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Materials of Construction in the Fatty Acid Industry

E.E. RICE, Vice President, Engineering, Humko-Sheffield Chemical, a Division of Kraft Inc., White Station Tower, PO Box 398, Memphis, TN 38101

ABSTRACT

The basic material of construction for the tankage and reactors that are used in the fatty chemical industry is one or another variant of the 300 series stainless steels. The use of these alloys essentially eliminates the possibility of iron and other metal contaminations which may either degrade the product or catalyze undesirable oxidation and other side reactions. With certain exceptions, it has been found that Type 304 stainless steel may be used in fatty chemical processing at temperatures up to 150 C and Type 316 stainless steel for tanks and vessels designed for use above that temperature. Where welding is involved in the fabrication of equipment designed for high temperature usage, it has been found necessary to use either a special low carbon stainless steel or an alloy which contains an extra ingredient that will inhibit carbide precipitation in the weld area since such precipitation usually results in a point of corrosion and ultimate failure. In the fabrication of pressure vessels, it is normal practice to use carbon steel plates of suitable thickness that have a minimal amount of the desired alloy bonded to the surface rather than fabricate of solid alloy. This not only reduces the cost of the vessel but adds greatly to the strength of the sheet since most high alloys lose tensile strength rapidly as temperatures are increased while carbon steel retains strength until very high temperatures are reached. In addition to the 300 series stainless steels, certain highly specialized alloys such as Inconel 825, Carpenter 20 Cb, or Monel are frequently used for extreme acid conditions. The lower cost of aluminum as compared to a high alloy makes it attractive for storage tanks but it can be used only when materials contain no moisture, since even traces of water accelerate the rate of corrosion and rapidly render the tank unusable. New materials on the scene are fiberglass-polyester tankage and applied linings of the phenolic or the epon-epoxy type. These materials do not have a wide application, but where their use is possible, it is a lower cost answer to the problem of iron contamination.

If it could be said that there are basic metals for the fatty chemical industry, they would have to be two of the so-called 18-8 series austenitic stainless steels, Type 304 and Type 316 in one or another of their variant forms (Table I).

Typically in this industry, Type 304 stainless steel is used for fatty chemical processes where the temperature does not exceed 150 C, and Type 316 is used for temperatures above this level. The principal difference in these two alloys is that Type 316 has added 2 to 3% molybdenum, which greatly improves resistance to corrosion particularly at elevated temperatures. Since this alloying component will act in much the same way as excess chromium in the promotion of a ferritic structure, the nickel is usually increased slightly in order to keep the alloy in the austenitic form, and consequently it remains less subject to intergranular corrosion as well as retains the nonmagnetic property that is typical of austenites.

One problem of any alloy containing both chromium and carbon is the precipitation of a chromium carbide as the alloy is subjected to what is called the sensitizing temperature range of 566 to 871 C, a temperature range that will always occur during any type of welding. In this range, the carbon leaves solution in the austenite and selectively reacts with chromium for precipitation as the carbide along grain boundaries. This leaves the area immediately adjacent to the carbide grain deficient in chromium since the carbon will tie up 17 times its own weight of this metal. This renders the boundary less resistant to corrosion, and the end result is eventual weld area failure. In extreme cases involving severe corrosive conditions, it can also result in an electrochemical action being initiated between the chromium-rich and the chromium-depleted areas and cause total failure due to destruction of the grain boundaries with resulting lack of coherency of the

TABLE I

Materials of Construction: 18–8 Stainless Steels

Type No.	Ni %	Cr %	C Max %	Mn Max %	Si Max %	P Max %	S Max %	Mo %
304	8–12	18–20	0.08	2.0	1.0	0.045	0.03	—
304L	8–12	18–20	0.03	2.0	1.0	0.045	0.03	—
316	10–14	16–18	0.08	2.0	1.0	0.045	0.03	2.0–3.0
316L	10–14	16–18	0.03	2.0	1.0	0.045	0.03	2.0–3.0

TABLE II

Materials of Construction: European Offsets for Type 316L

	Material No. (German)		DIN Marking (German)
AISI TYPE 316L	4404[a]		X3 CrNiMo 18 10
	4429[b]	–	X2 CrNiMo 18 14
	4435[c]	–	X2 CrNiMo 18 14
	4436[d]	–	X5 CrNiMo 18 12
	4571[e]	–	X10 CrNiMo 18 10

[a] Essentially same as Type 316L.

[b] Essentially same as Type 316L–Special Low Nitrogen Grade.

[c] Essentially same as Type 316L–Nickel content slightly higher.

[d] Same as (c) except Carbon specification is 0.07% max.

[e] Essentially same as Type 316 with Titanium added at 5XC level frequently referred to as Type 316Ti in Europe.

grains. For this reason, it is necessary to alter the alloy for equipment that must be fabricated by welding if such equipment is to be subjected to other than mildly corrosive conditions. The simplest method of doing this is to limit the amount of carbon present to not more than 0.03% since it has been found that this will not precipitate a continuous film of chromium carbide, and such alloy may then be welded without severely limiting the life of the vessel.

There are other methods of preventing intergranular corrosion through the use of additional alloying constituents that will selectively tie up the carbon rather than allow it to form a carbide with chromium. One such metal is titanium. If this metal is added at a rate equal to five times the carbon content, and if certain adjustments are made in the nickel/chromium ratio, a new resistant stainless known as Type 321 results. Another variant, Type 347, results when a mixture of tantalum and columbium is added at a level equal to 10 times the carbon content. Neither Type 321 nor Type 347 stainless steels is widely used in the fatty acid industry in this country, as their most important use is for the fabrication of equipment that is frequently heated and cooled through the sensitizing zone previously noted. These and similar alloys may be encountered, however, in equipment manufactured in Europe, particularly in Germany or Scandinavia, with some titanium added alloys being referred to as AISI Type 316Ti. Because of overlapping specifications for various alloying constituents, several material numbers are often listed by foreign vendor companies as being the same as AISI Type 316L. These may or may not be suitable replacements depending on the exact conditions to be encountered, Table II.

As to the uses of various forms of the 18-8 alloys for fatty chemical processing, the commonest is the basic Type 304 as used for the fabrication of storage tanks and pipelines which are not subjected to temperatures in excess of 150 C. Since none of the fatty acids are classified as severely corrosive at this temperature, it is not necessary to use the low carbon form even though welding may be used in fabrication. The majority of the processing equipment, however, is fabricated of Type 316L since most reactions or processes require temperatures in excess of 150 C. In this category are both batch and continuous splitters, hydrogenation vessels, esterification and other reactors and distillation equipment. In the case of the distillation equipment, the alloy is often used in the form of a solid sheet of ca. 5/8" or 3/4" thickness since it is not necessary to withstand high internal pressures, but only to prevent collapse under full vacuum. In the other cases noted, these are usually pressure vessels, and it is common practice to fabricate from a clad metal in which the sheet of the alloy of ca. 3/16" or 1/4" in thickness is fused to a sheet of the proper thickness of carbon steel before rolling or other fabrication. Since all wetted surfaces are of alloy, the equipment is as fully corrosion resistant as if it were solid, and an economic purpose is served by greatly reducing the amount of expensive alloy and substituting instead the much cheaper carbon steel. The previously mentioned Type 321 and 347 stainless steels, as well as their European offsets, may ordinarily be used for any fabrication where Type 316L is indicated excepting possibly for continuous splitter columns and distillation reboilers.

In addition to the usual 18-8 series of stainless steels, there are other highly specialized alloys such as Carpenter 20 Cb and Incoloy 825, (Table III). These are quite dissimilar in analysis but in properties related to use in the fatty chemical processing they are somewhat comparable, as their corrosion resistance is much the same for the uses where these alloys are indicated.

Of these high alloys, the Carpenter 20 Cb is probably the most corrosion resistant of all austenitic stainless steels, as it may be used to process items with up to a 40% concentration of boiling sulfuric acid and still maintain a controllable and permissable level of corrosion. This alloy is currently being used in the form of clad sheets for the fabrication of vessels where highly acidic conditions exist. The other alloy noted, Incoloy 825, is frequently used in clad form for the fabrication of esterification vessels where either short chain acids are processed or where sulfuric acid is used as a catalyst for other reactions. Another use of this alloy, also in clad form, is the fabrication of splitting vessels

TABLE III

Materials of Construction: High Alloy Stainless Steels

		Type 316L	Carpenter 20 Cb	Incoloy 825	AL 26–1 (E-Brite)
Ni	%	10–14	32.5–35.0	38–46 inc. Co	0.5 max
Cr	%	16–18	19–21	19.5–23.5	25.0–27.5
C	%	0.03 max	0.06 max	0.05 max	0.01 max
Mn	%	2.0 max	2.0 max	1.0 max	0.4 max
Si	%	1.0 max	1.0 max	0.05 max	0.4 max
P	%	0.045 max	0.035 max		0.02 max
S	%	0.03 max	0.035 max	0.03 max	0.02 max
Mo	%	2.0–3.0	2.0–3.0	2.5–3.5	0.5–1.5
Cu	%		3.0–4.0	1.5–3.0	0.2 max
Al	%			0.02 max	
Ti	%		8XC min, 1.0 max	0.6–1.2	
Co + Ta	%				
N	%				0.015 max
Ni + Cu	%				0.5 max
Fe	%			22.0 min	

TABLE IV

Materials of Construction: Alloy Comparisons

	Ni %	Cr %	C Max %	Mn Max %	Si Max %	P Max %	S Max %	Mo %
Type 316L	10–14	16–18	0.03	2.0	1.0	0.045	0.03	2.0–3.0
AL-6X (Typical)	24.5	20.25	0.025	1.5	0.5	0.025	0.01	6.25

TABLE V

Materials of Construction: Approximate Rates of Corrosion–Inches per Year Tallow Fatty Acids

	Storage tanks[a]	Ester reactors[b]	Ester reactors[c]	Still reboilers[d]
Aluminum 2S	0.0039			
Monel 400	0.0018		0.0110	0.0180
S.S. Type 304	<0.0001		0.0630	0.0035
S.S. Type 316	<0.0001	0.0017	0.0620	0.0002
Carpenter 20 Cb		0.0017	0.0130	0.0001
Incoloy 825		0.0013	0.0110	0.0001
Inconel 625		0.0005		0.0004
AL 26-1 (E-Brite)				0.0002

[a] Moisture free, 160 F.
[b] PTSA Catalyst, 195 F.
[c] 0.25% H_2SO_4 Catalyst, 295 F.
[d] Nominal 500 F exposure (465–550 F).

or columns that are designed to process coconut or other lauric oils since the superior resistance to corrosion over Type 316L is very useful in this type of processing. There is also a new alloy available that is properly known as Allegheny 26-1 but is commonly called E-Brite. This alloy is much different from the others in that it contains little or no nickel and is consequently ferritic rather than austenitic. This alloy also differs physically in that it is highly magnetic, a property that is usually not found in stainless steels. E-Brite is a vacuum refined steel, and in appearance seems identical to Type 316 except that the color is very slightly bluish by comparison. This alloy is relatively new and deserves a close look for many purposes. While it is somewhat more expensive than Type 316L, it is ca. 4% lighter in density so that a correspondingly lesser amount is needed for a given use. An important difference, however, is that the thermal conductivity is ca. 20% better than that of 18-8 alloys and this, combined with the lower density, can be valuable when designing a heat exchanger or a condenser when such design is hampered by available space for installation. As to resistance to acidic attack, E-Brite is in a class with Incoloy 825 and Carpenter 20 Cb as far as fatty chemical processing is concerned and should be basically interchangeable with them.

Before leaving the area of stainless steels, we should at least mention another very specialized Allegheny Ludlum steel, AL-6X, Table IV. This alloy is austenitic nickel-chromium steel containing over 6% molybdenum. The principal advantage of this alloy is its extreme resistance to chloride and stress corrosion cracking. For this reason, it is one stainless steel that may be used to fabricate condensers and heat exchangers that are to be cooled with brackish water or even with sea water. Since very few fatty acid plants are located directly on the ocean, this use is of little moment, but it could prove useful in a reverse condition such as the case of a sweetwater evaporator that is to be designed for a feedstock that has been acidified with hydrochloric acid. This water, even after being neutralized with an alkali, could be high in chloride ion content and thus result in deterioration of conventional 18-8 stainless steels through stress corrosion cracking.

There is one other ferrous metal which was not previously noted but which is widely used in the fatty chemical industry and is probably the commonest, plain carbon steel. The use of this metal by the industry is basically economic and not because of any unique properties. Carbon steel is widely used for storage tanks for low acid conditions such as the storage of glyceride raw materials and various solvents such as hexane, methanol and isopropanol. Another common use is for the storage of low acid byproducts such as ester and fatty acid pitches. Carbon steel may also be used for transfer lines in the above services as well as in others where trace iron pickup is not a problem. Tanks for the storage of 50° Be' caustic soda and 66° Be'' sulfuric acid may also be constructed of this reasonably priced metal as may storage bottles for compressed gasses such as hydrogen, nitrogen, air and dry carbon dioxide. Transfer lines for these chemicals and gasses may also be of carbon steel as may lines for steam, water and any liquid or gaseous fuels. Carbon steel is useful also, as previously noted, for the manufacture of clad metal sheets which can then be used in the fabrication of resistant vessels at much lower costs than when using solid alloy.

Certain nonferrous alloys are also used in some areas of fatty chemical processing. The more common of these are Inconel, Monel, and aluminum. Inconel 625 contains 61% Ni + Co, 21.5% Cr, 9.0% Mo, 3.5% Cb + Ta and 2.5% Fe. Monel 400 consists of 66.5% Ni + Co and 31.5% Cu. Aluminum alloys such as 2S contain typically 97–99% Al. In the past, these alloys have had varying uses in fatty chemical plants, but for the most of these they are being gradually displaced by one or another of the newer alloy steels shown in Table V. Inconel, basically an alloy of nickel and chromium, has been used for the high temperature exposure to fatty chemicals that would be common in distillation equipment and also in the fabrication of esterification vessels, particularly those where acid catalysts were to be used. These uses have now been replaced for the most part with high alloys such as Incoloy 825 or Carpenter 20 Cb, which offer essentially the same resistance to corrosion but with a distinct economic advantage. In many cases where only a high temperature is involved with no mineral acid present, as for example distillation equipment, this alloy has been replaced by an even more reasonably priced alloy such as Type 316L. There is one important use remaining for Inconel, however. Thin sheets of this alloy are used to line large boiler stacks to prevent corrosion when using high sulphur fuels, particularly residual oils that are also high in vanadium, the oxides of which catalyze the conversion of sulphur dioxide to sulphur trioxide and consequently increase the level of sulphuric acid formed.

Monel is another alloy that is being used to lesser degree in the fabrication of equipment for the processing of fatty chemicals. This alloy, basically of nickel and copper, was at one time widely used for esterification vessels and for tanks designed for sulphuric acid acidulation of soapstocks. It was also used almost exclusively in the fabrication of pressure vessels and storage tanks designed for the production of quaternary ammonium compounds from fatty amines. This latter use was primarily because of the excellent resistance of Monel to the extremely high concentration of active chlorides during this reaction. This alloy is still very satisfactory for the uses noted, but the cost has escalated far more than alloy steels and is now at a price nearly double that of Type 316L and about 1½ times that of Incoloy 825 or Carpenter 20 Cb. Because of the economic advantage of one or another of these alloy steels, they are now commonly substituted for Monel in the fabrication of esterification equipment, and Carpenter 20 Cb is frequently used for the fabrication of acidulation equipment. The use of Monel in the fabrication of equipment for the production and storage of quaternary ammonium compounds still continues, but it would seem that here, too, this alloy may be doomed since the introduction of alloys such as Allegheney AL 26-1 or E-Brite, and Al-6X as these alloys present economic advantages along with excellent resistance to chloride attack and the resultant stress corrosion cracking that follows.

The other metal noted earlier, aluminum, was at one time widely used in the fabrication of storage tanks and transfer pipelines because of its low price and ease of handling, coupled with a heat transfer rate far superior to any of the resistant ferrous alloys available. Over the years, this metal has been found to have many disadvantages and because of these the usage by the fatty chemical industry has declined. Primary among the disadvantages is the difficulty of cleaning an aluminum system since an alkaline cleaner rapidly attacks the metal leaving, at best, hard to clean pits, and at the worst, actual perforation. Another problem with aluminum is that in the presence of even traces of moisture the metal is subject to attack by fatty acids, and this attack, even though it progresses slowly, will eventually render the system unusable.. A further disadvantage of the use of this metal for large storage tanks is the fact that the low strength requires the use of very thick sheets of 5/8" or more for fabrication. Because of the stresses set up during welding, such tanks must then be normalized by furnace treating after fabrication. This makes field welding for either alteration or repair very difficult since on cooling, it is not uncommon to have virgin metal crack in areas adjacent to a weld. In order to avoid this situation, it is necessary to heat the areas adjacent to the weld with multiple acetylene torches during the welding procedure and then gradually cool by reducing such torch heat to allow the weld area to cool slowly, as the immediate withdrawal of the heat would cause a very rapid temperature reduction due to the high heat conductivity of aluminum. This is extremely difficult to do in the field, and consequently large aluminum tanks are seldom constructed for the modern fatty acid industry. Another problem that has arisen in the past with aluminum transfer lines is a sudden and apparently inexplicable explosion. These explosions have occurred when using compressed air to clear lines rather than using an inert gas such as nitrogen. The so-called explosion may occur when a complete or partial blockage occurs in an aluminum line that is both steam heat-traced and insulated. Under these conditions, the temperature of a partially filled line may easily rise to 150 C, at which point lower chain fatty acids will readily ignite and burn in the presence of compressed air. The resulting internal fire heats the pipeline to a temperature approaching the melting point where it may rupture due to the internal pressure, and the flame blowout leads to the supposition that an internal explosion has occurred. That such blowout is not a true explosion is shown by the fact that similar conditions involving stainless steel pipelines have resulted in the heating of the combustion area to redness without damage to the system other than an internal coking of char from the partially burned fatty material.

There is one nonferrous metal that is increasing in usage at the expense of stainless steels. This is titanium, and its use is indicated in equipment that is to be subjected to both corrosive and highly erosive conditions. One of the best examples of this application is in the fabrication of the plates of a plate-type heat exchanger when high velocities are involved, particularly when a liquid being heated may exceed the boiling point and internal flashing thus occurs. This highly erosive condition can cut through Type 316 plates in the relatively short time of a few weeks while titanium plates appear to be unaffected with exposures of a year or more, and the extra 40 to 50% cost is well justified.

In addition to the various metals commonly used in the fatty chemical industry, there are also several coatings that can be applied to carbon steel to make it corrosion resistant. One of the most useful of these is glass. In the manufacture of glass-lined equipment, a carbon steel vessel is first prepared, cleaned, fluxed and coated with the glass composition. The entire vessel is then fired in a kiln in order to fuse glass components to a continuous layer. Vessels of this type may be found useful where extreme corrosive conditions are involved such as a high acidity or a high level of active chlorides. In situations such as this, a glass-lined vessel will usually be somewhat cheaper in price than would be one constructed of a suitable high alloy. The glass-lined equipment, however, has many disadvantages which tend to offset the lower costs, the principal of which is susceptibility to both mechanical damage and thermal shock. When such a vessel is damaged, it is very difficult to repair satisfactorily and usually must be replaced or else relegated to a different operation. A further disadvantage is in the methods available for heating and cooling. If the material being processed is extremely corrosive even to high alloys, the only solution is to jacket the vessel and install adequate controls to prevent thermal shock. If high alloys are satisfactory, a bayonet bundle may usually be attached to a manhole cover, which cover must also be constructed of the same high alloy. A further drawback to the use of glass-lined vessels is the difficulty of adapting them to other purposes should the initial use become obsolete, since it is impossible to add nozzles or flanges. The uses indicated for glass-lined vessels are primarily for storage tanks, small reactors and systems with active chlorides such as quaternary ammonium compounds. It is also possible to line carbon steel vessels with elastomers such as Neoprene, Koroseal, butyl rubber, and so forth. Vessels of this type are widely used in deionization systems such as may be used in the processing of glycerine sweetwater. These linings are severely limited for temperature reasons and because of the difficulties of installing heating and cooling systems within the vessel. Repairs to a damaged lining can be made in the field and cured in place with heat lamps. These elastomers, and also Teflon, are very useful for the lining of pipes which are to be used for the transfer of severely corrosive liquids such as mineral acids as typically used in the regeneration of deionization resins since the structural strength of the metal pipe prevents breakage of the pipeline with possible harm to personnel and/or equipment.

The most common linings encountered in the modern fatty chemicals plant will be sprayed and cured coatings of either the epon-epoxy or the phenolic type. The principal uses of these coatings are for storage tanks to some degree and for tankcars to a major degree since the cost of stainless steel tank cars is almost prohibitive. Coatings commonly used are Lithcote, Amercoat, and Talicor. Of these, the most common and usually suitable for all around service is Lithcote #LC-19. The linings should be shop applied since closely controlled temperatures during curing are necessary. It is possible to coat storage tanks in the field and cure with propane or gas-fired heaters after insulating the tank with several inches of loose fiberglass batts, but this method should be used only as a last resort, as it is nearly impossible to have a coating which is not over-baked in some areas and under-baked in others. One common problem with these coatings is mechanical damage, and care must be taken not to scratch through the coated surface to the base metal or corrosion and/or iron contamination may result.

The use of sprayed and cured coatings presents a unique problem in that such a coating has a certain porosity even though it be very minor, and this causes the coating to act as a membrane in electrogalvanic action. Rate factors may be determined for the corrosion due to galvanic couples made up of metals commonly used in fatty chemical plants, Table VI. To compare corrosion rates when large areas of dissimilar metals are immersed in an electrolyte, the relative rate of corrosion may be obtained by subtracting the factor for the cathodic end from the anodic end, and this resulting number may then be compared with other couples to determine the most useful system. The rates of corrosion are also directly proportional to the surface area of the metal exposed. This becomes very important when dealing with sprayed and cured coatings in tankage involving an electrolyte such as crude glycerine sweetwater, since storage tanks with such a coating might well be fitted with stainless steel coils in an attempt to reduce corrosion of the coil. If we were to consider an uncoated 30,000 gallon storage tank with an interior surface of ca. 1,800 square feet and fitted with 100' of 3" stainless steel coil having ca. 90 square feet of surface, the ratio of carbon steel to stainless steel would be 20:1, and a given area of the carbon steel would therefore be very slowly corroded. If this tank, however, were lined with an epon-epoxy or phenolic coating, it would be expected that the total steel area exposed through pinholes would be something of the order of 1 square inch. This then changes the ratio from 20:1 steel to stainless to 13,000:1 stainless to steel. The rate of corrosion at these pinholes would therefore be increased by 260,000 times or an extremely severe condition, and the tank could be rapidly perforated. This can be avoided if the stainless steel coils are also coated with the resin to keep the ratio of exposed stainless to steel at a low level. In addition to corrosion rates through electrogalvanic action, there is also the phenomenon known as electroenosmosis which involves electrogalvanic action through a membrane. This corrosion must be avoided at all cost since it occurs behind the film and results in the total destruction of the bond and a subsequent sloughing off of the coating. It is, therefore, extremely important that no dissimilar metals be used in a coated system which is storing even a weak electrolyte.

TABLE VI

Materials of Construction: Dissimilar Metals Corrosion

Less noble anodic end	Rate factor
Aluminum	100
Carbon Steel	67
Brass	24
Monel	17
Inconel	13
SS-300 Series	7
Carpenter 20 Cb	4
Cathodic end more noble	

Further materials of construction for the fatty chemical industry are totally nonmetallic tanks such as fiberglass and wood. Tanks constructed of cypress have been common for acidulation of soapstocks for many years, but because of the problems of leakage, if the tanks are not kept filled at all times, the use of high alloys is increasing. Fiberglass tankage is increasing, also, due to its low initial cost and relative freedom from damage by either thermal or mechanical shock. These tanks and also fiberglass duct work are limited by the stability of the polyester resin used as a binder. These resins may be subject to chemical attack or to damage by temperatures of over 105 C. Some measure of selectivity is possible, however, if a tank is designed for a particular purpose since different resins may be employed in manufacture. In general, experience with fiberglass tanks has not been particularly good in fatty acid plants; however, considerable advances have been made in the past decade, and it would seem logical that further advances could result in more usable materials.

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