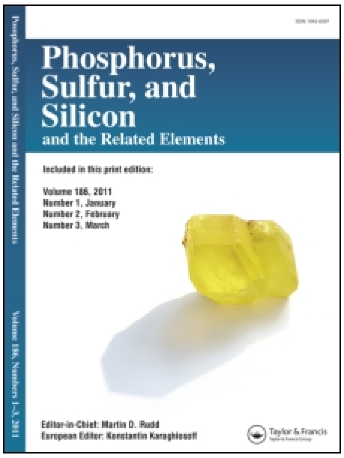

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Davis, Keith P. , Hoye, Peter A. T. , Williams, Michael J. and Woodward, Gary(1996) 'Development of an 'All Organic' Phosphorus Based Corrosion Inhibitor.', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 197 — 200

To link to this Article: DOI: 10.1080/10426509608545124

URL: http://dx.doi.org/10.1080/10426509608545124

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 197–200
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DEVELOPMENT OF AN 'ALL ORGANIC' PHOSPHORUS BASED CORROSION INHIBITOR.

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Abstract Albright and Wilson has developed a water soluble environmentally acceptable corrosion inhibitor, BRICORR288. Unlike current treatments for corrosion it does not contain chromium or zinc. Development of this organophosphorus corrosion inhibitor is described; both the process chemistry of manufacture and activity are discussed. BRICORR288 is manufactured by the aqueous radical reaction of phosphorous acid with maleic acid and is a telomeric mixture of phosphono succinic acid and 1-phosphono butane-1,2,3,4-tetracarboxylic acid. The general utility of the process chemistry is discussed with respect to the facile large scale manufacture of other water soluble phosphonates. BRICORR288 is now being manufactured on a multi tonne scale for sales in the UK and Europe.

INTRODUCTION

Corrosion is a serious problem, in the UK alone it accounts for the loss of £1000Ms each year as a result of direct damage and down time in industry. Treatments currently available to control corrosion often use materials which are now considered unacceptable. Chromium and zinc containing formulations in particular are used; they are toxic to marine life and persistent in the environment. In response to these pressures Albright and Wilson has developed an environmentally acceptable inhibitor system (BRICORR288) based on a water soluble phosphonate. Unlike currently available organophosphorus corrosion inhibitors it is stable to oxidation by bleach (currently used as a biocide in industrial cooling systems). The process for manufacture of BRICORR288 has minimal environmental impact; it has no by-products and uses a water solvent.

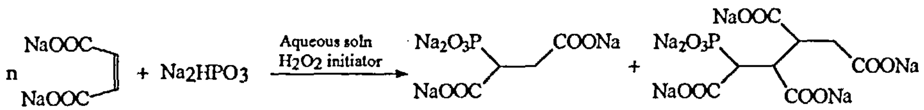
DISCUSSION

Choice of Compound

Any new potential corrosion inhibitor has to meet many criteria. These are:

(i) Good environmental profile in terms of toxicity, aquatic toxicity, environmental biodegradability and process chemistry / raw materials
(ii) Cost effective
(iii) Stable to oxidising biocides (e.g. bleach is commonly used in cooling systems)
(iv) Compatible with other water treatment agents (for formulation)
(v) Active over a wide range of water chemistry

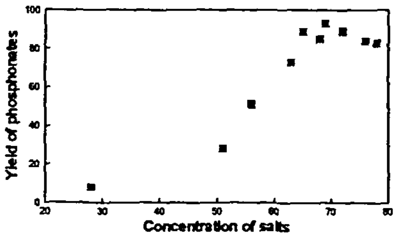
Many phosphonates are used in water treatment. The main products are hydroxy phosphonoacetic acid[1], aminomethylene phosphonates[2], 1-hydroxyethane-1,1-bis phosphonic acid[3], and 2-Phosphono butane-1,2,4-tricarboxylic acid. Over a period of two years we evaluated over 80 phosphonates in standard water conditions (60ppm active dose, 120ppm Ca, pH 7.5 at 20°C). Nearly half of the 20 'best' gave excellent corrosion inhibition (<2mils/yr); the final choice was not just based on activity but also on cost effectiveness, environmental profile of the process chemistry and chlorine stability. BRICORR288 is made by patented Albright and Wilson Technology:

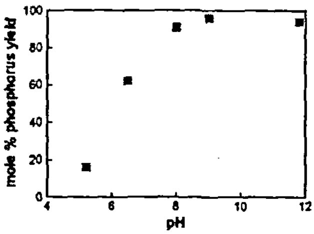


It is a telomeric mixture of phosphonosuccinic acid and 1-phosphonobutane-1,2, 3,4-tetracarboxylic acid made by the reaction of maleic acid with phosphorous acid. Variations have been made in the composition of BRICORR288. It has been discovered that an approximately 1:1 ratio of n=1 to n=2 gives optimum performance as a corrosion inhibitor. Details of this work will not be described here. No polymaleate is formed and oxidation to phosphate is <3%.

Choice of Process Chemistry

Raw material costs and disposal of by-products are vital considerations when designing a new process. The process must match the high environmental standards of the product. The chosen route uses phosphorous acid, this is a common feature in the manufacture of water treatment chemicals. In three of the above water treatment compounds phosphorous acid is used as the source of phosphorus[1,2,3]. All three of these compounds decompose in the presence of bleach. [2-phosphonobutane-1,2,4- tricarbox--ylic acid uses a base catalysed addition of dialkyl phosphite to dialkyl maleate in the first stage[4] of manufacture]. BRICORR288 chemistry uses phosphorous acid in a radical process. Radical addition of alkyl phosphites[5], or half phosphites[6] to olefins in the manu--facture of organophosphorus products is very well known in industrial applications. The direct radical addition of phosphorous acid to olefins in an organic solvents, e.g. dioxane, using organic radical initiators (e.g. alkyl peroxides or azo-bis initiators) has also been reported[7]. BRICORR288 process chemistry enables direct reaction of water soluble olefins in water solvent using hydrogen peroxide as the initiator for the radical chemistry [8,9]. As such the chemistry does not use toxic solvents, such as dioxane, has no initiator by-products to contaminate the product and therefore meets the required characteristics.





BRICORR288 Chemistry[9]

This chemistry is very sensitive to pH and concentration. The optimum concentration is 65% - this represents about 10 moles of water per mole of phosphorus; at a greater concentration the yield drops because the reaction mixture becomes too thick to mix effectively. Clearly radical transfer and termination processes dominate at lower concentrations. The pH must be above 6-7 to obtain a good yield. The pK_2 of phosphorous acid is 6.5. Although it is not valid to compare the optimum pH for reaction (at 110°C, 65% solids) with the pK_2 in dilute solution at 25°C, it seems reasonable to postulate that it is the radical dianion which is required for this chemistry. In the ^{31}P and ^{13}C nmr spectra of BRICORR288 it is clear that only two of the expected four diastereomers of the n=2 compound are formed. Clearly there is some preferred stereochemical orientation in formation of the C-C bond.

Activity as a Corrosion Inhibitor

Typical operating conditions are 10ppm of Ca as $CaCO_3$, 10-30ppm of inhibitor, pH 5.5-9.0 and max. of 600-900ppm chloride. Corrosion inhibition with BRICORR288 requires the presence of calcium; also, metal that has been treated with BRICORR288 has a surface film in which we have detected calcium, phosphorus and carbon, by surface analysis. Corrosion is an electrochemical process and for the above reasons we believe that BRICORR288 acts at the cathodic sites on the metal. At these sites oxygen and water are being converted to hydroxide ions; the surface pH can be 10.5 - 11[10], whereas the bulk water pH may be 5-7. This local high pH is believed to result in the deposition of a calcium salt of BRICORR288; this would stop corrosion by blocking the flow of water and oxygen to the metal surface. At anodic corrosion sites on the metal, rust (as mixed iron oxides) is being produced; it is not clear to what extent BRICORR288 modifies the metal surface and the iron oxide / hydroxide being formed at anodic sites.

Conclusions / Summary

BRICORR288 is now being manufactured by Albright and Wilson and sold into the European Market. It has an excellent environmental profile:

Ecological / toxicological information: *Toxicity*: Rat oral LD50 > 5000mg/Kg, Rat dermal LD50 > 2000mg/Kg, Ames test negative: *Aquatic toxicity*: 96h LC50 rainbow trout >100mg/L, 48h EC50 Daphnia magna>100mg/L, EC50 (30min and 3h) >1000mg/L (activated sewage sludge respiration inhibition assay). *Process*: Environmentally acceptable, No toxic by-products.

Activity :*Chlorine stable* - 5% BRICORR288 and 5% Cl_2 as bleach stable for >1week at 70°C, *Water soluble* - compatible with other water treatment agents, *Cost effective* 10-30ppm active dose and *Ease of use* -supplied as a solution in water .

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