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Technical Data Sheet

Zircadyne® 702/705 - in Organic Applications

INTRODUCTION

Laboratory studies and case histories have established zirconium as the most corrosion resistant material of construction in many production methods involving organic media. In fact, zirconium plays a pivotal role in production of a wide range of organic materials including formic, acetic, hydroxyacetic, lactic and methacrylic acids, urea, methyl methacrylate, rayon, and various alcohols and phenolic resins. The ability of zirconium to withstand high temperatures and concentrations coupled with the fact that the zirconium ions are colorless allows its use in dye manufacturing and other areas where the color of the final product is critical. Zirconium also appears to be nontoxic and biocompatible.

CORROSION RESISTANCE

Zirconium has excellent corrosion resistant in most organic media. Exceptions are chlorinated hydrocarbons and organic solutions that contain halogens or halides in the absence of adequate water. Under these conditions zirconium can experience high corrosion rates or suffer from hydriding.

For corrosion purposes, organic halides can be grouped into three categories. These are water-soluble halides,water-insoluble halides and water-incompatible halides. In the case of water-soluble halides such as aniline hydrochloride, chloroacetic acid and tetrachloroethane, insuring the presence of adequate water or stress relieving after fabrication can significantly reduce the tendency of zirconium to corrode or form hydrides. Water-insoluble halides, such as trichloroethylene and dichlorobenzene are not corrosive to zirconium. Waterincompatible halides, including acetyl chloride, are highly corrosive to zirconium. In each case the presence of adequate water is critical for the formation of the protective oxide layer on the surface of zirconium. Depending upon the solution and operating conditions, the water content needed to maintain zirconium's protective oxide file can be as little as 50 ppm to as much as 2-3%.

Acetic acid

Acetic acid is one of the basic starting materials for a wide range of organic materials. These include acetate esters, acetic anhydride, terephthalic acid, aspirin and other pharmaceuticals. Zirconium is considered the most corrosion resistant material in virtually all acetic acid solutions. As seen in Table 1, the few exceptions include acetic acid containing cupric ions, free chlorine and solutions with insufficient moisture to allow zirconium to reform the protective oxide surface layer. Under highly stressed conditions >650-ppm water is required in acetic acid to prevent stress corrosion cracking. If water addition is not practical, stress relieving may be considered.

TABLE 1. CORROSION DATA FOR ACETIC ACID

Media	Concentration (%)	Temp (°C)	Corrosion Rate (mpy)
Acetic Acid (anhydride)	99	Room-Boiling	<1
Acetic Acid	5-99.5	35-boiling	<1
Acetic Acid	99	200	<1
Acetic Acid (glacial)	99.7	Boiling	<5
Acetic Acid (glacial) + 0.5% methanol	99	200	<1
Acetic Acid (glacial) + 0.5% methanol + 200 ppm $FeCl_3$ + 1% H_2O	98	200	<1

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Acetic Acid (glacial) + 200 ppm $FeCl_3$	99	200	<1
Acetic Acid + 0.5% methanol + 200 ppm $FeCl_3$ + 5% H_2O	94	200	<1
Acetic Acid + 1% I - (KI) + 100 ppm Fe^{+3} ($Fe_2(SO_4)_3$)	99	200	<1
Acetic Acid + 10% methanol	90	200	<1
Acetic Acid + 10% methanol + 200 ppm $FeCl_3$ + 1% H_2O	88	200	<1
Acetic Acid + 10% methanol + 200 ppm $FeCl_3$ + 5% H_2O	84	200	<1
Acetic Acid + 10% methanol + 1000 ppm copper Acetate	89	89	<1 pit
Acetic Acid + 10% methanol + 1000 ppm Cupric Chloride	89	89	<1 pit
Acetic Acid + 10% methanol + copper metal	89	89	<1 pit
Acetic Acid + 1000 ppm copper Acetate	99	115	<1 pit

Acetic Acid + 1000 ppm copper metal	89	115	<1 pit
Acetic Acid + 1000 ppm Cupric Chloride	89	115	<1 pit
Acetic Acid + 2% HI	80	100	<1
Acetic Acid + 2% HI	98	150	<1
Acetic Acid + 2% HI + 1% methanol + 500 ppm formic acid	80	150	<1
Acetic Acid + 2% HI + 1000 ppm copper Acetate	97	115	<1 pit
Acetic Acid + 2% HI + 1000 ppm copper metal	97	115	<1 pit
Acetic Acid + 2% HI + 200 ppm Cl - (NaCl)	80	100	<1
Acetic Acid + 2% HI + 200 ppm Fe^{+3} ($FeCl_3$)	80	100	<1
Acetic Acid + 2% HI + 200 ppm Fe^{+3} ($Fe_2(SO_4)_3$)	80	100	<1

Data are typical and should not be construed as maximum or minimum values for specification or for final design.
Data on any particular piece of material may vary from those herein.

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Acetic Acid + 2% HI+ 1% methanol + 500 ppm formic acid, + 100 ppm copper	80	150	<1
Acetic Acid + 2% I - (KI)	98	150	<1
Acetic Acid + 48% HBr	50	115	<1
Acetic Acid + 50% Acetic Anhydride	50	Boiling	<1
Acetic Acid + 50 ppm I - (KI)	100	160, 200	<1
Acetic Acid + chlorine bubble	98	21	<1 pit
No control of moisture	98	21	<1 pit
Acetic Acid + chlorine bubble	98	21	<1 pit
Moisture controlled w/ argon purge	98	21	<1 pit
Acetic Acid + HCl bubble	98	21	<1 pit
Acetic Acid + HCl bubble (no control of moisture in vapor) Liquid	98	21	<1 pit
Vapor	21	<1 pit	

Acetic Acid + HCl bubble + chlorine bubble (liquid and vapor)	98	102	>50
Acetic Acid + Saturated, gaseous HCl and Cl_2	100	Boiling	>200
Acetic Acid + Saturated, gaseous HCl and Cl_2	100	40	<1
Acetic Acid + 1% acetyl chloride	99	Boiling	>50
Acetic Acid + .1% acetyl chloride	99	Boiling	wg
Acetic Acid + 200 ppm acetyl chloride	99	Boiling	wg
Acetic Acid + 2% HI, 1% methanol, 500 ppm formic acid, 100 ppm Fe	80	150	<1
Acetic Acid + 2% HI, 1000 ppm Fe (Fe powder)	80	100	<1
Acetic Acid + 25% sodium chloride +.1% sulfur + hydrogen sulfide	.5	150	<1

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Formic Acid

More corrosive than acetic acid, formic acid is used in the production of pharmaceuticals, dyes, and artificial flavors. The leather, textile, rubber and pulp and paper industries also use formic acid in their process.

TABLE 2. CORROSION DATA FOR FORMIC ACIDN

Media	Concentration (%)	Temp (°C)	Corrosion Rate (mpy)
Formic Acid	10-98	35-Boiling	<1
Formic (aerated)	10-90	Room-100	<1
Formic + 5% sulfuric	50, 70, 93	Boiling	<1
Formic + 5% hydrochloric acid	50, 70, 85	Boiling	<1
Formic + 1% Cupric	50, 70, 96	Boiling	<1
Formic + 1% iron powder	50, 70, 98	Boiling	<1
Formic + 5% HI	50, 70, 90	Boiling	<1
Formic + 2% hydrogen peroxide	50	80	<1
Formic + 4% hydrogen peroxide	50	80	<1

Other Organics

Zirconium is used in a wide range of organic media. These include sulfuric acid containing organic process streams such as methyl methacrylate (MMA), methacrylic acid (MAA), alcohols, hydroxyacetic (glycolic) acid, and rayon production. Other organic process streams involving hydrochloric acid include lactic acid, and methyl isobutyl ketone (MIBK). Production of phenolic resins and adipic acid are other areas that use zirconium extensively in production equipment. A limiting condition for the use of zirconium in organic process streams is maintaining minimum water content. A minimum of 50-ppm water, for example, is required for protection against hydriding in certain chlorinated organic compounds. To prevent stress corrosion cracking (SCC) in methanol solutions, with and without halogens or halides, >2% water may be required.

TABLE 3. CORROSION DATA FOR OTHER ORGANICS

Media	Concentration (%)	Temp (°C)	Corrosion Rate (mpy)
Acetaldehyde	100	Boiling	<2
Acetyl Chloride	100	25	>200
Aniline Hydrochloride	5, 20 5, 20	35-100 100	<1 <2
Bromochloromethane	100	100	<2
Citric Acid	10-50 10,25,50 50	35-100 100 Boiling	<1 <1 <5
Dichloroacetic Acid	100	Boiling	<20
Ethylene Dichloride	100	Boiling	<5

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Formaldehyde	6-37 0-70	Boiling Room-100	<1 <2
Formalin	100	98	<1
Hydroxyacetic Acid	70	205	<1
Lactic Acid	10-100 10-85	148 35-Boiling	<1 <1
Methanol	100	Boiling-200	Nil
Methanol + 0.1% KI + 0.1% formic acid	99.8	65	Nil
Melamine	100 100	260 427	<1 <1
Methanol + 1% KI	99	200	<1

Oxalic Acid	0-100	100	<1
Oxalic Acid + 41% sulfuric acid	17	74	<1
Oxalic Acid + 52% sulfuric acid	4	82	<1
Oxalic Acid + 52% sulfuric acid + 3% nitric acid + 2.5% ferrous sulfate	4	82	Gw*
Phenol Saturated Room	<5		
Phenol + 11% hydrochloric acid	60	70	<1
Phenol + 27% hydrochloric acid	7.2	100	<1
Sodium Formate	0-80	100	<2
Sodium Phenolsulfonate	100	185	<1
Succinic Acid	0-50 100	100 150	<2 <2
Tannic Acid	25	35-100	<1
Tartaric Acid	10-50	35-100	<1
Trichloroacetic Acid	10-40 100 100	Room Boiling 100	<2 >50 >50
Tetrachloroethane	100	Boiling	<5
Trichloroethylene	99	Boiling	<5
Urea	50	Boiling	<1
Urea Reactor Mixture (45% urea, 17% ammonia, 15% carbon dioxide, 10% water)	Mixture	193	<1

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Methyl Sulfide	100	21	<1
Methyl Sulfonic Acid	40	60	<1
Methyl Sulfonic Acid + 500 ppm Ceric +3	40	60	<1
Methyl Sulfonic Acid + 500 ppm Ceric +4	40	60	<1

*Gained weight

SPECIAL PRECAUTIONS

There is a special safety concern when using zirconium. Reactive metals like zirconium can develop pyrophoric films. Normally zirconium corrodes uniformly and all the zirconium is converted to zirconium oxide. If corrosion rates are low, <5 mpy, there is time to react all the zirconium uniformly. Under certain conditions, usually involving high corrosion rates under static conditions, it is possible that the corrosion process will liberate discrete un-oxidized zirconium grains. Under these conditions, the corrosion product may become pyrophoric. To passify the un-reacted zirconium, the trapped zirconium grains need to be completely oxidized before opening the equipment to the atmosphere. This is achieved by passing steam or hot air at 240ºC for 20 minutes or 120ºC for 3 days through the equipment to make sure all the zirconium in the corrosion product is reacted.

SUMMARY

As demonstrated above, zirconium can be the best alternative for material selection in many organic applications. 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.

Although, zirconium has proven its outstanding corrosion resistance performance in a wide variety of organic environments, the best way to determine zirconium's suitability for a particular environment is to perform a corrosion test. Zirconium corrosion test kits are available from ATI for use in on-line process equipment. These tests can show how zirconium will hold up under actual process conditions. For further information or any questions regarding the use of zirconium in organic applications, please contact Technical Services at ATI, phone 541-917-6777 fax 541-967-6987.

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