Selection and use of stainless steels and nickel-bearing alloys in organic acids

by C. M. Schillmoller

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Organic acids rank among the most important chemicals in industry today. Rather than being used as final products, they serve as a precursor for other chemicals. The reactive carboxyl group, -COOH, makes them a basic building block for many compounds, ranging from drugs and pharmaceuticals, such as aspirin, to plastics and fibres. Several million tons of organic acids are produced annually.

The most popular members of the carboxylic acid series are:

- Formic acid  C-1  HCOOH
- Acetic acid  C-2  CH₃COOH
- Propionic acid  C-3  CH₃CH₂COOH
- Butyric acid  C-4  CH₃CH₂CH₂COOH

The fatty acids generally comprise higher acids containing six or more carbon atoms; typical representatives include: lauric, oleic, linoleic, stearic and tall oil fatty acids; they are generated as by-products in the meat, agricultural and paper industries.

The corrosive action of organic acids is complicated because, as a rule, these acids are not handled in isolation but rather as process mixtures with inorganic acids, organic solvents and salts as well as in combination with other organic acids.

Formic and oxalic acids, as well as their higher homologues, are reducing acids. However, contaminants such as air, ferric or cupric ion or peroxides, will shift the redox potential to oxidizing, and this is a condition which favours the use of the nickel stainless steels. AISI types 304L and 316L stainless steels, Unified Numbering System, UNS, S30403 and S31603 represent the workhorses of this industry: aluminum, copper and its alloys play a more limited part. Copper alloys, such as copper, silicon bronze and inhibited aluminum bronze are employed under wholly reducing conditions. The stainless steels are readily available, easy to fabricate and proven in performance.

General considerations for alloy selection

Traditionally, the industry has chosen alloys conservatively, adhering to well established metallurgical practice which calls for AISI types 304L and 316L stainless steels and Alloy 20, UNS S08020. High nickel alloys were substituted whenever the former selections proved inadequate. Because of the possible shifting of the redox potential, the high nickel alloys are frequently selected because they can resist the most severe operating conditions.

The scope of this discussion does not permit a review of all the

<table>
<thead>
<tr>
<th>Table I Representative stainless steels and high nickel alloys used in the organic acid industry.</th>
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<tbody>
<tr>
<td><strong>Stainless Steels</strong></td>
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<tr>
<td><strong>Generic Designation</strong></td>
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<tr>
<td>Cb / Ta</td>
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<td>Others</td>
</tr>
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Cb | | | | | | | | | | | | | | | | | |
suitable alloys. Hence only a representative selection is shown in Table I which provides chemical compositions for the commonly used AISI types and the corresponding UNS designations.

Laboratory tests and in-plant corrosion rate determinations can be misleading, as the performance of a given alloy is either excellent or unacceptable. The mode of corrosion of stainless steel can vary from severe general attack, when passivity is lost, to an insidious localized attack (for example, intergranular corrosion, pitting or crevice attack or chloride stress corrosion cracking). Operating parameters and environmental factors exert significant influence on alloy performance; pH, temperature and the presence of chlorides and oxygen deserve particular attention.

One should assume that all warm organic acids can cause intergranular corrosion in the stressed, heat-affected zone adjacent to a weld. Titanium or columbium are frequently added to the alloy in order to convert carbon into a stable carbide and thereby avoid precipitation. Alternatively, a low carbon (0.03 per cent C max.) alloy may be specified to prevent intergranular corrosion from developing in service subsequent to welding. For cast structures, such as CF3M, as in pumps and valves, a high temperature anneal above 1000°C (1830°F) is recommended to homogenize the composition. For regular carbon or unstabilized grades, as in CF8M, CN7M, a rapid quench is required to prevent intergranular corrosion. The 18Cr-8Ni stainless steels are highly susceptible to chloride stress-corrosion cracking, CSCC, above 65°C (150°F), for instance, under conditions typically found in scrubber-liquid stripping stills in acetic acid processing. In general, alloys with a nickel content of 22 per cent and over, such as Alloy 904, N08904, Alloy 28, N08028, and Alloy 20, N08020, seldom experience CSCC while alloys with a nickel content of 42 per cent and over are fully resistant to it. As shown in Figure 1 this latter group includes Alloy 825, N08825; Alloy G, N06985; Alloy 625, N06625; and Alloy C-276, N10276.

Pitting and crevice corrosion are predominantly controlled by pH, chloride concentration, presence of oxygen or oxidizers, and by temperature. The resistance of alloys is enhanced by the addition of chromium and molybdenum. Alloy 825 weld overlays have been used to prevent crevice corrosion in gasketed AISI type 316L flange surfaces exposed to hot organic acids.

Whether or not to specify AISI type 304L and AISI type 316L can be a crucial decision. High nickel alloys such as C-276 have consistently rendered reliable service; they perform well in both oxidizing and reducing media; they resist high chloride levels as well as oxidizing salts.

This paper discusses materials selection for equipment used in the manufacture and storage of formic, acetic and propionic acid; it will also present selected data and recommendations relating to higher molecular weight organic acids. In general, the corrosive action of organic acids decreases with increasing molecular weight. However, at high temperatures, the acids can dissociate, forming more aggressive ion which can cause much faster corrosion rates than might otherwise be expected. As a rule, stainless steels are attacked more violently by anhydrous organic acids than by organic acids which contain traces of water.

**Formic acid**

Formic acid is the most corrosive of the common organic acids. It reacts readily with many oxidizing and reducing compounds.

*Figure 2* presents an alloy selection guide for the various alloys. It shows iso-corrosion rates of 3 mpy over the full range of concentrations up to boiling temperature. Alloy selection depends more critically on the temperature of the attacking acid than on its concentration. All of the listed alloys exhibit improved corrosion resistance in the presence of oxygen or oxidizing agents.

Type 304 stainless steel is the preferred specification for storage tanks. It can contain formic acid in any concentrations at ambient temperature. In process systems, type 316L is the

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**Figure 1** Relative resistance of stainless steels and nickel-chromium alloys to chloride stress cracking and crevice corrosion in hot systems containing chlorides.

**Figure 2** Alloy selection guide – Formic acid
alloy of choice in all concentrations at ambient temperature and up to a concentration of 10 per cent HCOOH at boiling temperature. It is appropriate to specify 316L with Cr and Mo in the upper AISI range or to consider type 317L, S31703 for borderline passivity.

For intermediate strengths of formic acid at elevated temperatures, Alloys 20, 28, 904L or 825 should be considered. They perform better than 316L and can withstand mixtures of formic and acetic acid. This group of alloys offers good resistance to pitting, CSCC and intergranular corrosion; it will also do well in contact with high velocity streams. Cast Alloy 20 is a standard selection for valves and pumps.

Several of the high nickel alloys, such as G, 625 and C-276, are suitable for all concentrations and temperatures up to the boiling point, whether or not oxidizing or reducing agents are present.

**Acetic acid**

Acetic acid is the source chemical for many products, including fibres, plastics, agricultural chemicals, pharmaceuticals and other compounds. It is consumed in quantities far exceeding those of other organic acids. Its role in the organic chemical industry compares with that of sulfuric acid in inorganic chemical processing. US production of acetic acid in 1987 exceeded 3 million metric tons. Therefore, a knowledge of its corrosivity is essential to ensure satisfactory service life of manufacturing equipment and to prevent product contamination.

Historically, acetic acid was produced by fermentation of grain and by destructive distillation of wood. Today virtually all acetic acid is made by one of three routes:

1. Acetaldehyde oxidation by direct air or oxygen in the presence of manganese acetate,
2. Liquid phase oxidation of butane or naphtha, and
3. Carbonylation of methanol (Monsanto process)

The most common current process is butane oxidation. An abbreviated, but typical flow diagram is shown in Figure 3. Air or oxygen is blown through butane in the presence of a catalyst. In addition to acetic acid, co-products such as formic acid, esters, and minor amounts of peroxides or reducing agents may be formed; these can materially affect the corrosion resistance of various metals and alloys. In hot acetic acid above the atmospheric boiling point, HCl can be generated by chloride ion contamination. Alloys 20, 904L or 904hMo may replace 316L in some parts of the column, although Alloy C-276 is preferred. At the outlet end of the process, the acids have become anaerobic and reducing.

Copper columns and high nickel alloy trays (Alloy C-276) have been routinely employed. Where air ingress cannot be prevented, or for hot-wall conditions, it may be necessary to design these items entirely in Alloy C-276 (e.g. in converter product stripping stills or calandria in the Dual Anhydride Process).

Type 304 stainless steel is the preferred construction material for storage tanks and tank cars handling pure, dilute acetic acid solutions of less than 90 per cent concentration. Type

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**Figure 3** Simplified flow diagram for production of acetic acid (butane oxidation process).
316L piping and heating coils are required to resist the effect of heat tracing or steam — hot-wall effects). Pumps and valves should be in CF3M. Where storage of contaminated acid, or storage at elevated temperature is anticipated, type 316L should be specified to maintain maximum purity and prevent turbidity or color pickup.

Type 316L is also preferred for bulk shipment of C.P. acetic acid to prevent excessive iron pickup in the product; the tank trucks are pre-seasoned, the initial lading being returned for redistillation, and only the second lading being shipped.

Low-carbon grades of stainless steels should always be specified for exposure above 60°C (140°F). Figure 4 is a selection guide for AISI type 304L and 316L stainless steels in contact with acetic acid. It shows that, in defining the relative limitations of AISI type 304L, the effect of acid temperature outweighs the effect of acid concentration.

With reference to the flow diagram, Figure 3, Alloy 20 is frequently used in the reactor. Alloy 316L can be specified for the product separator and hydrocarbon stripper, and also for distillation columns for removal of solvents such as esters and ketones, in dehydration equipment, piping and overhead condensers. Seamless or 'full-finished' welded construction should be chosen for the AISI type 316L heat exchanger tubing. Before its final anneal, a full-finished tube, for example, A249, is cold-drawn to reduce its wall thickness by at least 15 per cent or its cross-sectional area by at least 35 per cent. This procedure tests the entire length of the longitudinal weld and also promotes formation of a semi-wrought structure with corrosion resistance equivalent to that of the parent metal.

While type 316L resists most acetic acid concentrations at temperatures through their respective boiling points, the presence of certain contaminants, notably formic acid, various catalysts and chlorides can cause rapid general attack or pitting/crevice corrosion on stainless steel. Where such contamination cannot be eliminated, either a lowering of process temperature or upgrading to a more resistant alloy is indicated. Figure 5 illustrates the relative resistance of several representative alloys to pitting/crevice corrosion in chloride-containing systems under varying conditions of acidity.

While anhydrous acetic acid or traces of acetic anhydride will dramatically increase the corrosion rate, the introduction of a few tenths of one percent of water will reduce that rate. Oxidizing agents, such as permanganate, dichromate, cupric or ferric salts, peroxides or even the injection of air have on occasion proved effective as inhibitors of general corrosive attack. However, extreme caution must govern the application of oxidizing inhibitors as it may aggravate pitting and crevice corrosion.

The evolution of new processing methods for acetic acid has mandated larger and more sophisticated equipment. The presence of formic acid, higher acids, and/or halides, and the increased pressure and temperature levels characteristic of modern process technology necessitate the enhanced corrosion resistance provided by the high nickel alloys; the high-performance stainless steels and AISI type 316L are used in the less corrosive areas.

Alloy C-276 and its variants are specified for extremely hot or contaminated acetic acid. Alloy B-2 is used only under reducing conditions. For example, in the manufacture of acetic acid by carbonylation of methanol, ie by the Monsanto process, Alloy B-2 is preferred because of the presence of chlorides and iodides.

**Propionic and butyric acids**

The corrosion characteristics of propionic and butyric acids are very similar to, but somewhat milder than those of acetic acid. Type 316L is the preferred material for handling hot, concentrated solutions, while type 304L can be utilized for more dilute solutions up to the boiling point. A laboratory test (240 hours, unaerated) in boiling 100 per cent concentration propionic acid shows corrosion rates for type 304L and 316L stainless steel as 26 mpy and 1.2 mpy respectively. The corresponding rate for Alloy C-276 is 0.2 mpy.

**Fatty acids**

At lower temperatures, the fatty acids may be considered as harmless polar "oils". However, significant corrosion of steel can result at the higher temperatures required for processing. Most of the fatty acids are handled as a mixture of two or more compounds, rather than as pure compounds. Tall oil consists of the free fatty acids (mostly linoleic, oleic, linolenic and abietic acids), which are separated from the saponified fats and resins in the Kraft-pulp process, using sulfuric acid to "spring" the organic product.

![Figure 4](image.png)  
**Figure 4** Alloy selection guide – acetic acid.

![Figure 5](image.png)  
**Figure 5** Limits of usefulness of stainless steels and the high-performance alloys in a chloride environment under acid conditions (oxygen present).
Type 316L, usually specified as a high molybdenum grade (2.75 per cent min.), is widely used but, as processing temperatures increase, the higher molybdenum grades such as 317LM and 904L are needed. For the most aggressive conditions Alloy C-276 and Alloy 625 can be considered as they show negligible corrosion rates.

The effect of temperature must be carefully defined in these applications. Lower molecular weight acids remaining in the mixed fatty acids will result in a more aggressive environment, as will the products of decomposition which result from overheating of the acids. The ratio of fatty to rosin acids affects the corrosion rate, and the presence or absence of water or steam will have an effect. The oxidizing capacity of water reduces corrosion rates on the stainless steels appreciably. Pretreatment of the acids may leave contaminants that increase corrosivity.

Characterized by stearic and palmitic acids, the vegetable oils are less aggressive than the tall oil acids, while those derived from animal fats are more corrosive than the vegetable oils. Type 316L stainless has been used with good success in these applications.

**Naphthenic acids**

Naphthenic acids are present in many crude oils. They may be regarded as cyclopentane-substituted acetic acid. The higher molecular weight acids are bi-, tri- or poly-cyclic. The naphthenic acid content is usually expressed as a 'neutralization number'.

In oil refinery vacuum distillation columns, operating at 290-345°C (550°-650°F), type 316L (2.75 per cent Mo min.) is generally specified for bubble caps, trays and cladding. In extreme cases type 317L or Alloy 20 are required.

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### Summary

The performance of the various alloys largely depends on the characteristics of the contaminants contained in the organic acids, and on operating temperatures. Reference has been made to the principles of alloy selection and redox potential control as means to control intergranular corrosion, chloride stress corrosion cracking and pitting/crevice corrosion. At operating temperatures above 60°C (140°F), it is generally important to specify the type 316L stainless steel with Cr and Mo in the upper AISI range and carbon in the lower range of the specification.

Certain guidelines in alloy selection have been presented. It is recommended to conduct tests under field service conditions because the organic acids under consideration are frequently mixed with formic or acetic and/or inorganic acids, anhydrides, peracids and other oxygenated species. Much of the published literature appears contradictory because it fails to note the extent of minor contaminants in the system. Extreme caution should be exercised in extrapolating laboratory test work to plant scale operation.

*Figures 1 and 5 identify a group of alloys intermediate between the stainless steels and the high nickel alloys; these appear to offer long service life with relatively little chance of catastrophic failure. Particular attention should be focused on alloys in Zone II (Figure 1), such as Alloy 904L and Alloy 28. When compared with Alloy 20 and Alloy 825, these alloys have proven cost-effective in organic acid environments. Table II gives their approximate cost ratios in comparison with type 316L. Ratios are provided for plate as well as seamless and welded tubing. These ratios are intended as a guide for purchases in medium to large quantity; suppliers should be consulted for a comparison based on specific alloys and quantities.*

<table>
<thead>
<tr>
<th>Generic designation</th>
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<th>317LM</th>
<th>2205</th>
<th>904</th>
<th>904hMo</th>
<th>28</th>
<th>20</th>
<th>825</th>
<th>G-3</th>
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<th>625</th>
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<td>UNS designation</td>
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<td>N08925</td>
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<td>6.8</td>
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<td>1.2</td>
<td>1.6</td>
<td>2.2</td>
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<td>-</td>
<td>2.2</td>
<td>3.5</td>
<td>5.0</td>
<td>4.3</td>
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<tr>
<td>Tube (welded)</td>
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<td>0.6</td>
<td>0.6</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>1.8</td>
<td>2.1</td>
<td>3.8</td>
<td>3.3</td>
</tr>
</tbody>
</table>

**Table II Relative cost of stainless steels and high-nickel alloys, (316L plate = standard).**

Process development in the organic acid industry has tended toward evolution of larger and more sophisticated equipment, often operating at higher pressures and temperatures. Distillation columns of up to ten feet in diameter are not uncommon. Heat exchangers have grown much larger and they require many hundreds of thousands of feet of heat exchange tubing. An unexpected shutdown caused by material failure can result in very costly repairs and unnecessarily high losses in production. The high nickel alloys offer the highest level of reliability because they are able to cope with oxidizing and reducing conditions as well as providing a margin of safety to cover possible deviations from design.
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The Nickel Development Institute is an international nonprofit organization to serve the needs of people interested in nickel and nickel-containing materials.

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