

## Zirconium in Formic Acid Applications

### INTRODUCTION

Formic acid is a versatile player in the chemical industry. It is unique, in that it acts both as an aldehyde and as a carboxylic acid. It is more highly ionized and acidic than acetic acid. It is highly corrosive to most metals, plastics and rubbers. It reacts readily with many oxidizing and reducing compounds; because of this, formic acid has been gaining favor in industry. For instance, formic acid is used in the production of pharmaceuticals, dyes, flavors and perfume ingredients, textiles, leather and rubber. A large portion of formic acid production is earmarked for silage in Europe.

Formic acid is unstable under some conditions, decomposing to carbon monoxide and water or carbon dioxide and hydrogen. This instability is attractive because of heightened awareness to environmental pollutants. Formic acid is now being mixed with hydrogen peroxide to produce viable replacements for sulfur and chlorine solutions in the pulp and paper industries. Formic acid is produced in three main reactions: methyl formate, formate salts or as a byproduct of acetic acid production. Each of these methods produce formic acid in varying concentrations, but all require further distillation to retail grade material.

Formic acid has proven to be highly corrosive at concentrations over 50%; because of its corrosive nature at high concentrations material selection can be a challenge. Zirconium has distanced itself from other materials with its ability to withstand formic acid corrosion in all concentrations and a very broad set of other conditions. Acid concentration, vapor phase, temperature, heat transfer, aeration and other impurities do not affect the corrosion resistance of ZIRCADYNE 702 in formic acid; however, there are limitations which are discussed further.

### CORROSION DATA

Formic acid in its pure form is corrosive to many alloys. Formic acid as a reducing agent attacks stainless steels unless an oxidizing agent is added. Nickel base alloys perform better than SS 316, but are attacked if an oxidizing agent is present. Zirconium is resistant to reducing agents, as noted in **Table 1**.

**Table 1.**  
 ZIRCADYNE 702 and Three Other Corrosion-Resistant Alloys in Boiling Formic Acid Solutions (Data obtained after a 2-4-2 day cycle)

Formic Acid %	Zircadyne 702		Type 316 S.S.		Alloy B-2		Alloy C-276	
	NW*	W*	NW	W	NW	W	NW	W
50	<0.1	<0.1	24	25	0.9	1.0	2.0	1.8
70	0.1	<0.7	19	19	2.7	2.7	2.3	1.9
98	<0.1	<0.1	4.9	5.1	1.7	1.7	0.9	0.8

Corrosion Rate, mpy

Zirconium was tested with several different impurities to show its ability in corrosive media of differing chemical characteristics. Under both oxidizing and reducing conditions, Zirconium shows significantly better resistance compared to other alloys in formic acid media with impurities (See **Table 2**).

Zirconium was also tested at temperatures from ambient to 140°C. It showed no corrosion in the liquid phase, the vapor phase or the liquid/vapor interface of formic acid solutions of concentrations ranging from 10-90%.

Table 2.

Corrosion of Various Alloys in Boiling HCOOH Solutions with Impurity (Test results averaged from a 2-4-2 day cycle in most cases) \*NW: Nonwelded. W: Welded, \*\*Coupons were plated with copper, \*\*\*Weld metals were preferentially attacked.

Medium	Zircadyne 702		Type 316 S.S.		Alloy B-2		Alloy C-276	
	NW*	W*	NW	W	NW	W	NW	W
1%Fe Powder Containing								
50% HCOOH	<0.1	<0.1	26	28	73	86	6.4	4.8
70% HCOOH	<0.1	<0.1	22	21	28	28	8.1	8.1
98% HCOOH	<0.1	<0.1	1.8	2.0	1.5	1.5	1.2	1.1
CuSO4 Containing 1% Cu+2								
50% HCOOH	<0.1	<0.1	1.5	1.5	>200**	>200**	7.1	5.1
70% HCOOH	<0.1	<0.1	0.4	0.5	W.G.**	W.G.**	6.1	4.0
96% HCOOH	<0.1	<0.1	0.2	0.2	125**	152**	2.1	1.4
5% H2SO4 Containing								
50% HCOOH	<0.1	0.2	89	106	1.1	1.7	1.8	2.2
70% HCOOH	<0.1	<0.1	146	146	1.7	1.8	2.3	2.0
93% HCOOH	<0.1	<0.1	180	200	0.6	0.6	0.9	0.8
5% HCl Containing								
50%HCOOH	<0.1	0.1	>200	>200	1.8	2.0	107	126
70%HCOOH	0.1	0.1	>200	>200	1.5	1.7	37	38
85%HCOOH	<0.1	0.1	>200	>200	0.7	0.7	14	15
5% HI Containing								
50%HCOOH	<0.1	<0.1	24	44	1.3	1.5	9.0	9.8
70% HCOOH	<0.1	<0.1	172	>200***	59	75	129	123***
90% HCOOH	<0.1	<0.1	25	31	6.2	7.3	23	22***

\*NW: Nonwelded \* W: Welded

## SUCCESS STORIES

One company's search for the best possible formic acid process ended in 1980 when it adopted the basic technology of the Leonard Process. In redesigning the "Leonard-process," specifying materials of construction was a key issue.

Virtually all equipment and pipelines in the formic acid section handle hot formic acid solutions. There, ordinary stainless steels are not acceptable, not only because of their very short service life, but also because the product acid has to be free of all metal ions. For the same reason, high-performance alloys did not meet the service requirements.

The company's laboratory and plant performed lengthy tests on a variety of materials, including: glass linings, resin and plastic coatings, alloys and specialty metals. Test results showed that Zircadyne 702 was clearly the most economical construction material for use in the main equipment for this application.

## LIMITATIONS

Zirconium is a fantastic structural metal in many corrosive environments; it shows versatility to corrosion in media that is both oxidizing and reducing. If zirconium maintains a thin oxide layer in a particular media, it is then highly corrosion resistant. If the oxide layer does not form, it can corrode quickly. Zirconium in some formic acid concentrations does not resist attack well by acidic oxidizing chlorides and other contaminants such as Fluorides,  $\text{FeCl}_3$  and  $\text{CuCl}_2$ ; these materials should be avoided. It is important to disclose all possible metal ions to make a clear determination of the effectiveness of zirconium in formic acid.

## SAFETY

In some highly corrosive conditions, zirconium can form a pyrophoric film. This is caused by rapid uneven corrosion. Zirconium usually corrodes uniformly and all zirconium is converted to zirconium oxide. If the corrosion rate rises, it is possible that the corrosion can attack grain boundaries trapping small pieces of non-reacted zirconium. This can cause a pyrophoric film, which will need to be completely oxidized prior to opening to air. To pacify the zirconium it is necessary to pass hot air or steam through the equipment making sure the zirconium completely oxidized. At 250°C, air must flow for 20 minutes or steam for 30 minutes; at lower temperatures, several days of treatment may be required.

## SUMMARY/ CORROSION LAB SERVICES AND OTHER WAH CHANG RESOURCES:

Longer equipment life, reduced maintenance downtime, and higher purity product streams are all possible with the proper application of zirconium, making it the most cost-effective option when compared with other alloys. For further information or questions about zirconium in formic acid applications contact the Technical Services Division at Wah Chang.