

Oxidation And Degradation Products Of Common Oxygen Scavengers

There are numbers of reducing agent available, which works as oxygen scavenger. Different oxygen scavenger having difference characteristic. This article elaborate different characteristic and reaction hypothesis of various oxygen scavengers.

SULFITE

Sulfite reacts with and consumes dissolved oxygen in aqueous solutions: $2\text{SO}_3^{2-} + \text{O}_2$



At temperatures of 430°F and above, sulfite will react with iron oxide: $3\text{Fe}_2\text{O}_3 +$



However, because sulfite begins to decompose at higher temperature, this reaction is rarely encountered in boiler systems.

Sulfite is supplied to the water conditioning market via several common salts:

No.	Sulphite base Salt	Chemical Formula
1.	Sodium Sulfite	Na_2SO_3
2.	Sodium Hydrogen Sulfite	NaHSO_3
3.	Sodium Metabisulfite	$\text{Na}_2\text{S}_2\text{O}_5$
4.	Ammonium Sulfite	$(\text{NH}_4)_2\text{SO}_3$

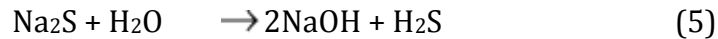
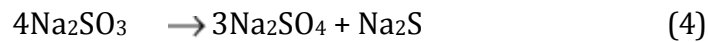
Each of these salts readily ionizes in aqueous solutions; solution pH levels determine which ions are released:

No.	PH of water	Present Species
1.	4-5	HSO_3^-
2.	7	HSO_3^- and SO_3^{2-} (1:1)
3.	8.5-9.0	SO_3^-

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Because of the alkalinity and sodium found in most boiler feed water and boiler water, sulfite ion is the species found regardless of the initial salt. In the high temperature/ pressure and alkaline atmosphere of the boiler, sodium sulfite will decompose. As a result, the sulfite salts are limited to pressures below 900 psig.



Large amounts of sulfur dioxide and hydrogen sulfide gases are usually the result of an overfeed of the sulfite salt.

Both gases volatilize with the steam, reducing the condensate pH at the point of condensation. Generally, this is considered undesirable, but a deliberate overfeed of sulfite will frequently prevent the buildup of water soluble deposits found in turbines operating in the 600-900 psig range.

HYDRAZINE

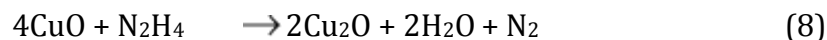
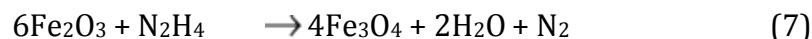
Hydrazine has been used in high purity and high pressure systems, where sulfite compounds in the steam could foul a catalyst, or where feed water is used for attemperation.

Hydrazine reacts with dissolved oxygen:



The reaction is slow at ambient temperatures but increases as temperature and pH increases. The presence of a catalyst reduces the reaction temperature to ambient levels. However, the reaction rate is, at best, slower than that of sodium sulfite. Neither hydrazine nor its reaction products contribute dissolved solids to the boiler water. This has been an important feature of the use of hydrazine.

Hydrazine also reacts with CuO and Fe₂O₃ forming protective passive oxide films:



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A reaction temperature of 250°F or higher is required for these reactions to take place.

Hydrazine begins to decompose at about 400°F and is virtually gone at 600°F. The reaction at the lower end of the temperature range is believed to be:



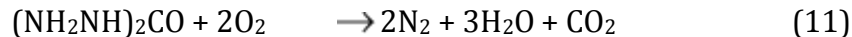
At the higher temperature the reaction appears to be:



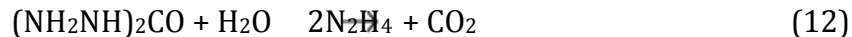
In either case, a significant amount of ammonia is formed when hydrazine decomposes. The ammonia can attack copper and copper alloys in the condensate and feed water system. This is a good reason to keep excess hydrazine in the feed water low.

CARBOHYDRAZIDE

Carbohydrazide is the dihydrazide of carbonic acid. It can react with oxygen directly:



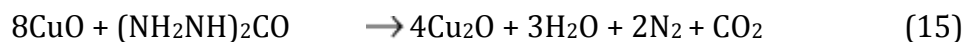
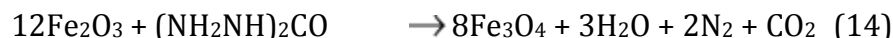
and indirectly through hydrolysis to hydrazine:



At room temperature, reaction 11 takes place significantly faster than reaction 12, and slightly faster than reaction 13. However, at boiler feed water temperatures, reaction 12 is fast enough to produce hydrazine in the boiler feed water.

Carbohydrazide is relatively stable at or near room temperature. At elevated temperatures, hydrazine and carbon dioxide are released followed by the degradation reaction shown above for hydrazine.

Carbohydrazide reacts with iron and copper oxides to form protective passive oxides:

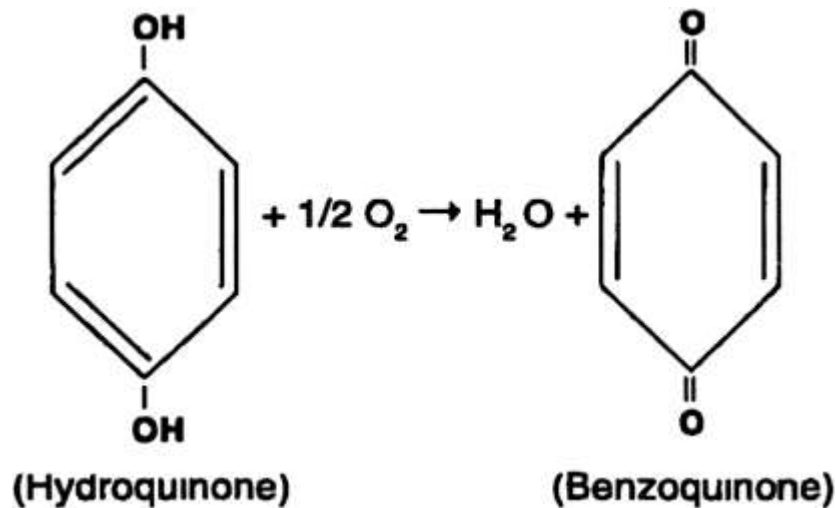


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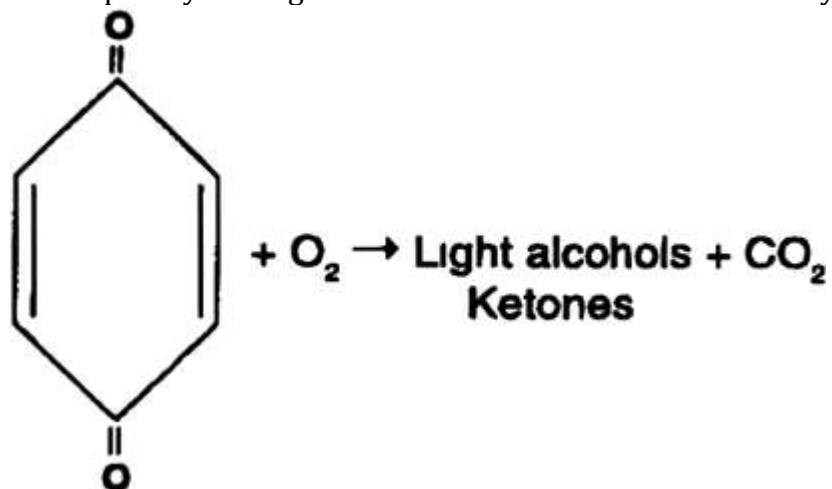
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HYDROQUINONE

Hydroquinone reacts with dissolved oxygen in an aqueous system. The reaction rate is a function of temperatures, solution pH, and the ratio of hydroquinone to dissolved oxygen present in the system. Unlike the reaction of oxygen with sulfite or hydrazine, the hydroquinone reaction is quite complex and appears to go forward in more than one stage. Autoclave studies have shown that the first stage reaction is believed to be:



The Benzoquinone subsequently undergoes further reaction with dissolved oxygen:



Because the amount of hydroquinone required in a well-maintained system is small, the

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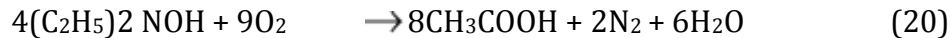
quantity of the final reaction products is very low. The end products have neither caused a problem, nor are problems to be expected. As a result of the secondary reaction, less than stoichiometric amounts of hydroquinone are frequently required to scavenge dissolved oxygen from boiler feed water.

Because there is no nitrogen in the molecule, it does not contribute ammonia to the system. Hydroquinone will also form protective passive oxides with iron and copper.

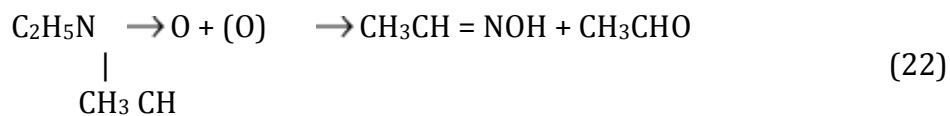
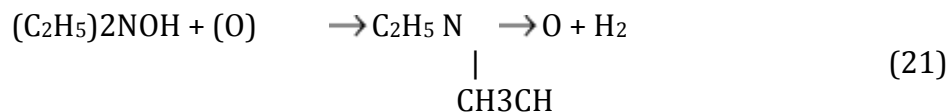


DIETHYLHYDROXYLAMINE (DEHA)

Diethylhydroxylamine (DEHA) is most privileged oxygen scavenger due to its non-carcinogenic properties and used widely by food grade industries, where usage of hydrazine is restricted. DEHA reacts with oxygen in aqueous solutions. The reaction rate is dependent upon solution pH, temperature, and the ratio of DEHA to dissolved oxygen. Similar to hydroquinone, the reaction of the DEHA with dissolved oxygen is quite complex and several reaction products have been identified. Theoretically, DEHA reacts with dissolved oxygen thusly:



In practice, the reaction does not proceed stoichiometrically to acetic acid. The first stage reaction with oxygen produces a nitron, which is further oxidized to acetaldoxime:

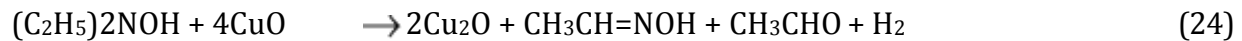


When sodium hydroxide is present in the boiler water, the acetic acid produced is trapped as sodium acetate and removed by blowdown. The other products are volatile and pass through the condensate system and are vented.

DEHA will also react with iron and copper oxides to form protective passive film:

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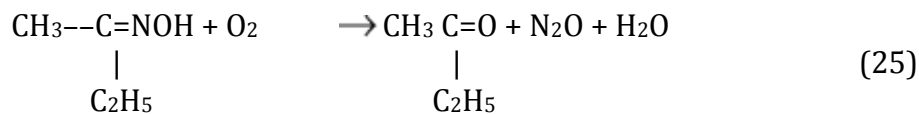
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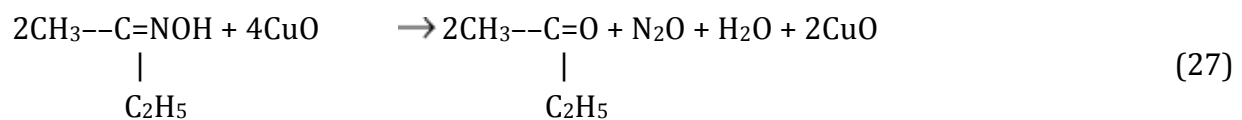
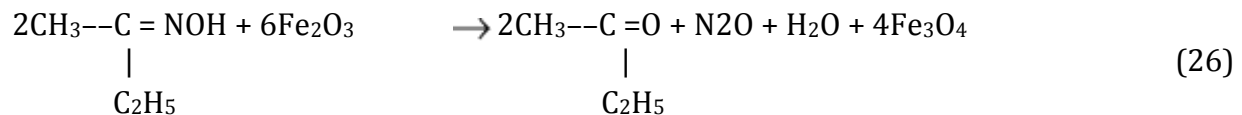
DEHA degrades as the pressure increases above 1,250 psig. The major degradation product appears to be diethylamine, a volatile neutralizing amine that will contribute to the pH control of the condensate.

METHYL ETHYL KETOXIME

Methyl Ethyl Ketoxime (MEKO) reacts with dissolved oxygen in an aqueous system. The reaction is virtually non-existent at room temperatures, but at elevated boiler conditions it is reported to react with oxygen:

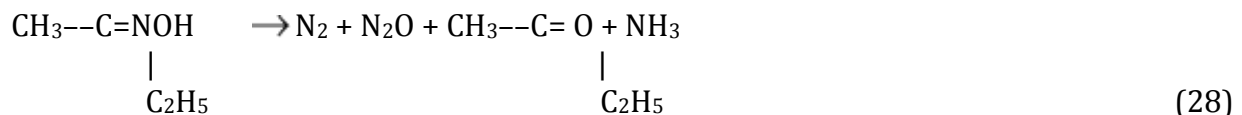


MEKO is claimed to react with iron and copper oxides to produce passive protective oxides:



Because the reaction with oxygen is slow at low temperature, the reaction is probably also very slow under normal condensate temperature conditions.

MEKO will degrade under boiler conditions:



At 1800 psig MEKO will produce the same amount of ammonia that would be produced from an equivalent amount of nitrogen in the form of hydrazine.

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ERYTHORBATE:

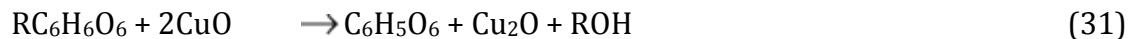
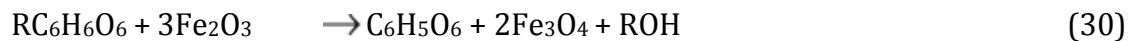
Erythorbate reacts with dissolved oxygen in aqueous solutions:



Note: R could be hydrogen, sodium or an amine.

However, as with most complex organic molecules, the reactions are also quite complex. The dehydroerythorbic acid readily hydrolyzes to 2,3-diketo- D-gluconic acid, which in turn can undergo further oxidation. Under alkaline conditions, the reaction can proceed to D-erythronate and oxalate, and finally to CO₂ and water. The final products will depend upon the amount of oxygen, the pH and the temperature during the reaction. The presence of metal ions also impacts upon which of the final reaction products are produced.

Erythorbate is a relatively strong reducing agent capable of reducing oxidized forms of iron and copper.



As with oxygen, these reactions can proceed beyond the dehydroerythorbic acid. The path will be similar to that described for the oxygen reaction and the final products will be dependent upon the amount of oxidized metal, the pH, temperature, and level of exposure.

Erythorbates will degrade in aqueous solution. The pathway and route of degradation is dependent upon the chemical environment. The pH, temperature, the presence or absence of oxygen and the presence or absence of metal ions are all important parameters of the degradation reaction. Under acid conditions (without oxygen) the molecule degrades to carbon dioxide and furfural, under alkaline conditions (without oxygen) erythorbate is quite stable.

CONCLUSION:

Oxygen scavengers remove dissolved oxygen in boiler water by a reduction reaction, and thereby inhibits corrosion caused by oxygen. The desirable functions of an oxygen scavenger are to have a chemical potentiality high enough to reduce oxygen, and a thermally decomposed reaction product that does not have an aggressive effect on the boiler or on the steam and condensate lines. These two conditions have been met for the above discussion of oxygen scavengers.

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Oxygen Scavenger	Volatile	Contribute			Hazardous Material	Flammable/ Combustible	Theoretical Dosage
		Solids	CO ₂	Organics			
Hydrazine	Yes	No	No	No	Yes	No	1:1
Carbohydrazide	Yes	No	Yes	No	No	No	1.4:1
Sodium Sulfite	No	Yes	No	No	No	No	8:1
DEHA	Yes	No	Yes	Yes	Yes	F	1.2:1
MEKO	Yes	No	Yes	Yes	Yes	C	5.4:1
Erythorbate	No	No	Yes	Yes	No	No	11:1
HQ	No	No	Yes	Yes	No	No	6.9:1

Reference Source:

- 1. John Zupanovich- Staff Technical Consultant with ChemTreat, Inc.**
- 2. Trends in boiler water treatment: EA Water Issue: May June 2003**
- 3. Inorganic Chemistry -P.L.Soni**

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