systems in many industries for the past 20 years. Its unique combination of properties, such as volatility; the ability to passivate steel surfaces; and its very low toxicity makes it the oxygen scavenger of choice for many applications. The application of DEHA in a number of different systems is discussed in this article and its performance is compared with hydrazine and sulfite.

Introduction
The presence of dissolved oxygen in boiler feedwater can present serious problems in a steam generating plant by promoting corrosion in the feedwater system, the boiler, and the steam condensate system. Therefore, it is important to remove oxygen from the feedwater and also from the condensate where inleakage can occur.

The first step in the elimination of oxygen from the boiler feedwater is mechanical deaeration. With good deaeration oxygen values as low as 7 μg/L (ppb) can be attained.

The second step involves chemical oxygen scavenging to remove the residual. For many years sodium sulfite and hydrazine were the chemical oxygen scavengers of choice. However, sodium sulfite contributes solids to the boiler water and hydrazine was found to be toxic. These factors led to the introduction of alternative oxygen scavengers including diethylhydroxylamine (DEHA). DEHA was introduced as an alternative oxygen scavenger to hydrazine, offering the advantages of very low toxicity and the volatility of a neutralizing amine. Like hydrazine, DEHA also promotes the formation of a passive magnetite film on low carbon steel surfaces minimizing corrosion in the system (Schneider, 1986).

Deha Performance Characteristics
DEHA has a number of beneficial properties as an oxygen scavenger in boiler feedwater systems:
1. Rapid complete oxygen removal under typical boiler feedwater temperature and pH conditions.
2. Promotes passivation of internal surfaces in the boiler system.
3. It is volatile similar to a neutralizing amine with the ability to distilled off the boiler, and is available to protect the entire steam condensate system as well as the feedwater and boiler system.

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4. Under the action of heat, some of the DEHA is degraded to yield two neutralizing amines which assist in elevating the pH in the condensate.
5. It has very low toxicity making it safe and easy to handle in typical boiler application systems.

The goal of the water treatment professional is to provide clean corrosion free surfaces throughout the entire boiler feedwater/boiler/steam condensate system. The unique feature of DEHA based products is that they can provide corrosion protection in a simple package, which is safe and easy to use.

1. Reaction with Oxygen
From a stoichiometric standpoint, 1.2 mg/L of DEHA is required to react with 1 mg/L of oxygen, however for practical purposes 3 mg/L DEHA per 1 mg/L oxygen is recommended. The oxidation of DEHA is a complex process involving several reactions, which are dependent on temperature, pH and the concentrations of both DEHA and oxygen (Ellis et al, 1987).

The overall reaction of DEHA with oxygen can be summarized as:

$$4(C_2H_5)_2NOH + 9O_2 \rightarrow 8CH_3COOH + 2N_2 + 6H_2O$$

The total oxidation of DEHA through to acetic acid, nitrogen and water involves six steps. Extensive application experience over more than 20 years has shown that the formation of acetate is minimal in the presence of the other reducing agents generated in the oxidation process.

2. Metal Passivation
The primary objectives of a boiler water treatment program are the prevention of both scale formation and corrosion on internal surfaces in the system. Minimizing corrosion in boiler systems involves removing all traces of oxygen from the boiler feedwater and creating conditions, which promote the formation of a passive magnetite film on the internal surfaces.

At high temperature iron corrodes in water to form magnetite as follows:

$$Fe + H_2O \rightarrow FeO + H_2$$
$$3FeO + H_2O \rightarrow Fe_2O_3 \cdot FeO + H_2$$

Under normal boiler system conditions magnetite forms a stable tightly bonded surface layer, which inhibits further corrosion (Bain et al, 1994).

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3. Volatility

In addition to oxygen scavenging and metal passivating capabilities, another key advantage of DEHA is volatility. Not only does DEHA scavenge oxygen and passivate metal in the feedwater and boiler portions of a steam boiler cycle, it also volatilizes with the steam to provide complete system protection (Rossel et al, 1991).

The fact that DEHA is volatile represents an enormous advantage in condensate system treatment because most of it is transported and absorbed into the condensate system allowing it to:

• Passivate condensate system metallurgy preventing corrosion
• Scavenge oxygen if it enters the condensate system preventing corrosion
• Reduce corrosion byproduct transport to the boiler minimizing the potential for boiler deposition and corrosion
• Improve equipment reliability and efficiency
• Minimize overall condensate system corrosion reducing the related maintenance costs

4. Thermal Degradation

Under the action of heat in the system DEHA degrades to form two neutralizing amines, diethylamine and ethylmethylamine. In many instances it will be possible to reduce or eliminate neutralizing amine feed while maintaining the condensate pH in the desired range with DEHA in the system. Over the past 20 years DEHA has been used in many systems to elevate condensate pH as well as remove oxygen from the system eliminating the requirement to apply neutralizing amines (Ellis et al, 1987).

5. Toxicity

DEHA has very low toxicity making it safe and easy to handle in typical application systems. One standard acute oral toxicity test measures LD_{50}, the amount of a substance required to kill 50% of the laboratory population of a given species under test conditions. The LD_{50} numbers for DEHA are 2190 mg/kg on rats and 1300 mg/kg on rabbits. These are very high dose rates. As an example from a safety and handling standpoint, in this type of testing DEHA exhibits less than 10% of the toxicity of hydrazine (Cuisia et al, 1983).

6. DEHA Applications

DEHA has been successfully utilized to treat a variety of low pressure and high-pressure boiler systems replacing both hydrazine and sulfite as well as competitive organic oxygen scavengers. It can be used in any type of boiler system where the feedwater temperature exceeds 180°F under alkaline conditions (pH 8.5 or higher). However, DEHA does not have FDA approval. Therefore, it cannot be used in systems where the steam comes into direct contact with food. DEHA has also found many applications aside from conventional boiler feedwater treatment over the years.

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Wet storage or lay-up of a boiler system:
DEHA should be recommended in accounts when wet storage of a boiler is being considered. Use 500 mg/L DEHA (active) with morpholine to adjust the pH to 10.0-11.0 (> 400 mg/L). Test for DEHA and pH on a weekly basis (Thompson, 1986).

Systems where air in-leakage is a problem due to operation schedules requiring regular downtime:
Examples are steam systems involving surface condensers and condensate systems with atmospheric vents. DEHA will remove the oxygen, which is causing corrosion in these situations (Schneider, 1986).
Systems where steam and cooling water interchange:
Batch chemical manufacturing systems with jacketed reactors, and tire manufacturers are examples. DEHA will passivate the metal surfaces in the system during steam introduction, reducing the corrosive impact of the cooling water.

Applications where rapid surface passivation is required:
For example nail, nut and bolt manufacturing systems. DEHA will passivate metal part surfaces. In the production of semi-finished goods, this may eliminate a two-step procedure for the application and removal of temporary corrosion protection on inventoried parts.

Processes where an organic reducing agent is used:
For example, refinery process side reducing agents.

Any industrial application requiring oxygen scavenging and passivation with minimal solids added to the boiler water:
For example pulp and paper utility applications (Rossel et al, 1991).

7. DEHA Application and Control
A. Dosage Recommendations
The dosage demand for DEHA will fluctuate, as it is very difficult to anticipate how much product will be consumed in the passivation of system metallurgy. In general, the dosage recommendations for DEHA feed are dictated by:

- The amount of oxygen present
- The feed point of the product
- The state of passivation of the system
- The operating parameters of the system (pressure, temperature)

In low to moderate pressure industrial boiler systems, an initial feedwater DEHA dosage of 300-500 ppb (active DEHA) is recommended. Adjust product feed rates until a consistent DEHA residual of 80-120 ppb has been established in the condensate.

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In moderate to high-pressure industrial or utility systems (>600 psi), passivation is much more prevalent. Product demand requirements are generally low and residual requirements are lower due to reduced upset potential. In many instances, as little as 75-100 ppb of DEHA in the feedwater will generate at 40-50 ppb residual in the condensate and promote the maintenance of a passive magnetite surface.

B. Product Feed Points

DEHA products can be fed to a number of different points in a standard steam/condensate system. The impact of DEHA may vary, depending upon the point of application. There are a number of application points for DEHA.

Deaerator – The most common introduction point of DEHA into a steam generating system is to the storage section of the deaerator. This is the furthest upstream point in the system where a chemical oxygen scavenger should be added. Care should be taken to insure that the product is not added to the dome section or the dropleg of the deaerator, causing excessive product losses to occur through venting.

Avoid feeding DEHA and sodium sulfite at the same point in the system since DEHA will react with the sulfite. If sodium sulfite is being fed to the deaerator, the feed point for DEHA should be moved downstream, preferably into the steam header. The use of hydroquinone as a feedwater oxygen scavenger is preferable to sulfite when using DEHA.

Feedwater – DEHA can be fed to the feedwater, either by itself or in combination with other treatment chemicals.

Boiler – If the boiler itself is the only point in the system where chemicals can be injected, DEHA can be combined with other products and fed at that point.

Steam Header – The optimal point of application for DEHA products used for post boiler protection is to the steam header because product application changes will have immediate and measurable impact.

Deha Versus Competitive Oxygen Scavengers

The following information describes how DEHA technology compares with hydrazine, and sulfite.

Hydrazine

DEHA functions extremely well when applied as a hydrazine replacement. From an oxygen scavenging standpoint, 40% more DEHA is required than hydrazine (N_2H_4). The competitive advantages, which DEHA has over hydrazine, result from its volatility and low toxicity (Schneider, 1986).

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While hydrazine is a strong passivating agent, it functions as a reducing agent in the feedwater/boiler phases of the system. Not only does DEHA perform the same oxygen scavenging/passivating functions in these areas, it also passivates the entire steam condensate system due to its volatility. In addition, hydrazine thermally degrades to ammonia, which can be very corrosive to yellow metals in the presence of oxygen. By comparison, ammonia generation from DEHA is only 10 to 20 % of that generated by hydrazine.

The second significant advantage of DEHA over hydrazine is its toxicity (Cuisia et al, 1983). The LD_{50} for hydrazine is 82 mg/kg on rats and 91mg/kg on rabbits. This is the dosage of hydrazine necessary to kill 50% of a laboratory population of these species under test conditions. The same LD_{50} numbers for DEHA are 2190 mg/kg on rats and 1300 mg/kg on rabbits. In essence, from a safety and handling standpoint, DEHA exhibits less than 10% of hydrazine toxicity. Hydrazine has also been identified as a suspected animal carcinogen by the U.S. government. In today's changing marketplace, with a heightened emphasis on employee health and safety in the working environment, employee health and safety is a significant issue with all water treatment customers.

Sulfite

Sodium sulfite has been widely used as an oxygen scavenger in boiler systems particularly at lower pressures. It is non-toxic and relatively easy to apply. It can be used in either solid or liquid (sodium bisulfite dissolved in water) form.

On a stoichiometric basis 7.9 mg/L of sodium sulfite is required to react completely with 1 mg/L of oxygen. In lower pressure systems it is generally recommended that an excess of 20-40 mg/L of sodium sulfite be maintained in an operating boiler.

Use of sodium sulfite adds considerable solids to the boiler water, which limits its use in systems utilizing high purity boiler feedwater.

Sodium sulfite does not promote passivation in boiler feedwater or boiler water systems. The ability of sulfite based products to minimize corrosion stems solely from their capability to remove oxygen from the water.

Sodium sulfite is totally non-volatile. It is used exclusively to protect the boiler feedwater system and the boiler system. Sulfite based products cannot be used to protect the steam condensate system.

Compared with sulfite, DEHA offers many benefits due to its volatility and ability to promote passivation of steel surfaces in the system.

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Conclusion

Many years of application have clearly demonstrated the excellent performance of DEHA as a passivating agent and oxygen scavenger for the entire boiler feedwater, boiler water and steam condensate system. Its many advantages in application and cost-effectiveness make it the oxygen scavenger of choice for most types of steam generating facilities.

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Technical Article Review Quiz

The Questions for the exam may be answered by reading and understanding the Winter 2001 Analyst Article titled “Diethylhydroxylamine (DEHA) A Volatile Oxygen Scavenger for Boiler System Treatment “by Frank Kasinecz. The correct answers are derived from that article and any disputed answers will be referred back to that article for justification.

1. From a stoichiometric standpoint, for every 1 mg/L of Oxygen you will need to add,
    a. 0.5 mg/L of DEHA
    b. 1.2 mg/L of DEHA
    c. 22.0 mg/L of DEHA
    d. 60.0 mg/L of DEHA

2. DEHA has the ability to
    a. remove all traces of Oxygen.
    b. prevent scale formation.
    c. degrade to a single neutralizing amine
    d. prevent formation of a passive magnetite film

3. DEHA also has the ability to
    a. passivate only the condensate system.
    b. scavenge magnetite in the condensate system.
    c. reduce corrosion byproduct transport to the boiler.
    d. remove oil contaminants in boiler vessels

4. Under the action of heat in the system DEHA degrades to form,
    a. Cyclohexylamine
    b. Sodium Sulfite
    c. Hydrazine
    d. Diethylamine and ethylmethylamine

5. Successful DEHA treatment requires boiler system feedwater temperature to be at least,
    a. 100°F
    b. 100°C
    c. 180°F
    d. 180°C

6. For wet storage or lay-up of a boiler DEHA should be maintained at,
    a. 5 mg/L
    b. 50 mg/L
    c. 500 mg/L
    d. 5000 mg/L

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7. In low to moderate pressure industrial boiler systems, an initial feedwater DEHA dosage should be
    a. 3-5 mg/L
    b. 30-50 mg/L
    c. 300-500 mg/L
    d. 3000-5000 mg/L

8. When replacing Hydrazine with DEHA the dose rate will
    a. remain the same as hydrazine
    b. have to increase by a factor of 2.
    c. reduced by 50%
    d. have to increase by 40%

9. Sodium Sulfite and DEHA
    a. add considerable solids to the boiler water
    b. promote passivation in the boiler feedwater or boiler water systems.
    c. can be fed separately to the same boiler system.
    d. have FDA approval for use in direct steam contact applications with food.

10. DEHA has been utilized as an oxygen scavenger in boiler systems for the past
    a. 5 years
    b. 20 years
    c. 50 years
    d. 75 years