



Speciality Chemicals Magazine

DECEMBER 2008
Volume 28 No. 10

The right priorities

Prioritising chemicals
of concern

Liquid diet

Progress in HPLC

Also:

Outsourcing ... Oilfield chemicals
... Peptides & proteins ... Process
development ... Informex USA
2009 preview

... and all the latest news

www.specchemonline.com

Phosphate esters & alkoxyated

Alan Russell of **PChem** reviews the basic chemistry behind systems involving phosphate esters and alkoxyated amines

As the world develops greater oil and gas production from marginal sources, there is a need for more effective corrosion inhibitors under more extreme conditions. Molecular structures that contain both amines and phosphate groups may be used in corrosion inhibitor formulation in these severe applications.

There is already number of products that combine phosphate ester technology with amine technology to provided highly effective corrosion inhibition under severe conditions of elevated temperatures, high velocity, and extreme acidity.

Current formulations

Fatty nitrogen compounds, such as coco diamine, or imidazolines, such as tall oil amino ethyl imidazoline, are frequently formulated with acidic compounds, generally to achieve a pH in the slightly acid range from 5.5 to 6.5.

In spite of the belief that there are stoichiometric considerations in these formulations, they are largely empirical and are described as salts, even though both the amine value and the acid value of the components can be measured using standard acid-base titrations.

The word 'salt' is more typically used to describe compounds like sodium chloride, where neither the acid nor the base can be measured by titration. A common lubricant additive, the compound of equivalent amounts of oleic acid and oleyl amine, is frequently called a salt, even though both the acid number and the total amine value can easily be measured.

The acidic chemicals used to make these formulations fall into two categories: the stronger acids are used to make more water-soluble formulations, the weaker acids to make more oil-soluble formulations. Examples of weaker acids are tall oil fatty acids (TOFAs), their dimers and trimers and naphthenic acids.

In order to achieve the desired pH of the formulation, it is typical to use two or more equivalents of acid for each amine equivalent. For example, coco diamine (amine equivalent weight 135) can be formulated with TOFA dimer (equivalent weight 305). A formula of 11% diamine, 49% tall oil dimer acid and 40% hydrocarbon solvent would conform to this principle, as would a formula of 11% tall oil imidazoline, 29% dimer and 60% solvent.

Stronger acidic materials include acetic acid, substituted acetic acids (i.e. glycolic acids), and 'detergent acids' (i.e. detergent alcohol sulphates and phosphates (Figure 1, 1). In general, stronger acids are used to prepare water-soluble or at least water-dilutable and, hence, highly water-dispersible formulations.

Empirically, some of these formulations have a lower (5.5) pH, such as mixture of 35% coco diamine, 15% glacial acetic acid and 50% alcohol/water solvent, while some with have a higher pH (7.5), for example a mixture of 43% tall oil/DETA imidazoline, 7% glacial acetic acid and 50% alcohol/water solvent.

The discussion to date has described formulations with a surface-active ammonium ion as the active ingredient. These compounds are generally referred to as cationic surfactants. These surfactants form a thin chemical film on a metallic surface, which protect the metal from corrosive gasses (CO₂ and H₂S) dissolved in brine.

Also described are anionic surfactants: carboxylates of fatty acids, poly acids, such as dimers, and naphthenic acids. These anions are also film-forming chemicals. This latter group seem to work better when the corrosive gas is O₂ (air).

In addition to the carboxylates, phosphate esters are frequently employed to prevent atmospheric corrosion. A phosphate ester can be manufactured from virtually any chemical that has a hydroxyl (alco-

hol) group. Specific compounds used are too numerous to mention, but the acidic compounds, which would be corrosive, can be made into corrosion inhibitors through the neutralisation process.

Polyol phosphate esters (Figure 1, 2) are frequently manufactured as scale inhibitors. Some of these esters also function as atmospheric corrosion inhibitors when formulated as an alkali salt.

Many of the cationic or the anionic surfactants used as corrosion inhibitors have other applications. For example, the hydrochloride salt of tallow diamine is used in the manufacture of cationic rapid set asphalt emulsion. Similarly, the sodium salt of tallow fatty acid is called soap.

It is important to understand all of the potential unintended consequences of the use of corrosion inhibitors, which are part of the formation. These unintended consequences can include emulsification of the crude and 'gunking' caused by the adhesion of heavy crude oils to sand and clay, as well as other factors.

Using a combination of a cationic and an anionic surfactant can overcome this problem if the surfactants remain water-soluble over a wide pH range. Fatty amines are water-soluble only at low pH, but ethoxylated fatty amines are cationic surfactants over a wide pH range.

Some detergent alcohol ethoxylates, which are either water-dispersible or water-soluble in cold water, are quite water-soluble but only at high pH. This problem can be overcome by converting the detergent alcohols into phosphate esters, making them anionic surfactants over a wide pH range.

Combinations of water-soluble fatty amines and water-soluble phosphate esters can be formulated to make effective corrosion inhibitors that will not emulsify the hydrocarbon. Both the amine and the ester might cause emulsion problems if used individually, but when they are combined, the anion (phosphate) and the cation (ammonium) are part of the film.

The assumption is that when an amine salt is used as a corrosion inhibitor, the film is composed of ammonium ions, with the anions being part of the brine. The theory is that when both the anion and cation are part of the film, the film is much less likely to be washed away and, hence, is more persistent. This has the advantage of being much more effective under the conditions of high velocity, high temperature or high acidity.

Phosphate ester derivatives

Phospholipids are very common surface-active molecules, which are understood to form the bi-layers that make up cell membranes. This understanding has led to the technology that allows testing of the corrosiveness of chemicals without the torture of albino laboratory animals.

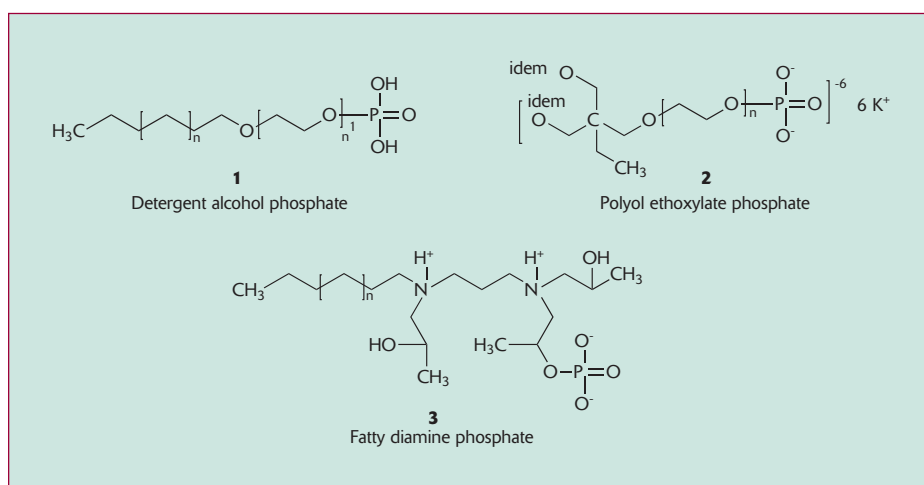


Figure 1 - Common formulations of corrosion inhibitors

amines for severe corrosion

We use this as an example of commonly occurring phosphate ester of a hydroxylamine. A commonly manufactured product is the phosphate ester of triethanolamine. Obviously, the occurrence of phosphate esters of hydroxyamines is quite common.

As discussed previously, tallow diamine, or coco diamine, are building blocks for corrosion inhibitor formulations. These formulations contain carboxylic acids as pH reducing agents or contain ethylene oxide additions to make the amine more water dispersible or entirely water-soluble. Obviously, an amine alkoxyate can also be converted into a phosphate ester in a manner similar to the manufacture of phosphate esters from detergent alcohols.

Alkoxyated amines

Previously we also looked at ethoxylates of tallow diamine. The simplest propylene oxide addition to tallow diamine is the three-mole addition, where two moles are added to the primary amine and one mole is added to the secondary amine. The resulting molecule can have multiple phosphate ester groups added.

Empirically, it has been found that when one mole of phosphoric acid is added to one mole of propoxylated tallow diamine, the resulting molecule, on the average, contains two amine equivalents and two phosphate equivalents. This molecule becomes an internal salt that has a resulting pH in the mildly basic range, about pH 9.

I refer to this as an internal salt because only one half of the original amine value can be titrated and it is quite unusual for a substance to have a pH above 7 and have twice the acid value as the amine value. In this example, one amine equivalent is a salt and the other is still measurable.

When the ammonium group and the phosphate groups are on separate molecules, these molecules have differing water and oil solubility as the pH changes. Raising the pH, in general, makes the phosphates more water-soluble and the amines less so. The reverse is true when the pH is lowered.

This means that the phosphate molecule could emulsify the amine molecule at high pH and that the amine molecule could emulsify the phosphate at low pH. Conversely, the phosphate ester of the alkoxyated amine (Figure 1, 3) just becomes less surface-active at either high or low pH and hence an effective corrosion inhibitor over a wide pH range.

These empirically formulated internal salts are not to be confused with the amphoteric compounds known as the betaines, which are not identified as corrosion inhibitor intermediates. Research has identified molecules that have both the amine group and the hydroxyethyl group present. The molecules are then converted to phosphate esters using the common synthesis techniques.

Phosphate esters can be manufactured using 85% phosphoric acid, 105% super phosphoric


acid, 115% polyphosphoric acid or phosphorous pentoxide. Each of these reagents will produce a differing result.

This paper just scratches the surface of corrosion inhibitors for the oilfield industry. With the many different reactants that can be combined into interesting chemicals, and the potential interaction of those chemicals in a finished formulation, it is important to work with suppliers that provide a high level of technical support. A chemistry degree will never replace a formulator's industrial experience.

For more information, please contact:
 Alan Russell
 Vice President of Technical Operations
 PChem, Inc.
 100 Old Latexo Road
 Latexo
 TX 75849
 USA
 Tel: +1 936 544-5174
 E-mail: alanrussell@pcheminc.com

Your Specialist for Hazardous Reactions.

Visit us at the InformexUSA 2009 Booth No 1112


 dottikon
 EXCLUSIVE
 SYNTHESIS

Dottikon Exclusive Synthesis AG
 P.O. Box, 5605 Dottikon, Switzerland, www.dottikon.com