Taking the Mystery Out of Boiler Additives

By Tony Fleming and Joe Montecalvo, PhD

Process inspectors are trained to look for boiler additives that carryover onto products via steam, such as “volatile amines”. But what exactly does that mean? Making sense of the boiler additives used at a processing facility—or even obtaining the actual chemical names—can be a frustrating experience for the chemistry-challenged. Of the boiler additives listed above, for example, two are acceptable for organic processing, not because they lack toxicity, but because their chemical properties prevent them from being transmitted via steam and contacting food—note that the sentence says “acceptable” and not “allowed” (as in 205.605). Another one is prohibited from having any direct contact during organic processing. Still another is allowed in a very limited instance. One of them is listed in a way that makes it impossible to tell its status without prior knowledge. And all of them can be removed from the steam with the use of an activated carbon filter, right?

Beyond the challenges of determining what additives may be present and how they behave in the boiler system, the inspector also has to be on top of the processes being inspected, in order to recognize the myriad ways boiler steam can contact equipment, packaging, and, especially, ingredients and products, at which point it is known as culinary steam. In this article, we attempt to take the mystery out of boilers and boiler additives by outlining the major classes of boiler additives in common use at food processing facilities, what they are used for, and how to recognize them. We also present a simple decision tree that should help to streamline the boiler aspect of a processing inspection. But first, we begin with a brief review of how boilers work and why they often require chemical treatment.

Boiler Systems

The role of a boiler system is to produce hot water and/or steam and transmit them to various points in the plant where they are used in processing and cleaning. Issues affecting both the performance of the boiler system and the quality of the steam or water produced can arise at any point in the system. Most issues are ultimately related to the chemical properties of the feedwater: alkalinity, pH, dissolved oxygen, and dissolved minerals such as calcium, magnesium, and iron are the feedwater components most problematic for boiler systems. In addition, heating the water changes the stability of dissolved minerals, alters the pH, and increases the reactivity of dissolved oxygen, all of which negatively affect the system. Finally, the phase change from steam to condensate that occurs in steam lines, condensate traps, and at the point of use promotes acidification and oxidation, with attendant corrosion and mineral deposits.

All of these chemical processes can cause costly problems if left unchecked, such as greatly reduced boiler efficiency, higher energy use, scale and rust buildup on steam lines and processing equipment (with greater potential for contamination of products), and severe corrosion leading to premature equipment failure. These issues are typically dealt with by conditioning the feedwater via several kinds of mechanical and chemical methods (e.g., de-aeration, filtering, clarifying, ion exchange), and by employing a variety of chemical additives inside the boiler system itself to address specific problems. An important consideration for inspectors is that feedwater conditioning should be a key part of the boiler program at facilities with water-quality challenges, because it can significantly reduce, or even completely eliminate, the need for employing problematic kinds of boiler additives.

Classes of Boiler Additives and What They Do

Boiler additives fall into several distinct chemical classes, each of which is typically suited to deal with a particular type of problem in boiler systems. Thinking about boiler additives in terms of the issues they are intended to address also makes sense from an organic certification perspective, much like a process...

Water Quality and Boiler Additives at Processing Inspections: Two Sides of the Same Coin

Exactly which of these undesirable chemical processes are present in a particular boiler system, and the methods used to mitigate them, depend to a large extent on the quality of the feedwater. This relationship suggests the importance of considering the water quality component of a processing inspection in conjunction with the boiler system. If the water supply is derived from groundwater, for example (i.e., a municipal or private well), the boiler system challenges are likely to revolve around controlling alkalinity and hardness, whereas surface water supplies tend to have low alkalinity and hardness, but higher acidity and levels of dissolved oxygen. A review of water quality data at the inspection can be very helpful in understanding the facility’s boiler program, and perhaps identify inconsistencies between the two. Typical sources of comprehensive water-quality data include consumer confidence reports (for public water supplies) and outside testing programs (for private wells), often performed by the boiler service company specifically for that purpose. A broader discussion of water quality issues is beyond the scope of this article, but can be found in the TAP area of the members-only section of the IOIA website.
inspector looks at the hierarchy of pest management practices in a facility. As it turns out, only two widely-used classes of additives exhibit behavior that is of direct concern for culinary steam systems in organic handling facilities. The most important chemical characteristic for purposes of organic integrity is not the toxicity per se, but whether or not the compound enters the vapor phase and is transmitted with the steam. This is determined by a property known as the distribution ratio, which is a temperature-dependent expression of how much of the compound resides in the vapor phase (steam) versus the liquid phase (hot water). Compounds with a distribution ratio greater than zero are said to be volatile. A wide range exists, however, with some boiler chemicals having ratios as high as 10 (highly volatile), while others have ratios approaching zero (low volatility). Below, we highlight the commonly-used classes of boiler additives in terms of the three most common issue(s) they are intended to address.

**Dissolved Oxygen:** One of the most troublesome components in boiler systems is dissolved oxygen (DO). When boiler water is heated, DO becomes increasingly reactive and can cause severe corrosion of metal parts throughout the system if not controlled. It is very difficult to completely prevent DO from entering the boiler system: some invariably gets past the de-aerator (if present), while minute leaks at steam fittings and exposure to air in the condensate system allow additional oxygen to enter the system, where it is often returned to the boiler along with the condensate.

Boiler additives are designed to address this issue in two different ways. The first is by chemically eliminating the oxygen through the use of inorganic compounds known as oxygen scavengers (sometimes called reducing agents), which readily accept oxygen into their chemical structure by transforming into soluble salts. Sodium sulfite (or sulfide, or sulfonate) is the most widely used oxygen scavenger because it is cheap, effective, and of comparatively low toxicity (though not without hazard). As a rule, oxygen scavengers do not enter the vapor phase, and therefore pose no risk of being transmitted to products via the steam.

The other type of additive used to manage DO involves a completely different approach, namely creating a film on the surfaces of steam lines and other equipment. Such **filming amines** are formulated with emulsifiers and dispersants to form a protective barrier that inhibits corrosion from both oxygen and carbonic acid (our next topic). By design, they are highly volatile in order to carry over in the steam and effectively coat steam lines, and they are most often found in older facilities, which tend to have less modern boiler systems with more corrosion-prone components. Currently, octadecylamine is the only FDA-approved filming amine; it is limited to 3 ppm in steam, and prohibited in dairy plants. In organic handling situations, it is allowed only in steam used for packaging sterilization.

**Carbonic Acid:** The other major cause of corrosion in boiler feedwater is carbon dioxide (CO₂), which readily dissolves in water to form carbonic acid. This reaction accelerates at higher temperatures, such as those found in a boiler system, resulting in enhanced rates of corrosion. The primary source of CO₂ in feedwater is carbonate minerals, such as calcium carbonate (limestone) and calcium-magnesium carbonate (dolomite), both of which occur abundantly in many aquifers and are major components of hardness. These minerals are readily soluble in groundwater and produce both carbonate and bicarbonate, which are the key components of alkalinity and the main chemical precursors to CO₂ and carbonic acid. While mechanical de-aeration does remove most dissolved CO₂, it has no effect on carbonate or bicarbonate; conditioning the feedwater via ion exchange (e.g., softening or reverse osmosis) is effective at reducing alkalinity, however.

Boiler additives employed to combat carbonic acid attack have two primary modes of operation. As their name implies, see [Boiler, p 14](#).

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**Chemistry 101: Boiler System Corrosion and Treatment**

Dissolved oxygen causes steel to corrode into iron oxides and hydroxides (rust) according to the following 3 equations:

(1) Fe + 2H₂O → Fe(OH)₂ + H₂
(2) Fe(OH)₂ → Fe⁺² + 2OH⁻ → Fe₂O₃ + 3H₂O
(3) 4Fe + 6H₂O + 3O₂ → Fe₄O₇

Another mechanism of corrosion results when carbon dioxide dissolves in water to form carbonic acid (1). Carbonic acid then reacts with steel to form ferrous bicarbonate (2):

(1) CO₂ + H₂O → H₂CO₃
(2) 2H₂CO₃ + Fe → Fe(HCO₃)₂ + H₂

Boiler additives used to treat corrosion work by interrupting these chemical processes. For example, oxygen scavengers, such as sodium sulfite, accept oxygen into their structure, thereby forming non-scaling sodium sulfate: 2Na₂SO₃ + O₂ → 2Na₂SO₄

Neutralizing and filming amines both neutralize acid (H⁺) created by the solution of carbon dioxide in the condensate: R-NH₂ + H₂CO₃ → R-NH₃ + HCO₃⁻

The former are a systemic treatment that creates a condensate pH of 8.5 to 9.0, whereas the latter form a protective barrier that coats susceptible surfaces.

For a more comprehensive chemical treatment of this topic (highly recommended), see [Mechanisms of Boiler and Steam Condensate Corrosion](#), posted on the IOIA website.
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Neutralizing amines are high-pH chemicals that react with carbonic acid to neutralize acidity and maintain a strongly alkaline pH in the boiler system. Morpholine, cyclohexylamine, diethylenetriamine, and hydrazine are all in this class, and are all readily transmitted in the vapor phase. Together with the aforementioned octadecylamine, they comprise the so-called “volatile amines” inspectors should be on the lookout for. The second mode of action against acid attack uses a film-forming agent to coat susceptible surfaces with a protective barrier. The film forming amine octadecylamine, and acrylamides are the primary additives of this type. The latter belong to the class of additives broadly referred to as polymers (resins), which are not volatile except for trisodium nitrilotriacetate, a rarely used amine substitute.

Mineral Deposits: Mineral deposits wreak havoc by reducing boiler efficiency, raising energy costs, and coating the surfaces or plugging orifices of processing equipment (with attendant functional and sanitation challenges). Referred to generically as “scale” or “rust”, these deposits include several kinds of minerals with different sources and chemical properties. Calcium-magnesium carbonates typically form in systems fed by groundwater, which often comes from limestone- and dolomite-bearing formations. Iron oxides (rust) can occur both as a result of corrosion, which liberates iron from steel surfaces, and naturally: some groundwater sources are high in dissolved (reduced) iron, which becomes insoluble in the presence of oxygen inside the boiler and precipitates as oxides or hydroxides. Silicates are less common but sometimes occur in acidic feedwater, and subsequently become unstable and precipitate as scale in the alkaline environment inside a boiler system.

Feedwater conditioning methods available to reduce the mineral content include ion exchange, and clarifying with quick lime (for calcium and magnesium) or soda ash (for silicates). A variety of additives are also used, most of which react with the dissolved phase of the mineral to either keep it in solution or to cause it to precipitate out in a soft and easily removable form. Phosphates, for example (mono-, di-, and tri-sodium phosphate; sodium polyphosphate) react with calcium and magnesium to form soft rock phosphate, while chelating agents (ethylenediamine tetra-acetic acid, or EDTA, is a common example) enhance the solubility of minerals and prevent them from precipitating on surfaces. Polymers work similarly to chelating agents and are among the best methods for controlling both iron and silicate deposits. None of these three classes of additives are volatile, except for the polymer, trisodium nitrilotriacetate.

Tips for Effective Boiler Additive Inspections

The first question that must be answered is whether or not there is direct contact between boiler steam and any product or food-contact surface, including during sanitation. The answer to this question should be clear from the Organic Handling Plan, but it must be verified at the inspection, both by operator interview and by direct observation of the process flow. We have encountered situations where the OHP is wrong! Pay particular attention to any schematic facility diagrams and flow charts. Be clear about whether steam-based processes use indirect heating (e.g., plate pasteurizer, double-wall kettle, tube-in-shell) or direct heating (e.g., sparging, capping-lidding operations, blanching, peeling, and extrusion). Beyond these common processes, direct steam may be used in a number of less obvious places: scalding (chicken processing), tempering (grain processing), steam barriers in pasteurizers, and sterilization of transfer carts and other ancillary vessels are examples.

Second, if direct contact does occur, then you must identify the chemical names of all boiler additives used, not just the trade names. This can’t be emphasized enough! This information should also be clear from the OHP, but we have seen many cases where the OHP lists only the trade name.

A Simple Decision Tree for Inspecting Boiler Systems:
1) Is a boiler system present at the facility? If the answer to any of the first three questions is "NO", there are no compliance issues related to boiler additives. If it is "YES", continue on.
2) Does steam have direct contact with ingredients, products, packaging, or food-contact surfaces at any point during processing or sanitation?
3) What boiler additives are used, and are any of them volatile?
4) Does the operation utilize an "integrated boiler management" program in which alternatives to volatile boiler additives (e.g., feedwater conditioning, excellent system maintenance, and non-volatile additives) are or have been tried first? If yes, continue to #5. If no, or the boiler program is not documented, a minor noncompliance may exist. Continue to #5.
5) Is the steam used in organic processing limited to packaging sterilization? If yes, go to question #6. If no, jump to question #7.
6) Are cyclohexylamine, diethylenetriamine, and/or octadecylamine the only volatile additives in use, and is the concentration measured in the steam within FDA limits? If yes, the operation complies with the NOP. If no, go to the next question.
7) Are measures in place to prevent contact of prohibited boiler additives with organic food, and are they documented to be 100% effective? If the answer to either of these is no, a major noncompliance exists.
Regulation of Volatile Boiler Additives: FDA vs NOP

The seven volatile boiler additives currently regulated by the FDA for use in food processing plants are cyclohexylamine, octadecyclamine, diethylamino ethanol, hydrazine, morpholine, ammonium hydroxide, and trisodium nitritriacetate. In practice, ammonium hydroxide is seldom if ever used in food plants because it can create odor issues. In all cases, the maximum concentration allowed in culinary steam is regulated. The first five are "volatile amines", the last two are not. This is why keying on the phrases "amine", "amino", or just plain "-ine" is helpful, but not infallible, for identifying additives that transmit through the steam. The first three are allowed at 205.605 for package sterilization only (as limited by FDA); otherwise, none are allowed to have any contact with organic food. To learn how and which boiler additives are regulated by the FDA, visit 21 CFR 173.310.

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(e.g., “Marathon 84”), and if you don’t obtain the chemical name, you would have no way of recognizing this additive as morpholine (prohibited). Moreover, the boiler additives used at a given facility can do change over time, and those changes may not be communicated between the boiler service staff (usually an outside company) and the individual who updates the OHP. Thus, don’t rely solely on the OHP: always visually observe the boiler room and compare both the trade and chemical names of the additives listed on the containers to the OHP and any MSDS provided with it. Note that MSDS for boiler additives must be maintained on site.

Third, there is a strong case to be made that an organic handler should be using an “integrated boiler management” program to reduce or eliminate the need for volatile additives. Look for evidence that the facility has a viable boiler system maintenance program that includes regular feedwater and condensate testing and inspection of system components. How often are water-quality tests performed on the plant’s water supply, and are the results consistent with the boiler treatments used? Is there evidence that alternatives to volatile additives are or have been attempted, such as appropriate feedwater conditioning methods and non-volatile additives? Oxygen scavengers such as sodium sulfite, and acrylamides such as 2-acrylamido-2-methyl-propane-sulfonic acid copolymer are often excellent alternatives to volatile additives.

Some operations that use volatile boiler additives in culinary steam may shut off the additive feed at some predetermined time before organic handling begins in an effort to prevent contact with organic products. This raises a host of difficult questions. How is the appropriate shut-off interval determined, and are the results repeatable (as in any good science experiment)? Boiler systems are complex systems with many variables that affect the "half life" of additives. For example, was the condensate test done on a Monday, after the boiler was off or running on low power for the weekend? Was more than one test performed? Perhaps most importantly, what is the sensitivity of the test method that was used? Testing of condensate for volatile additives is a fairly simple operation using colorimetric kits from familiar suppliers (e.g., Hach, Ecolab), but just like quat test kits, the sensitivity varies from kit to kit (or it may be geared to FDA maximum limits) and may not definitively indicate "zero" residue is present in the condensate. If this is the situation, you must ask a lot of questions and request documentation. In some cases it may not be possible to conclusively verify that shutting off the additives is a scientifically sound approach to compliance. Such problematic operations may be better off using a portable steam generator during organic handling, an elegant and comparatively inexpensive solution that requires no additives.

Finally, keep in mind that, despite some claims to the contrary, none of the steam traps and filters in use today in processing plants are capable of removing volatile boiler additives. This includes activated carbon filters, culinary filters, condensate traps, and any other kind of filter!

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Eric Feutz, Treasurer, is the senior member of the BOD and ably chairs the Finance Committee. During 2011, he convened the Finance Committee to plan the audit and draft the 2012 budget. The BOD met in person at the AGM, 11 times via conference calls, and at the 3-day retreat. BOD minute highlights are published in each newsletter. Full minutes are available on the “Inspectors Only” section of the website.

Staff:

Margaret Scoles continues as Executive Director. IOIA benefits from a staff of highly skilled and dedicated individuals. In addition to adding the Training Services Director full-time, IOIA transitioned from a part-time to full-time Office Manager.

- Danalyne Miller, Office Manager (thank you to Renee Higgins, who left in 2011 as the position was expanded)
- Jonda Crosby, Training Services Director
- Sacha Draine, International Training Manager (.6 FTE)
- Kathy Bowers, U.S. Training Services (.6 FTE)
- Lynell Denson, Administrative Assistant (.4 FTE)
- Diane Cooner is contract Newsletter Editor, Website Manager, and moderator of the IOIA Forums.

Your help as volunteers and committee members is necessary and greatly appreciated!