Corrosion at and near the Welded Joints

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Introduction

Replacement of costly machinery or parts can be prevented by the proper utilisation of welding processes in repairing and reclaiming techniques. Welding processes are being widely used in construction of various types of structures and overhead tanks and have, with advantage, replaced rivetted constructions in many instances. Processing tanks made of stainless steel and aluminium are also welded. Welding processes are helpful in many ways but if proper precautions are not taken during and after welding, this may lead to serious defects and premature failure due to general and intergranular corrosion at and near the welded portions.

This paper deals with the various causes of premature corrosion due to welding. The following effects have been considered :

1. Temperature

2. Dissimilarity in the composition of the parent metal and the welding rod.

3. Flux residues

4. Gases

5. Type of welding

6. Passivation treatment to the welded metal

7. Stray current during welding

8. Design

9. Cathodic protection

Effect of temperature

The effect of temperature on the welding process is a very important factor. When certain austenitic stainless steels are heated in the range 800 to 850°C for some critical time and then exposed to corrosive environment, preferential attack occurs along the grain boundaries. This critical temperature is attained by the steel during the welding process and the attack is generally described as 'Weld decay' (Fig. 1). The parent metal on both sides undergoes heating and subsequent cooling. Among the infinite variety of heat treatments thus unintentionally carried out at points situated at different distances from the weld, it is not surprising that some will adversely affect the corrosion resistance. The two materials in which this unintended heat treatment leads to most deterioration are austenitic stainless steel and the temper hardening aluminium alloys[2]. The welding of austenitic stainless steel or their heat treatment causes formation of chromium carbide (with larger grain size compared to the original fine grain)[3] in the grain boundaries. A continuous grain boundary net work of these carbides can lead to severe intergranular attack in certain corrosive environments.

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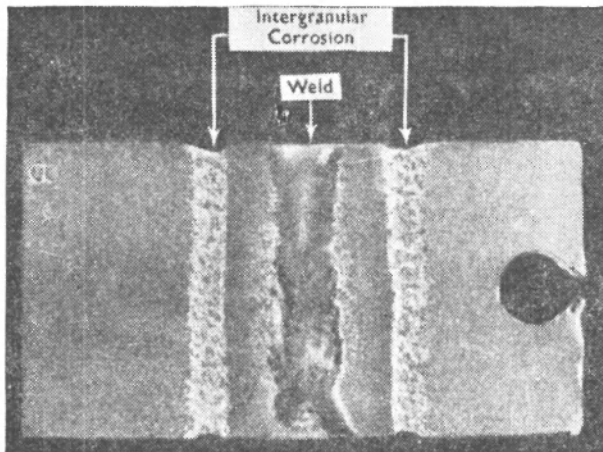
Fig. 1. Example of weld decay 2X. Specimen after sensitization was exposed to 25% HNO_3.

Intergranular corrosion of the austenitic stainless steel can be controlled or minimized by employing high temperature solution heat treatment, commonly termed quench-annealing or solution-quenching.[1] Commercial solution-quencing treatments consist of heating to 1050-1100°C followed by water quenching. Chromium carbide formed due to welding is dissolved at these temperatures and a more homogenous alloy is obtained. Most of the austenitic stainless steels are supplied in this condition. If welding is used during fabrication, the equipment must be quench-annealed to eliminate susceptibility to weld decay. This poses an expensive problem for large equipment and, in fact, furnaces are not available for heat treating very large vessels[1]. Quenching, or rapid cooling from the solution temperature, is very important. If cooling is slow, the entire structure would be susceptible to intergranular corrosion. It is advisable not to temper martensitic steels at temperatures between 350 and 650°C.[4]

If pretreatment is performed by quenching and drawing or spheroidizing, the sensivity of the steel to intercritical temperatures is greatly lessened. It is suggested that localized gas-torch post heating may be an easy and practical way of restoring the properties of the welded plate.[5]

Welds of steel containing C—0.10, Cr—16.35, Si—0.34, Mn—0.51, P—0.19 and Ni—0.25% are not corrosion resistant. This is due to formation of a reactive layer along the grain boundaries at above 900°C. In 60% HNO_3, whole grains fall out ; if the steel is kept at 1100°C for a longer time (more than 1 hr) the loss of weight in 60% HNO_3 is less since the grains are larger. Annealing at 700-800°C restores the corrosion resistance. The resistance of a steel containing C—0.05, Mn—0.56, Si—0.43, Ni—1.02, Cr—15.72 and Ti—0.35% is not impaired by welding[6].

The temper hardening class of aluminium alloys (which acquire strength by carefully regulated heat treatment) presents special difficulties in welding. Treatment at certain combination of time and temperature produces susceptibility to stress corrosion and it is fairly certain that around the weld line there will be places where such unfortunate combinations have existed, so that there will be zones of low resistance to corrosion cracking.

Oxyacetylene welded aluminium samples containing (a) 0.48% Si, 0.67% Fe and 0.002% Cu (b) 0.09% Si and 0.009% Fe respectively are attacked in 15 and 50% HnO at 60°C due to the segregation of Si and Fe_3Al in the contact zone of the weld[7]. Aluminium joints after welding should finally be heated to 380°-400°C and cooled in air or water.

Austenitic stainless steels containing higher percentage (more than 0.08%) of carbon are attacked intergranularly due to welding.[1] The deterioration is usually caused by the precipitation of chromium carbide, leaving a zone depleted of chromium, the element responsible for the protective film on stainless steel. Certain ferritic steels become susceptible to intergranular corrosion but the dangerous precipitation occurs more rapidly at a lower temperature than with the austenitic steels. Martensitic steels can also suffer from a form of selective attack caused by local depletion of chromium associated with the formation of chromium bearing carbides, although the corrosion need not necessarily be intergranular.

Lowering the carbon to below 0.03% (type 304L) does not permit sufficient carbide to form to cause intergranular attack in most applications. The original 18/8 steels contained around 0.20% carbon, but this was quickly reduced to 0.08% because of rapid and serious weld decay failures. Lowering the carbon content much below 0.08% was not possible until it was discovered that it was possible to blow oxygen through the melt to burn out carbon and until low carbon ferrochrome was developed[1].

The strong carbide formers or stabilizing elements, *columbium (or columbium plus tantalum) and titanium are used to produce types 347 and 321 stainless steels respectively. These elements have a much greater

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* This element is now known as Niobium.

affinity for carbon than does chromium and are added in sufficient quantity to combine with all of the carbon in steel. The stabilized steels eliminate the economic and other objections of solution-quenching the unstabilized steels after fabrication or weld repair[1].

Both the intergranular precipitation of chromium carbides and the formation of sigma phase may be prevented in steels containing adequate amount of titanium by heating at 850°—950°C for 1 to 4 hrs. This so-called "stabilizing treatment"[1] precipitates TiC, which ties up carbon and removes titanium from austenite. As a result, during subsequent heating at about 675°C there is no carbon available for formation of chromium carbide and because removal of titanium from austenite increases its stability, there is less possibility for transformation of austenite to sigma phase.

When certain grades of austenitic stainless steel such as type 316, 316L and 321 are heated in the 550° to 950°C temperature range, another microstructural constituent known as sigma phase[8] can form in the grain boundaries of the steel. This phase is an intermetallic compound consisting principally of iron and chromium and enriched in other ferrite forming elements that may be present in the steel such as Si, Mo and Ti. Little is known about the influence of sigma phase on the corrosion resistance of stainless steels. However, it has been established that sigma phase can cause accelerated corrosion of stainless steel in boiling 65% nitric acid and in hot, concentrated (40 to 80%) sulphuric acid solution. Aside from these media, there has been no evidence to indicate that the presence of sigma phase is necessarily damaging to the corrosi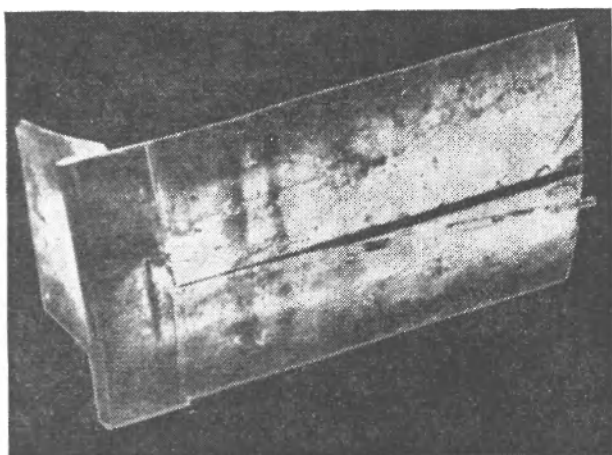on resistance. Moreover, there are no records of field corrosion failures that can be directly attributed to sigma phase.

Intergranular corrosion by fuming nitric acid of type 347 stainless steel[9], 18-8, stabilized with columbium may occur in this way. (Fig. 2). The attack is confined to a very narrow band in the parent plate immediately adjacent to the weld metal. This should not have occured because columbium is known to stabilize 18-8 against intergranular corrosion. This problem was studied and the basic mechanism determined.

Sometimes columbium or titanium added to the austenitic stainless steel to minimise weld decay may not overcome the trouble and this type of steel may undergo "knife line" attack (Fig 2). The mechanism of such a type of attack is based on the solubility of columbium in the stainless steel. Columbium and columbium carbides dissolve in the metal when it is heated to a very high temperature and they remain in solution when cooled rapidly from this temperature. The columbium stays in the solution when the metal is then heated in the chromium carbide precipitation range, columbium carbide does not form, and the metal behaves (sensitizes) as though it was 18-8 without columbium. The grain boundary susceptibility occurs, in practice, mostly in parts welded by argon arc since in this method a brief heating of the seam edges to a high temperature takes place. Therefore, the high temperature susceptibility range occurs as knife like corrosion, while the 600-900°C range occurs at a certain distance from it.

From the above it may be summarised that the problem of weld decay can be overcome by (a) reducing the carbon content to less than 0.02% (b) by heat treatment followed by rapid quenching or (c) addition of stabilising agents e.g. columbium and titanium which have greater affinity for carbon and chromium so that chromium carbide formation is prevented. Local heating with flame torch and water spraying are sometimes used. The stabilizers are often used in the welding rod so that they may have almost the same effect as being present in the parent metal.

Effect of dissimilarity in the composition of the parent metal and the welding rod

It is difficult to match the composition of welding rod and the parent metal exactly and this difference in the compositions constitutes an infinite number of galvanic cells. The electrochemical contrast between weld metal and parent metal is considerably smaller

Fig. 2. Knife line attack of type 347 stainless steel vessel.

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than that between solder and the plates joined by it. At first sight, it would be seen that the electrode chosen should be such as to make the weld metals cathodic to the plates:, but often other considerations prevail. In welding aluminium intended for service with nitric acid, there is a danger that the acid will pick out closed-in blowholes along the weld-line ; this is least likely to happen if pure aluminium, which develops a highly protective film, is used as weld metal despite the fact that pure aluminium is, in many liquids, anodic towards commercial aluminium.

Use of more electropositive materials for rivets or welded seams are beneficial from the bimetallic corrosion point of view. It is recommended, for instance, that copperized steel[9] or even stainless steel be used for rivets.

The problem of weld metal corrosion in ships has been more difficult because use is often made of basic weld metals from consideration of their better weldability and better mechanical strength. Exceedingly severe corrosion amounting to as much as 6-10 mm per year in weld joints of certain ships, especially in ice-breakers delivered from Finland to the USSR, provided cause for investigations of several years duration. An inducement to undertake such investigations was furnished by the fact that no corrosion whatsoever of weld joints occured in some other ships manufactured with the same weld materials in the same shipyards and identical conditions. The causes responsible for the said corrosion were sought everywhere, but no rational explanation of its occurence could be found until potential measurements were undertaken with different steel plates and weld joints. It was then found that the corrosion potentials both of steel plates and of the

Fig. 3. *Detail of welded steel—stainless clad tank construction.*

weld metals of a certain type display a tendency to become anodic in connection with certain brands of parent plate[9].

Combination of carbon steel and stainless steel may set up galvanic corrosion of the latter, particularly in the welded region[10]. Figure 3 represents a section of a large number of huge welded steel-stainless steel clad tanks which failed by complete penetration in a few months. Most of the holes were in the carbon steel within a narrow band just above the weld. The steel surface was coated with a protective coating but the stainless steel was left bare. Small defects in the coating on steel resulted in small anodic areas connected to large cathodic areas (18-8 stainless steel) about 20 feet in diameter. The problem was solved by coating both the steel and stainless steel surfaces. Over a quarter million dollars were at stake on the decision regarding the mechanism of these failures[10].

Flux residues

The danger of flux residues exists also in welding[2]. It may be necessary in some cases to use mechanical methods such as impact tools, to remove residues. Corrosive constituents may be fluorides, chlorides and, for some metals, alkali, even where the metal is resistant to alkali, alkaline residues may cause deterioration to a paint coat if applied subsequently (here vinyl coatings or alkali resisting types may prove useful[2]) On welded articles made from magnesium alloy, flux residues are the most likely cause of corrosion when a chloride flux is used.

Magnesium alloy containing 1.5% manganese can be welded with a fluoride flux[2] which is non-corrosive, magnesium fluoride being sparingly soluble.

Effect of gases

Hydrogen in the metal arc welding process enhances cracking of the metals. Studies of under bead and toe cracks in welds of many types and grades of steels including NE 8620-26-30-35-40-45 and SAE 4130, have led to the hypothesis that (a) chemical composition of steels to be welded in a protective hydrogen atmosphere greatly affects the weldability ; (b) chemistry restrains cracking of many steels and (c) dispersion of carbides in and around the weld zone permits escape of entrapped hydrogen which causes cracking. Such a type of attack is generally called weld embrittlement.[11]

In welding of aluminium-magnesium alloys, blistering due to hydrogen uptake causes serious problems[2].
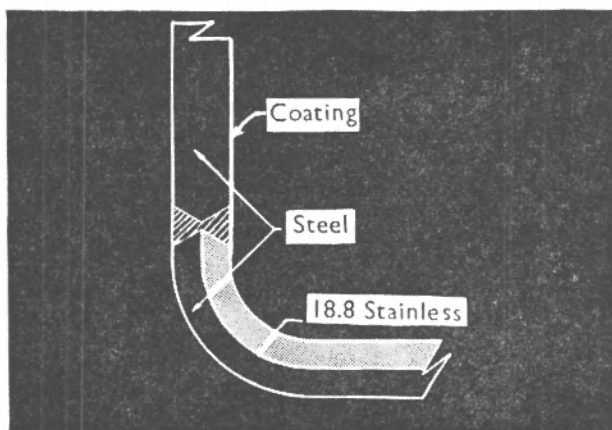
Various types of gas welding give rise to 'blow slips' during welding which reduce the strength of the metal structure. These blow slips are generally caused due to entrapped gas and by the use of improper weld rod.

Precaution should also be taken against oxygen uptake during welding, otherwise welded steel containing oxygen shows pitting type corrosion in 3% sod. chloride solution[2].

Effect of type of welding

Characteristics of the various welding process should be considered from the point of view of the material with which they may be concerned. In welding high purity aluminium, special consideration should be given to the selection of type of welding and the welding rod[12]. Flash welded high strength aluminium alloy corrodes severely at the weld lines.[13]

In recent years the use of the argon shielded arc—with elimination of flux—has greatly eased the situation both for magnesium and aluminium alloys. The argon should be substantially free from nitrogen[2].

Time and temperature effects provide one reason why electric arc welding is used more than gas welding for stainless steel. The former produces higher and more intense heating in shorter time. The latter would keep a wider zone of metal in the sensitizing range for a longer time, which means greater carbide precipitation.[1]

Effect of passivation treatment of welded areas

Effect of water and gasolene 70 Octane on welded portions of untreated and MBV (Modified Bower Vogel chromate) treated aluminium jerricans has been investigated.[14] Panels 7.5 cm×2.5 cm were cut from
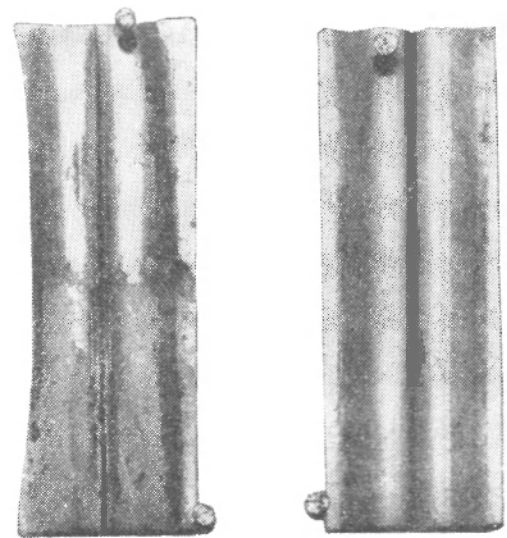
UNTREATED   M.B.V. TREATED
STUDY OF CORROSION ON
ALUMINIUM
WELDED JERRICANS

Fig. 4.

welded portions of MBV treated and untreated NS4 (IS 737) jerricans. The panels were suspended half immersed in fuel and half in water in 50 : 50 water-gasolene mixture and was kept at 84°F. The periods of test were 15 & 45 days. The gain in weight and metal loss after the test periods are given in the table below.

Portion of the untreated weld showed greyish film in the aqueous phase. Portion of the MBV treated weld did not show any discolouration in aqueous phase.

From the weight increase and loss of metal data it will be seen that overall attack on the untreated weld was comparatively much higher than on the MBV

TABLE

Type of panel	Environment	Wt. increase in mg after		Loss in wt. in mg
		15 days	45 days	
weld from MBV	70 Octane	-3	No change	not done
treated jerricans	fuel+water	7	4	,,
		12	4	,,
weld from untreated	-do-	12	22	,,
jerricans.		12	13	17
		22	23	20

treated weld. Welded areas were found to be susceptible to corrosion by fuel-water mixture. The MBV treatment, however, completely eliminated the corrosion at welds. Fig. 4 shows the condition of the treated and untreated welded joints.

Effect of stray current

Serious damage can be caused by stray current from welding sets leaking into unwelded regions and leaving the structure through electrolytes. An example of this was provided by the failure of a hull of a ship during welding.[15] The welding set was placed on shore away from the ship. During the welding of the hull, stray current leaked from the hull through sea water electrolyte to the welding set terminals. At points where the current left the hull, into the electrolyte severe damage occured. Thus while welding was used for repairing at one part of the hull another part of the hull suffered corrosion due to stray current electrolysis.

This type of defect can be avoided by (i) by transfering the welding set on to the ship so that the possibility of leakage of current through the electrolyte is avoided. (ii) Complete elimination of single wire systems of electrical energy supply on ships and strict requirement for electrical insulation of conductors. In carrying out welding on ships, there is danger of accelerated corrosion from stray currents. This is especially the case when single-conductor systems are used with the ship as the positive pole. This danger can be eliminated by using a more perfect two-wire power supply without grounding the generator at its station.

Effect of design

In good design, as little surface should be exposed to corrosion as possible. This can be done by removing surfaces from exposure to corrosive environments by seal welding the rivets all round, using standard welds for sealing crevices and using butt type joints wherever possible[16] (Fig. 5). Where fillet, lap, or strap joints must be used, the weld should be made continuous and sound to prevent any fluid getting into the joint and jointing compound and putty should be used to fill crevices wherever possible and compatible with the environment or where welding is not economical or desirable.

Cathodic protection[14]

Corrosion of the welded joints of stainless steel vessels containing corrosive liquids e.g. (a) mixture of
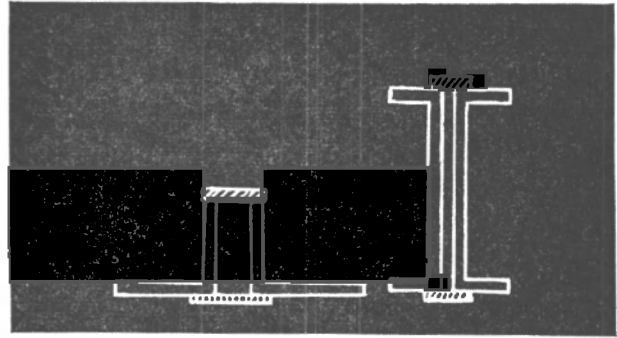

Fig. 5. Angles and channels joined back to back. Removal of exposed areas by seal welding with straps.

chromic 5% and sulphuric acid 15% and (b) bleaching liquor has been successfully prevented by the application of cathodic protection. General and pitting type of corrosion was reported of the welded joints and on the internal surface of stainless steel tanks containing a mixture of chromic and sulphuric acids used for etching of aluminium surface prior to anodising. Corrosion was so severe that either replacement of the tank as a whole or welding of stainless steel plates had to be carried out frequently to avoid leakage.
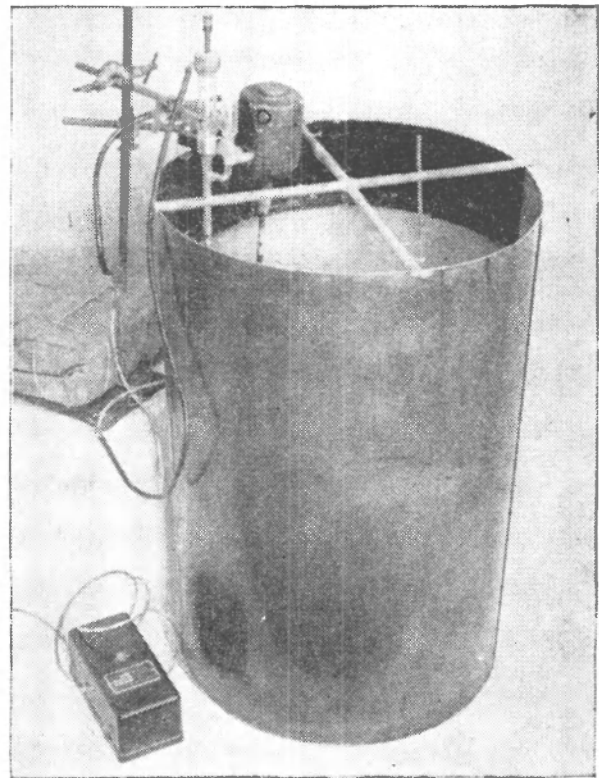

Fig. 6. Arrangements showing cathodically procted stainless steel drum.

Cathodic protection of internal surface of the stainless steel tank containing the acid etching solution was carried out by using lead anodes. The current density of 7 mA/sq.cm. was maintained during the entire period of test (6 months). The potential of cathodically protected tank varied from +300 mv to +250 mv vs SCE while that of the unprotected tank was +800 to +1000 mv during the test period. After expiry of the test period the cathodically protected tank did not show any thinning or cracks at the welded joints. The sides of the unprotected tank had thinned down considerably and showed perforation when lightly hammered. The welded joints also showed general corrosion.

In another experiment, stainless steel tanks containing bleaching liquor were used for the bleaching of yarn in the textile industry. Pitting type of corrosion and severe corrosion of the welded portion was reported by the textile industry. In a few cases the corrosion of the weld was so severe that the weld cracked and there was lifting or separation of sheets. In order to overcome the attack, the feasibility of cathodic protection of internal surface of stainless steel tank containing bleaching liquor (3-5 mg/litre chlorine) (Fig. 6) was examined. Aluminium rods used as
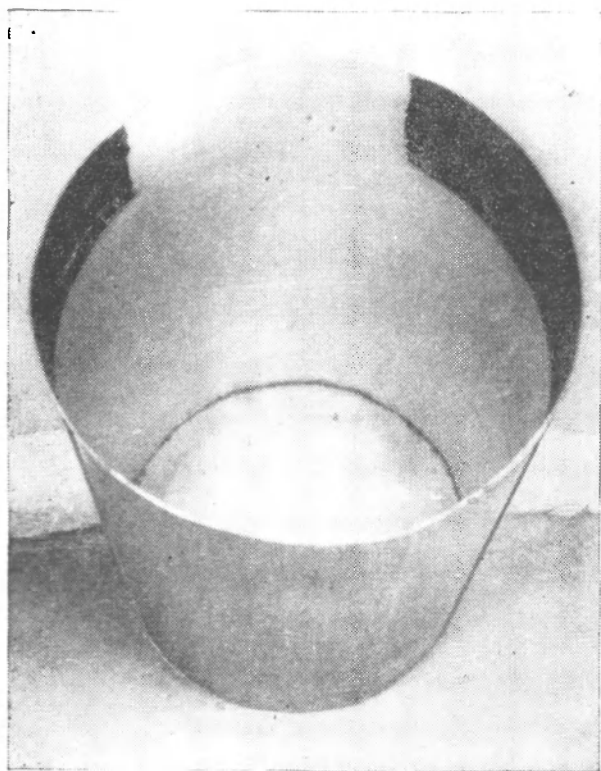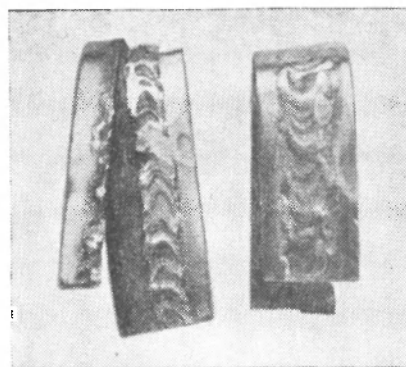

Unprotected   Protected

Fig. 8. Welded portions cut from the Panels of Stainless Steel and given a Bend Test.

sacrificial anodes were encased in porcelain pots to avoid contamination of the bleaching liquor with the corrosion products. The current was adjusted to 5×1000 μA initially which fell to 21 < 100 μA after 6 days and thereafter remained 8 < 10 μA for the entire period of test (one year). The potential of the cathodically protected tank was maintained between -200 to -300 mv vs SCE. The potential of unprotected tank was initially -50 mv, which rose to --250 mv during the test period. Stainless steel coupons, unwelded and welded, were also placed at different depths in the cathodically protected tank and were coupled with the aluminium anode. The potentials of these panels also were maintained between -200 to -250 mv. Panels immersed in the cathodically protected tank but not connected to anode showed a potential of +250 mv. The tank was emptied after a year and general observations were taken after cleaning (Fig. 7) The internal surface of the tank was free from any corrosion and the welded areas were also free from any damage. The cathodically protected unwelded and welded coupons were free from any attack. There was severe pitting type corrosion on the unprotected metal coupons and the welded portions showed cracks and there was lifting and impairment of welded joints (Fig. 8)

Fig. 7. Inner View of the Cathodically Protected Stainless Steel Drum after one year.

Cathodic protection is thus a practical means to prevent attack on welded chemical processing equipment. A still more economical method is to subject the equipment to anodic protection techniques. In the latter case, current is applied so as to make the equipment anode instead of cathode (as in the previous case). The mechanism of protection in the two cases is, however, entirely different.

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