

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.

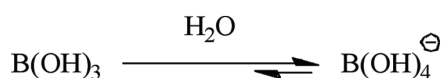
One of the repercussions of classification is that suppliers of a classified mixture containing over 0.1% of a toxic to reproduction substance are required to identify the presence of that reproductive toxin on the product's Safety Data Sheet. Products which have levels of free boric acid below 0.1% 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