

Determination of residual free boric acid in amine borate condensate reaction products by ^{11}B NMR spectroscopy

Introduction

Boric acid derivatives have been the general purpose corrosion inhibitors of choice in aqueous metalworking fluids for over thirty years. They were introduced to replace nitrates which had been found to produce nitrosamines in the presence of certain amines. In addition to corrosion inhibition, borates provide a number of well-known and beneficial attributes including buffering, reserve alkalinity and hard water tolerance amongst other properties when used in aqueous synthetic and semi-synthetic cutting fluids. In recent years the use of boric acid itself has come under the spotlight, in particular by the European Chemicals Agency. The use of boric acid has not been restricted, but growing concerns over its use is prompting metalworking fluid producers to question the additive producers regarding the boric acid content in the additives they do use. As a responsible additives supplier with a range of metalworking fluid additives incorporating boric acid as a precursor, Afton Chemical has responded to these concerns and undertook a project to determine the levels of free boric acid in the borate condensate products manufactured and supplied to the metalworking fluid producers.

Regulatory requirements for boric acid

In 2008 within Europe, boric acid was identified as a Category 2 reproductive toxin requiring it to be labelled with Risk Phrases R60 and R61 (may impair

fertility; may cause harm to the unborn child). Mixtures containing 5.5% or more of free boric acid would also need to be similarly classified and labelled. In 2010, the new European CLP, (Classification, Labelling and Packaging) of substances and mixtures regulation entered into force, implementing the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) within Europe. The equivalent classification for boric acid under the CLP Regulation is toxic to reproduction, Category 1B, with hazard statement H360FD (may damage fertility; may damage the unborn child) and the Health Hazard pictogram.

A consequence of the toxic to reproduction classification is that boric acid has been added to the EU's Candidate List of Substances of Very High Concern [SVHC]. All SVHC substances may be put forward for assessment under the Authorisation process in REACH, although there is no timescale when this assessment may take place. Placing a substance on the SVHC Candidate List does not in itself change the regulatory status of that substance.

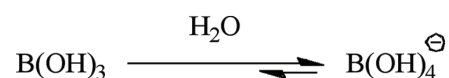
One of the repercussions of classification is that suppliers of a classified mixture containing over 0.1% of a toxic to reproduction substance are required to identify the presence of that reproductive toxin on the product's Safety Data Sheet. Products which have levels of free boric acid below 0.1% require no such identification or notification.

Previous investigations to determine the level of free boric acid [Lube-Tech 65 August 2009] concluded that it was very difficult to determine the exact level of the substance in undiluted blends of boric acid, MEA and water. The conclusion at the time was that the boric acid MEA salt blend must contain below 5.5% boric acid but could not stipulate beyond that.

Afton Chemical uses boric acid as a raw material in the production of a number of corrosion inhibitors marketed as the POLARTECH® BA series. The conditions used to manufacture the borate alkanolamine condensates ensure that complete reaction has taken place consuming all of the boric acid. In line with Afton's Health Safety and Environmental Policy, Afton Chemical has undertaken to demonstrate the absence of unreacted (free) boric acid in its POLARTECH® BA series of products.

Boric acid

Boric acid is a weak Lewis acid with a $\text{pK}_a = 9.0$ at 25°C and maximum solubility in water only 5.5%. This means that in dilute solutions of boric acid in water, below 0.025 molar, the boric acid will be present in two principle forms depending on the pH.



Example

At pH <5, boric acid $B(OH)_3$ is the dominant form and at pH > 12 then borate anion $B(OH)_4^-$ is the dominant form. At pH between these two values and excluding outside factors, both forms will be present. The higher the pH, the greater the tendency to form the borate anion.

For solutions at concentrations higher than 0.025 molar, boric acid in water tends to form polyborate complexes of various types, all dependent on concentration, pH and the environment.

Afton Chemical manufactures a range of boric acid derivatives for use as metalworking corrosion inhibitors. These derivatives are produced at a high temperature to ensure full reaction between boric acid and the various alkanolamines used. Water of reaction is evolved during the process generating a complex mixture of borate and polyborate reaction species. With this as the starting point, Afton Chemical undertook a program to develop an analytical method, based on ^{11}B NMR capable of determining the free boric acid content in the POLARTECH® BA series additives at a level of 0.1%.

^{11}B NMR analysis is difficult in comparison to the more familiar 1H and ^{13}C NMR. With a spin number of $I=3/2$ and a relative sensitivity approximately 4% that of 1H , determination of boric acid at low levels is always going to be a problematic. There were a number of challenges to be overcome for this program.

NMR method development

A Bruker 400 MHz spectrometer, capable of multi-nuclear analysis and equipped with a BBO probe was used for this analytical programme. Conditions were developed to maximise the sensitivity towards ^{11}B and required the use of ultra-low boron quartz tubes, Norrell® S-5-500-QTZ-7. This methodology was established as part of the calibration process and it was possible to calibrate the instrument down to very low levels of free boric acid.

Calibration was achieved by preparing boric acid in deuterated water [D_2O] at various concentrations from 5.0 to 0.05% by weight. Boric acid is set at 0 ppm chemical shift. Chemical shifts other than 0 ppm indicate the boron atom is

chemically associated with other chemicals such as alkanolamine or present in more complex forms such as polyborate. With boric acid arbitrarily set at 0 ppm, this leads to other boron species having negative chemical shifts away from the boric acid. Each boron species has its own unique chemical shift.

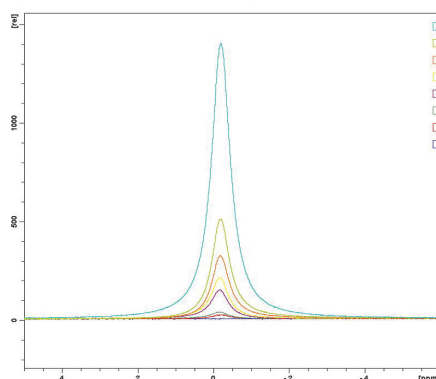


Fig 1 ^{11}B NMR of boric acid solutions, aqua = 5% by weight, light green = 2%, brown = 1%, yellow = 0.5%, purple = 0.2%, green = 0.1%, red = 0.05% and blue = 0%.

A more detailed observation of boric acid in D_2O at calibration points at 2.0% and 0.05% are seen in figures 2 and 3.

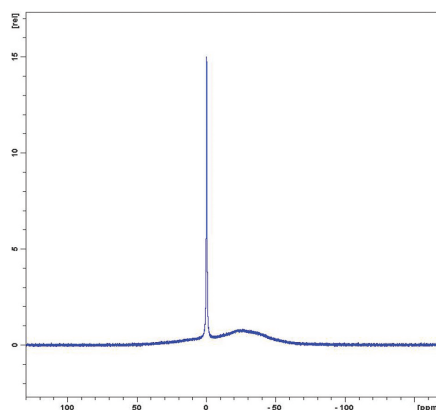


Fig 2 Boric acid in D_2O at 2% by weight.

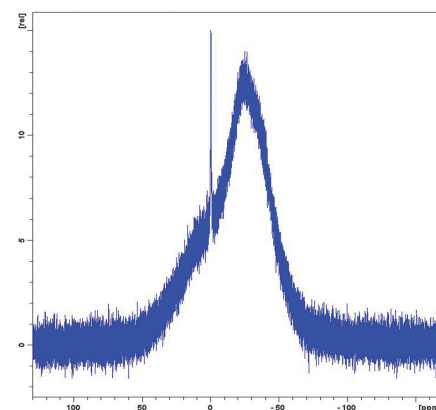


Fig 3 Boric acid in D_2O at 0.05% by weight

In both cases the free boric acid is clearly visible as the sharp peak at 0 ppm and the limit of detectability is thought to be below 0.02% by weight. The broad peak is borate anion and hydrated polyborate anions.

Additive analysis

A series of investigations were conducted to first determine how to analyse for boric acid alkanolamine condensate derivatives, then determine the free boric acid content.

The first phase of the program was to determine how to analyse the additives. A laboratory prepared reference product was prepared under conditions designed to replicate the typical plant conditions. The reaction was monitored by the normal QC analytical methods and water of reaction was evolved and collected. The sample prepared was determined to be indistinguishable from the typical plant product by normal QC analytical methods.

As produced, the borate condensates are viscous concentrates which makes them difficult to analyse in the neat form. Analysis of the neat additives gave an unsatisfactory broad spectrum from which it was difficult to extract meaningful data.

Starting with the lab prepared borate condensate sample, the reaction product of boric acid and monoethanolamine, sequential dilution in D_2O significantly improved resolution and enabled isolation of single species peaks. We found that dilution of borate condensate 50% to 10% active in D_2O was sufficient to provide the resolution necessary, with the greatest resolution at 10%. However as we were looking for boric acid, which we expected to be at a low initial level, we decided to accept a compromise resolution at 50% active.

An interesting observation from this dilution work came from assessing the hydrolytic stability of the borate condensates. Many formulators have experienced precipitation when using boric acid products; the common belief is that it is boric acid that is precipitating. This may be the case where boric acid salts are used, but even at the low

10% active dilution we did not see any sign of precipitation.

Boric acid salts are typically prepared by addition of boric acid to alkanolamines in water at temperatures too low for the condensation reaction to take place. This observation is taken to be a result of the borate condensates being more water soluble and containing a negligible level of boric acid.

The next phase of additive evaluation assessed laboratory prepared materials based on commercial additives. The reactions were controlled to minimise by-product formation and thereby simplify the analysis. The condensation reaction is carried out at a temperature sufficient to ensure water of reaction is evolved, with a subsequent measurable mass loss in the reaction product. The condensation product is a complex mixture of polyborate amides, polyborate esters, ionic polyborate species, monoborate amides and monoborate esters and unreacted MEA. The lab products were based on boric acid and monoethanolamine at 2% molar excess MEA, to give nominal elemental boron content of approximately 6%. We selected this material as it is at the upper limit of elemental boron found in most metalworking fluid formulations. As it has a relatively high initial boric acid charge, this material should have the greatest level of residual boric acid remaining after the condensation reaction.

Analysis of the lab samples at 50% active by ^{11}B NMR gives strong peaks at -6, -10 and -13.5 ppm, a weak peak at -18.3 ppm and a broad tail of unresolved species between -13 to -20 ppm. No peak is visible at the reference 0 ppm for the materials at 100%, 50% or 10% active in D_2O . This suggested that either the sample did not contain boric acid or that boric acid was not detectable in the complex product. To validate the analysis and confirm whether the interpretation of 'no detectable boric acid' was genuine or an artefact of the analysis, boric acid was spiked into the samples. A 10% addition of boric acid spike to the sample gives very strong peaks at 0 ppm and -18.3 ppm chemical shifts, indicating the presence of free boric

acid and the simple borate anion.

As the analytical methodology was found to be suitable to detect boric acid spiked in the additive, the next stage was to evaluate a wider range of additives. Lab prepared additives as controlled references and plant prepared products were assessed. Products prepared using a range of alkanolamines and boric acid expressed as elemental boron from 2% to 5.5% were analysed under the same conditions at 50% active in D_2O . These samples covered the full range of Afton metalworking fluid borate additives.

In each case key peaks were identified at -6.3, -10, -13.5, -15.4 and -18.3 ppm, with the relative peak heights varying dependent on the nature of the raw materials and the products formed. In each case no evidence of any free boric acid at 0 ppm was observed.

As the analysis of lab prepared samples all indicated no boric acid present, this work was repeated on freshly prepared plant products. Samples of the various borate additives were taken from recent plant retained production samples, all less than four weeks old. The analysis of these plant retained samples was indistinguishable from the lab prepared samples, indicating a high level of consistency between the lab and plant prepared materials. Again the analysis indicated no boric acid present. Further this analysis demonstrated that the lab samples were truly representative of the plant materials.

The logical question was asked; "How do these additives behave in real formulations?" Metalworking fluid formulations are complex products with between 10 to 20 individual components, of which borate corrosion inhibitor is only one component. Several industry typical formulations were prepared using a selection of borate condensate additives. Typical metalworking fluid concentrates have between 10 to 40% active borate additives. The fluid concentrates had between 0 to 50% oil content to cover the range of synthetic oil-free to medium oil semi-synthetic working fluids. We were concerned that incorporating the borate additives into these

complex formulations may cause any number of potential interactions to take place which could potentially liberate boric acid.

As anticipated when analysed, the same range of key NMR peaks at -6.3, -10, -13.5, -15.4 and -18.3 ppm were seen, with peak heights varying dependent on the additive used. We did observe in some formulations a small shift in the relative peak heights of these major peaks, which we attribute to interaction with the various acid and alkali components and possible complexation with hydroxyl species. However, despite the complex nature of the formulated fluids, no evidence of free boric acid at 0 ppm was seen.

The final evaluation was to assess the long term stability of the borate condensates. Two representative borate condensate products at 4.8% & 5.6% elemental boron were selected. Plant retained samples spanning 18 months, stored under typical warehouse conditions were obtained. The warehouse, located in Manchester UK, is typical in as much as it does not have active climate control. This means that the samples depending, on age have been exposed to cold and warm extremes of normal storage conditions, with outside air temperatures of between -12 °C to +25 °C recorded over the time period.

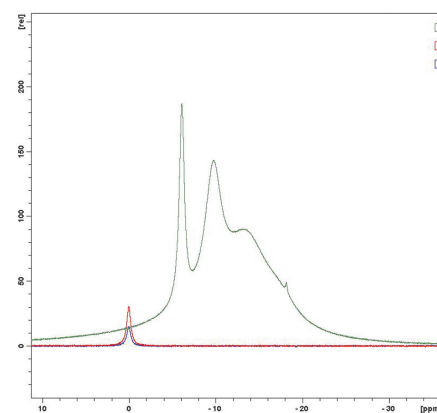


Fig 4a Nov 2010

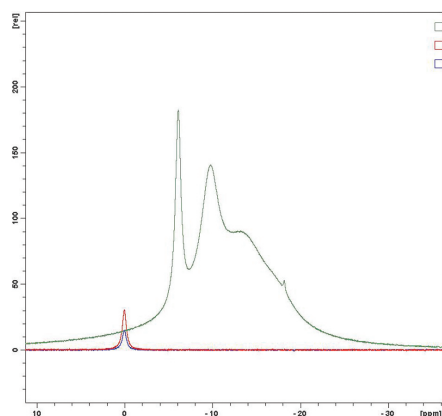


Fig 5a April 2011

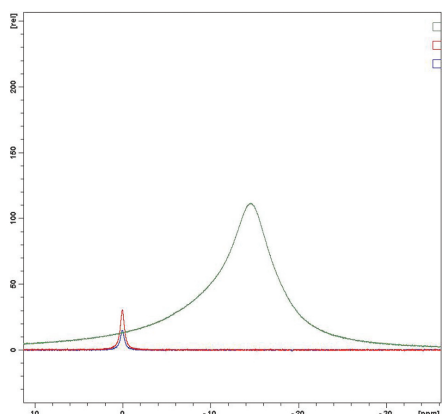


Fig 4b April 2012

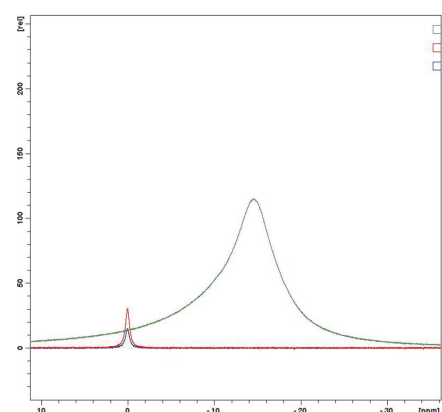


Fig 5b March 2012

Figures 4a, 4b, 5a & 5b

In all, eighteen samples were analysed during this final stage and again no evidence of free boric acid was seen at the 0 ppm chemical shift. In each case the sample is indicated in green, boric acid at 0.2% in red and boric acid at 0.1% in blue. As can be seen in figures

4a & 4b and 5a & 5b, plant retained samples give essentially identical spectra when aged 12 or 18 month. This demonstrates the high stability of borate condensate additives when stored under typical conditions, regardless of the additive composition. This analysis of the aged samples clearly indicates that the condensation process is complete and prevents the possibility of reverse hydrolysis and release of boric acid on storage. Visually the aged and fresh samples are indistinguishable, with no change in colour and no signs of precipitation or splitting.

Throughout this program, there has been considerable debate regarding the analysis and the implications. Afton Chemical has undoubtedly developed a far deeper knowledge of the borate condensate additives, their chemistry and manufacturing processes. Information such as long term stability and hydrolytic stability is clearly of significant value and it is reassuring to see stable long life products. Developing an analytical method capable of reliably detecting boric acid at very low levels and further demonstrating the lack of measurable boric acid in the condensate additives is a real technical achievement.

We have been able to determine that the additives manufactured do not contain boric acid. However, this is not the end of the investigation. Most metalworking formulations that use borates have a moderately high pH around 9.0 – 10.0 and under these conditions, the working fluid is stable and offers optimum corrosion protection for most metal. These are also optimum conditions to maintain the stability of the borates. Afton continues to investigate the use of borates to develop a more comprehensive picture of the stability over time and under different metalworking conditions.

Conclusion

Afton has developed a NMR method capable of identifying free boric acid down to very low levels. The limit of detectability for free boric acid is below 0.02%. A selection of boric acid condensation products were analysed and the analysis confirmed that these products do not contain a detectable level of free boric acid.

During the course of this investigation over 50 individual borate condensate samples have been analysed. These include samples used in the method development phase, lab prepared borate condensates, plant manufactured borate condensates, typical formulations using a range of borate condensates and plant samples aged up to 18 months. Great care has been taken to ensure the analysis of each sample and product was consistent and of a high standard.

We conclude that Afton Chemical's fully reacted Borate condensation products are free from detectable levels of boric acid (where the limit of detectability is 0.02% free boric acid).

Based on this work, and the evidence from formulated fluids, Afton Chemical is confident that these fully reacted borate corrosion inhibitors, manufactured to the process described used in aqueous MWF under normal metalworking conditions and pH do not contain detectable levels of free boric acid. The supply and use of these additives and fluids incorporating them are therefore not required to carry labelling or notification regarding the presence of boric acid.

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