Organic Water Treatment Inhibitors: Expansion of Current Guidelines, Myths, Disinformation, and the Next Generation of Novel Chemistries—Part II

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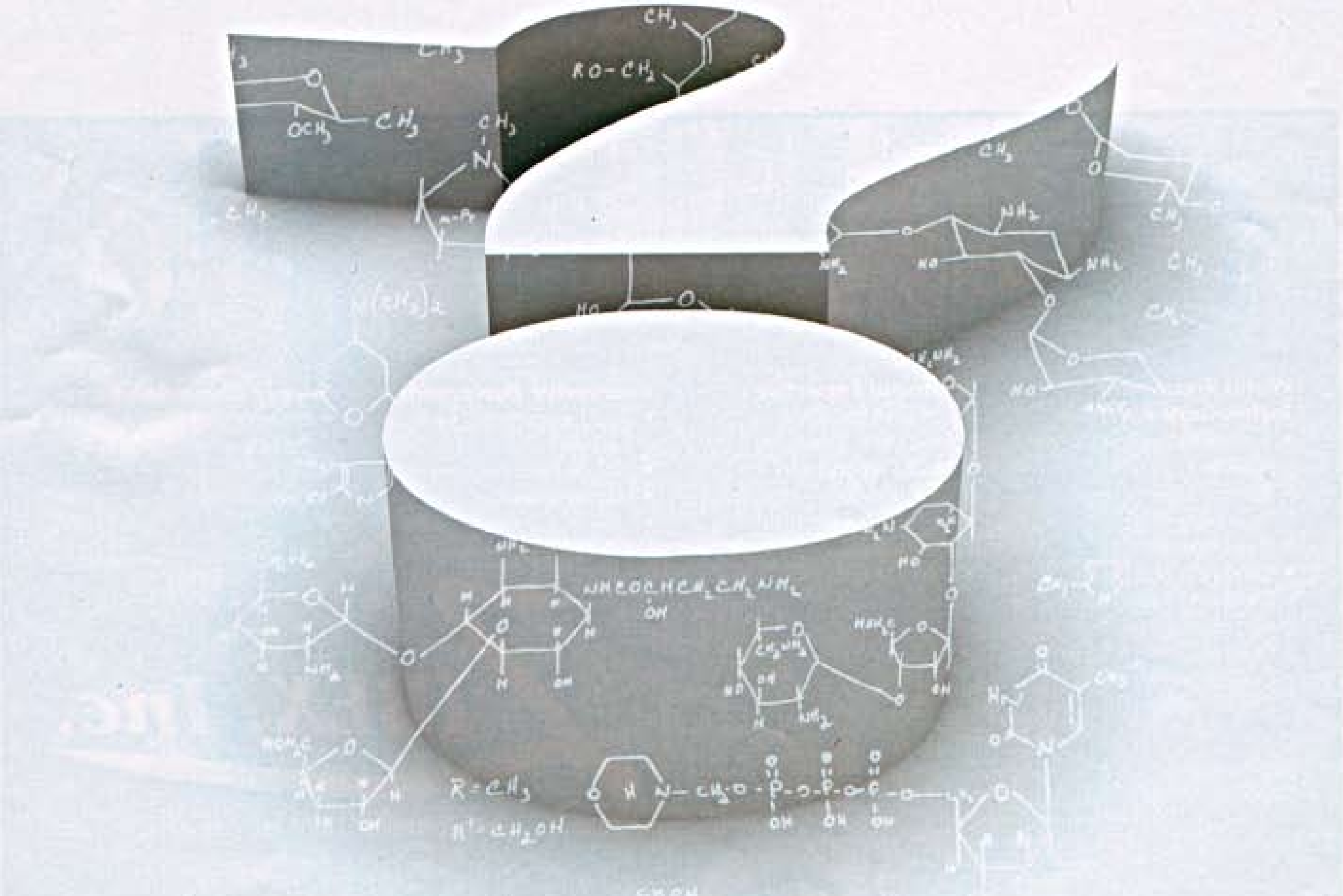

Introduction

This is the second of a two-part article written in response to a request for comments by Robert R. Cavano,[1] following the 2008 *Analyst* publication of his four-part series entitled "Developing Cooling Water Treatments." This final part discusses some technical and green chemistry considerations in formulating with organic inhibitor chemistries, plus requirements for inhibitor actives, some novel and green chemistries, and the next generation of inhibitors.

Part 1: The first part of this two-part article on organic water treatment inhibitors and formulatory chemistries discussed the background to modern industrial water treatment chemistry. It also reviewed marketplace problems myths, and disinformation, as well as the magnitude of the problems in developing a cohesive approach to formulations.

Further Technical and Green Chemistry Considerations in Formulating Blends

The formulation of inhibitors for cooling water must also consider system pH—usually within the range of 7.5 to 9.5. Lower pH values tend to render the recirculating water excessively corrosive, while higher pH values will result in both amphoteric metal corrosion (as with zinc, brass and aluminum) and scale-forming conditions. At these pHs, modification of corrosion risk is controlled by corrosion inhibitors, which usually form a passive protective barrier on a metal surface by chemical reaction with the surface, or by physical or chemical adsorption. As Cavano[1] has stated in his articles, a review of Calcite Saturation Index (CSI), Langelier Saturation Index (LSI), and inhibitor calcium tolerance is primary, and problems associated with silt, clays, soluble iron, manganese, phosphate, calcium, sulfate, and silica will also need to be considered. Also, it is important to evaluate corrosion potentials for iron (Fe), copper (Cu), zinc (Zn), aluminum (Al), and magnesium (Mg), especially when associated with chlorides, sulfates and biocorrosion. Certain process industries may have problems with barium, strontium, oxalates, and titanium dioxide. The inhibitor package will need to cater to any, or all, of these risk factors. Also, the formulator has to consider the stabilization of oxide films on stainless steel, transport of metal ions, and risks of calcium phosphonate formation with low calcium-tolerant organics.

Some inorganic inhibitors may be proposed, including less common agents such as manganese (Mn) and tin (Sn). However, a current worldwide marketplace issue is the growing pressures for sustainable (green) chemistry, which will urge further reduction of inorganic chemistries (e.g., molybdenum (Mo), phosphorus (P), zinc (Zn)) on grounds that they may be considered harmful to human health and the environment. Also needed for consideration are the many blended inhibitor formulations labeled as "Class 8 corrosive." If caustic or potash is removed for a greener product, then we may have to rethink our use of fully neutralized polymers and phosphonates, as well as the TTA component. In the not-too-distant future, we might need to formulate based on a simpler, but more multifunctional, green chemistry approach, using only fully degradable and non-toxic organic inhibitors.

However, for now, we know that calcium carbonate is the most common foulant and will preferentially scale as calcite if the solubility product is exceeded (i.e., if the water is saturated or supersaturated with $CaCO_3$). Generally, the higher the CSI, the higher the risk of other supersaturation-related problems developing, such as from sulfates, phosphates, iron, or silica. We also know that organic inhibitors can help by exhibiting combination effects against scaling, deposition, and fouling by a variety of mechanisms, including threshold stabilization, sequestration, crystal modification, and dispersion. Ferguson[3] believes that the critical parameters relating to dosage are induction time, temperature, and the degree of supersaturation, to which Cavano has added system residence time. We would also add system cleanliness and, especially, freedom from waterside surfaces biofilms.

Additionally, we know that some of the very same organic inhibitors employed for scale control can simultaneously provide a corrosion inhibiting effect; it is simply a matter of degree. Thus, from a technical perspective, ranking chemistries solely on their ability to provide a specific benefit (such as control over calcite scale) can be misleading, as all organic inhibitors will exhibit more than one beneficial effect and the economics of feedrates can improve many a second-tier inhibitor.

When formulating for any particular problem, it is often useful to mix a primary and backup inhibitor together. This does not mean, however, that the formulation package must, of necessity, contain a great many chemistries, as a specific chemistry may be primary in one effect, secondary in a minor effect, and tertiary in still another effect. Thus, by careful selection and mixing of vendor blends, we can provide synergistic inhibitor effects with only a very limited number of chemistries. This aids simplicity, reduces inventory costs, and is likely to be the way of the future.

Formulating With Organic Inhibitor Chemistries

The organic chemistries employed in formulations for control of scaling, deposition, fouling, and corrosion include a wide range of branded generics available from a great many sources (most often from China and India these days) and some strong international OEM brand names. The key chemistry groups discussed below have well-recognized basic functionalities, but much subtlety exists in the individual branded products and derivatives within each group. Readers are urged to reread Cavano's articles[1] (and others) for the details, as we have no desire to simply duplicate their findings.

Polyacrylic acids (PAA), polyacrylates, and polymethacrylates—most popular are those with molecular weights (MW) ranging from 2,000 to 10,000 daltons, e.g., Lubrizol K752 is a brand name for a 2,000 MW polyacrylic acid and K732 is a 5,000 MW PAA. Forty-five hundred (4,500) MW homopolymers are good dispersants for $CaCO_3$, silt, and iron under normal lower-stress conditions, as the backbone molecule tends to curl at high temperatures. Two thousand (2,000) MW homopolymers are decent scale control agents for HVAC, RO, sugar evaporators, especially if blended with PMA or HEDP. Blending a 2,000 MW and 4,500 MW PAA provides for synergy and increased scope of application.

Copolymers and terpolymers to consider include SS/MA, AA/AM, AA/SA, AA/COPS, AA/HPA, AA/AMPS, AA/SA/NI, AA/SA/SS, and PBS/AM. Betz Dianodic polymer is an acrylic acid/hydroxypropylacrylate, Versa TL4 is a sodium SS/MA, Calgon TRC 233 is a 60/40 AA/AMPS, Acumer 3100 is a strong brand for AA/SA/NI, and Alco Versaflex ONE is a copolymer. This group has a range of properties too wide for blanket recommendations, and individual polymer performance strongly depends upon specific polymer architectures.

AA/SA or AA/AMPS extend the calcium tolerance of phosphonates, especially HEDP. AA/HPA was the original dispersant for the Betz Dianodic stabilized phosphate programs. Note: globally, stabilized phosphate/sulfuric acid and alkaline phosphate/dispersant programs are still the first choice in developing countries.

AA/SA/SS (ionic) terpolymer performs significantly better at preventing calcium phosphate precipitation than copolymers such as (neutral) AA/AM.[10] AA/SA/SS also exhibits better tolerance to metal ions (e.g., Fe, Mn, Al, Cu, Zn) than AA/SA (even though AA/SA is a good iron oxide dispersant because it is not affected by the presence of calcium—unlike PAA homopolymer).

Polymaleic acid and maleates to consider include PMA, AA/MA, SS/MA. Belclene 200 is a brand of PMA, and Belclene 283 is a maleic terpolymer. We have successfully used PMA as an antiscalent for MSF evaporators in the Middle East, hardness stabilization for water-storage tanks in the African Kalahari Desert, and sugar evaporators in Central America. It is a great antiscalant, but lacks good dispersive powers. Use with 4,500 MW PAA.

Carboxylates, phosphinocarboxylates (PCA), and phosphoncarboxylates (POCA) include Belclene 494—a POCA, Belclene 161 and Unisperse 124—both brands of PCA, and Bricorr 288—a phosphonated oligomer. PCA is regarded as an excellent, thermally stable dispersant for steam boilers, but is also a decent calcium carbonate scale inhibitor. Bricorr 288 is a corrosion inhibitor alternative to HPA, but our experience is that it often performs better in closed loops than in open recirculating systems, and thus, is a good alternative to Belclene 590 (which is itself an organic replacement for nitrite).

Straight phosphonic acids and phosphonates include HPA (HPCA), HEDP, and PBTC. For example, Belcor 575 is hydroxyphosphonoacetic acid, and Bayhibit AM is a brand of PBTC. HEDP and PBTC have become the defacto multi-functional inhibitor standards for calcium carbonate, iron, and silt, although HEDP has very poor calcium tolerance. HEDP and PBTC also function as useful corrosion inhibitors by forming calcium-phosphonate complexes at the metal water interface. Because each of the phosphonates exhibit subtle (or sometimes not so subtle) changes in effect for different contaminants under different waterside conditions, it is common to blend them, for example HEDP/ATMP. HPA is a very good steel corrosion inhibitor and functions by a self-limiting corrosion process, and so is good for soft water (where calcium is limited), but it may need higher feed rates (greater than 5 mg/L). It is not halogen stable, but this negative can be limited by use of MEA in the formulation. HPA also has scale-control properties and, based on work by Boffardi[11], has been found to be a good solubilizer for Fe and Mn.

Aminophosphonic acids, aminophosphonates and derivatives, such as ATMP, MAPA, DETA phosphonate (DETPMP), DTMPA, MDTP, PAPEMP, and PAP (polyaminophonates) blends. For example, Dow Versenex CSI is a manganese-aminophosphonic acid (MAPA) blended with AA/AHA. Buckman BSI 319 is a blend of DTMPA and MDTP, Wujin XF 335 is PAPEMP, and Unichem Technologies' Multicor 400 is a PAP blend. ATMP is a decent, low-cost, general purpose scale and corrosion inhibitor, but can be uneconomic in the presence of iron.

DETA phosphonate is also a good general purpose inhibitor, useful as a corrosion inhibitor for Al. Also, DETA has a high sequestration value, making it valuable for chelating Fe, Mn, and Cu. PAPEMP is a good example of a multi-functional phosphonate, exhibiting excellent scale-control performance at very high calcite saturation levels. It is also good for iron stabilization, sulfates, silica and silicate deposit control. Also, being an aminophosphonate, it is an effective corrosion inhibitor. Polyaminophosphonates (PAP), of which Multicor 400 is the prime example, is a developing group of blended phosphonates that offer even more multi-functionality than PAPEMP.

Azoles

Azoles include tolyltriazole (TTA), benzotriazole (BTA), and sodium mercaptobenzothiazole (NaMBT), and are selected for corrosion control of copper and brasses. For example, Wintrol B-40Na is a 40% sodium BTA solution. TTA is normally the first choice, but it is not very soluble, necessitating incorporation in strongly alkaline inhibitor blends. BTA is more soluble, but perhaps price and overall effectiveness, in some circumstances, may be a deterrent. NaMBT is more suitable for closed loops. Products are typically employed to provide from 1 to 2.5 mg/L active azole in open recirculating cooling water systems.

Amines, Amides, Esters and Amine Derivatives

These inhibitors include volatile corrosion inhibitors, primary amines and fatty diamine salts. Examples include Cortec VCIs, Buckman's DMAD, phosphate esters such as TEAPE, and acrylate silicate esters such as Buckman's SACE. Belcor 590 [6,6,6-(1,3,5-triazine-2,4,6-triyltriimino)trishexanoic acid] is an organic replacement for nitrite in closed loop systems. Cocoalkylamine (Armeen C from AkzoNobel) is a solid/paste and can be formulated for use in small cooling systems, via basket feeders. N-tallow-1,3-diaminepropane (Duomeen T), can be formulated into an acetate salt for corrosion inhibition of once-through cooling systems and for hydrostatic testing of large international gas pipelines. It is also an effective molluscide.

Requirements for Organic Inhibitor Actives

Cavano has indicated that, in general, phosphonates should be present in recirculating cooling water systems at minimum levels of 3 mg/L for lower-stressed systems, rising to 5 mg/L for higher-stressed systems. He also recommended HPA as a corrosion inhibitor at 3 mg/L for higher-hardness waters, rising to greater than 5 mg/L for soft waters. To these notes we would add an earlier guideline of ours: namely, in a cooling system, the total of all organic phosphonates and polymers derived from an inhibitor formulation is unlikely to exceed 12 to 20 mg/L, depending upon stress. Cavano also warns against overdosing. We suggest the "less is usually more" approach for any particular chemistry in a multiple-organic blend.

Thus, understanding that for many inhibitor chemistries there is a minimum threshold level, below which a beneficial effect is zero or negligible, and that there is some latitude to increase feed rates to cater to higher stresses. We can formulate a product designed to provide a total of 15 mg/L active organic inhibitors at 100 mg/L product in the cooling system, so that for:

Low-stress systems: feed product to achieve 75 to 90 mg/L in the system, equating to 11.25 to 13.5 mg/L total active organic inhibitors.

Medium-stress systems: feed product to achieve 90 to 110 mg/L in the system, equating to 13.5 to 16.5 mg/L total active organic inhibitors.

High stress systems: feed product to achieve 110 to 125 mg/L in the system, equating to 16.55 to 18.75 mg/L total active organic inhibitors.

Finally, Some Novel and Green Chemistries, and the Next Generation of Inhibitors

The current poor global economic situation further reinforces our collective need to reexamine many of our inhibitor product formulations. Much of what is out there is too complicated. In general, our raw material inhibitor inventories are too high. We use too many formulatory components, and have too many variant product offerings. (An analogous situation exists in the market for microbiocides). As a result, many formulators are looking to limit their range of formulations, bring them up to date with novel and green chemistries, yet simplify them and add more flexibility in application. Thus, when examining the marketplace for novel inhibitors, we naturally tend to think that some are just that—novel! But the reality is that water treatment is a relatively small market sector and it borrows chemistries from other industries. (In fact, both phosphonate and phosphonosuccinate chemistries are employed not just in other industrial fields, but as medicaments in bone disorders.) Much of what we think is new has been available for at least 20 years or more, and many of the patents for polymers and phosphonates date back to the 1970s and 1980s. For example, the development of PBTC relied, in part, on an American Cyanamid 1962 patent for sequestration of metal ions.[12] Universal Oil filed for a patent of a synergistic polyaminophosphonate/polymer blend in 1976.[13] Ciba-Geigy filed for its HPA (Belcor 575) patent in 1987.[14] Dow received a patent for its MAPA technology in 1988.[15] Albright & Wilson (now Rhodia) filed for a patent on phosphonosuccinate chemistry in 1994.[16]

This borrowing of chemistries is not necessarily a bad thing, but it confirms that our market for water treatment chemistry inhibitors is relatively small and, as we are all aware that some segments are fully mature and commoditized, for any novel chemistry to succeed, it has to offer some really special benefits and value-added economics. Some chemistries attracting considerable current attention because of novel or green issues, or that might be the next generation of inhibitors include the following:

Polyaspartic Acid, Aspartates, and Succinates:

The starting point for these chemistries is succinic acid (butanedioic acid), which is made from maleic anhydride. They are based on peptide chemistry and were borrowed from the detergents industry. They are now promoted as biodegradable, green, and scale and corrosion inhibitors for water treatment. There is a growing interest in these chemistries, although some doubts exist about their in-use cost structure and strength under high-stress conditions. Examples include Bayer's IDS (iminodisuccinic acid) and polyaspartic acid. Also, Nanochem/Donlar CB-105, which is a 5000 MW sodium polyaspartate for hard water. However, the major water treatment companies have embraced these chemistries, for example, Nalco's Inulin (sodium dioctylsulfosuccinate) and PSO [phosphonosuccinate oligomer (i.e., A&W/Rhodia's chemistry)]. Also, GE Betz has PBTC/PESA (polyepoxysuccinic acid) blends.

Aminophosphonates and Polyaminophosphonates:

This group of chemistries has been briefly discussed above, but in view of the need for simpler, more flexible, and greener formulations, and the growing interest in polyaminophosphonates (PAP), it is worth discussing them in more detail. This technology initially started with Dow's MAPA chemistry. Versenex SCI (scale and corrosion inhibitor) was based on an EDTMPA phosphonate with partially chelated manganese, to improve corrosion inhibition, and blended with AA/HPA. Drew and Betz produced derivatives by removing the manganese, improving the aminophosphonate chemistry and changing the dispersant. Versenex CSI is no longer available in the market, but Chemco and Telomer have their own variants.

Amines and their derivatives are well-known corrosion inhibitors and, when incorporated into a phosphonate molecule, provide additional corrosion inhibiting functionality. The presence of a hetroatom in the unsaturated organic compound causes an adsorption process on the metal surface, which reduces metal dissolution and significantly retards metal corrosion. Thus, the aminophosphonates can function as both scale and corrosion inhibitors, with good dispersive action. There are many similar amine-derived chemistries that provide good corrosion inhibition in oil field and water treatment markets, for example, N,N-dipropynoxymethylamine-trimethylphosphonate, which can protect iron in sulfuric acid.[17] Also, Dabdoub has taken the concept of using aminophosphonates as true multifunctional inhibitors and developed low-phosphorus, polyaminophosphonate blends (PAP blends) with additional cyclic and alkyl amino groups increasing corrosion inhibiting properties of the molecules.[18] These are used in oil field, pulp and paper, and kaolin industries. The primary PAP blend for the water treatment market is Multicor 400, which is a mix of cyclic and linear polyaminophosphonates derived from amine reaction with ATMP/DETA phosphonates.

In his articles on developing cooling water treatments,[1] Cavano recommends that "all formulas should contain PBTC, HPA, and a terpolymer." However, with PAP chemistry in mind, we would respectfully disagree. We would argue that, under many circumstances, the polyaminophosphonate can fully protect both iron and copper metals, and so, by using PAP chemistry, we can eliminate the requirement for HPA (and the MEA necessary for its stability), plus TTA (and the caustic needed for its solubility). We cite the previously discussed Demadis and Ketsetzi[8] article, which showed that aminophosphonates do not dramatically degrade in the presence of high levels of halogen, and suggest, therefore, that PAP blends are an appropriate and novel technology that can provide the basis for green water treatment inhibitor products, with benefits of maximum use of the molecule, and simpler and lower-cost formulations. We can envisage formulations for lower-stress waters based on PAP and blended with other economic chemistries such as PAA and ATMP. Also, in the near future we may see formulations for higher-stress waters based on PAP with IPPA/PIPPA co- or terpolymers and PCA (e.g., Unisperse 124).

Iso- and Polyisopropenylphosphonic Acid (IPPA, PIPPA)

The chemistry of the IPPA, PIPPA molecule is that it is a combination of both polymer and phosphonate—two of the key fundamental technologies employed in modern water treatment. Here again, we tend to believe that this chemistry (which was introduced to the Association of Water Technologies by Dabdoub, at the 2008 AWT Convention[19] in Austin, Texas) is also novel, whereas in fact, it has been selectively used for a number of years. (Scale-inhibiting isopropenylphosphonic acid copolymers were patented by Betz Laboratories in 1984[20].) Although it is a tremendous technology and represents a significant step forward in treating very high-stress, high-temperature applications, it has, until now, been difficult to fully commercialize due to manufacturing constraints (and hence had a high cost structure). To date, the chemistry has only been used in a limited number of applications, such as high-pressure industrial boilers and some nuclear power installations.

Dabdoub has been involved in the development of IPPA/PIPPA since the earliest days of the chemistry's invention, and what he has now done is to find a way to synthesize the monomer in a simpler and more cost effective way, thus opening up a new market sector for IPPA and PIPPA products and a new generation of highly stable, co- and ter-polymer-phosphonate derivatives. Current examples of this technology include Betz's HTP2 (IPPA copolymer), Ashland Hercules's Optisperse HTP (PIPPA) and Unichem Technology's Unisperse 210.

A practical example of the benefits obtained from IPPA/PIPPA is discussed in a presentation at the 4th Middle East Refining & Petrochemicals Conference and Exhibition, in Bahrain in 2003.[21] The paper, written by Brown, Moore, and Al-Ben Hamad of Saudi Aramco, and Didden of GE Betz Belgium, mentions the successful use of the anionic PIPPA polymer for on-line boiler cleaning in a U.S. petrochemical plant. It then discusses successful on-line cleaning trials for the removal of iron and copper deposits using a maximum of 20 mg/L of polymer in 625 psig industrial boilers in Saudi Arabia. The next generation of novel chemistries should see IPPA/PIPPA with specific functional groups taken from, perhaps, the following list:

- Acrylic acid or methacrylic acid
- Acrylamide or t-butylacrylamide
- Methyl methacrylate, ethyl acrylate, 2-hydroxyethyl- or 2-hydroxypropyl acrylate
- Maleic acid or maleic anhydride
- Vinyl- or 2-acrylamido-2methyl propane sulfonic acid
- Vinyl acetate or phosphonic acid
- Styrene, or styrene acetate, phosphonic, benzoic, or sulfonic acid

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