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# The Effect of Electrochemical Potentials on the Durability of Rubber/Metal Bonds in Sea Water†

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A study of the role of electrochemical potentials on the durability of rubber/metal bonds in seawater is described. In electrochemically inert conditions, these adhesive bonds are shown to be extremely stable—even after more than 3 years immersion in seawater. However, some bond failure is shown to be possible within days—when the rubber is bonded to the more noble of a pair of metals in electrical and electrolytic contact. Resistance to bond failure increased as the cathodic potential was decreased. Mechanical strain in the elastomer layer was shown to have no effect on bond durability.

## INTRODUCTION

The difference in electrochemical potential between dissimilar metals in electrical and electrolytic contact causes electron flow between them which usually increases the corrosion attack of the more active metal and reduces that of the more noble metal. While corrosion attack of the more noble metal is decreased, it has been shown<sup>1</sup> that the rate of adhesive bond failure between it and rubber

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can be strongly increased. This phenomenon is of potential importance for a number of applications in the Offshore Oil and Gas industry,<sup>2</sup> where rubber/metal composite bearings or rubber coated pipework are used in close proximity to steelwork protected from corrosion by means of sacrificial anodes or impressed currents. The usual assumption that the rubber coated regions will be unaffected by such cathodic protection are not always true since the latter can cause bond failure between the rubber and the metal.

Previous work<sup>1</sup> reported a study of this effect for rubber/carbon steel, Inconel and titanium. Electrochemical potentials were provided by the natural differences arising from their combination with carbon steel. In addition to the laboratory tests, the results of steel, Inconel and titanium. Electrochemical potentials were provided by the natural differences arising from their combination with carbon steel. In addition to the laboratory tests, the results of parallel deep sea trials at a water depth of 450 ft are also discussed. Finally, the results of some model experiments with testpieces immersed with a positive compressive stress applied to retard the progress of bond failure and with testpieces immersed in a very high pH solution are presented. The results of all these experiments are discussed in terms of the evidence they provide for the likely physical mechanisms involved.

## EXPERIMENTAL DETAILS

The testpieces were of the double shear type, consisting of 2 rubber and 3 metal discs of 25 mm diameter alternately bonded in the configuration shown in Figure 1(a). Each testpiece thus has 4

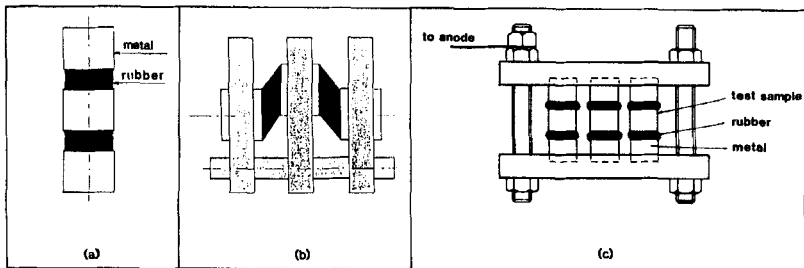


FIGURE 1 Testpiece geometry (a) unstrained (b) simple shear @ 100%. (c) compression @ 25%.

TABLE I  
Metal surface preparation and bonding technique

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All adhesive bonds were formed in accord with the procedure below:

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1. Metal surface degreased with trichloroethane
  2. Metal surface grit blasted to white/grey finish with grade 60/80 Aluminium Oxide
  3. Cleaned with trichloroethane
  4. Within 30 minutes of drying—primer coat (Chemlock 205) applied
  5. Within 30 minutes of drying—bonding agent (Chemlock 220) applied
  6. Within 30 minutes of drying—metal parts placed in rubber mould
  7. Cured *in situ* with rubber—2 hrs @ 125°C
- 

rubber/metal bonded surfaces. The 2 rubber layers were each of 10 mm thickness. The different types of metal used were: (A) carbon steel, (B) Inconel, (C) stainless steel, (D) pure titanium and (E) titanium alloy. The composition of the rubber used was the same for all testpieces. This was a sulphur cured Natural Rubber filled with carbon black.

All metal endpieces of all types underwent the same procedure for forming the adhesive bonds. This is described in Table I. During the test program about 500 testpieces were produced in this way in several batches. Quality control checks were performed on about 25 testpieces removed at random before commencement of the main body of tests. Of these, some were pulled to failure dry, in shear, on a Zwick test machine and some were immersed in sea water for 3 days and then pulled to failure. Such a quality control testpiece was considered to be a failure if there was any sign whatsoever of failure at the metal surface (i.e. 100% rubber failure was required). If a single quality control failure was discovered, then the whole batch was rejected. In addition, the shear modulus of each testpiece produced was measured over the strain range 0–25%. This was required to be within 5% of 0.8 MPa. For some batches, the shear modulus was within 2% of the mean value. This checked the cure and quality of the rubber. Standard tensile, tear and fatigue tests were also performed for each batch of mixed rubber.

At an early stage of the program it was found that the surface roughness of the metal could have a strongly detrimental effect on bond durability after 3 days in sea water—although dry control tests showed no difference. Too fine or inadequate grit blasting could lead to premature failures and one batch of testpieces was rejected for this reason. However, when the procedure in Table I was

TABLE II  
Summary of bond failure penetration depths at different imposed cathodic potentials during sea water exposure at 23°C

Cathodic potential	Induction period (days)	Rate of bond failure {mm/(day) <sup>1/2</sup> }	Maximum penetration depth (mm)
1050 mV	1	1.0	15
950 mV	5	1.0	9
850 mV	5	1.0	9
750 mV	20	1.0	7
610 mV	30	1.0	4
0 mV	>1000	—	0

followed carefully there were no failures of this quality control test and no rejects at all.

After the quality control checks, most testpieces were mounted in jigs to hold the rubber layers at 100% shear strain, (see Figure 1(b)), and immersed in sea water. These holding jigs were fabricated from the same grade carbon steel as the carbon steel testpieces. All parts of the jigs were coated in Chemlock 220 to inhibit gross corrosion. However, on fitting the testpieces, metal at the inner faces of the holes was bared so that the metal of the testpiece and the carbon steel jig may be considered to have been in electrical contact from the outset. In this way, when carbon steel was not used in the testpiece there would be a local electrical potential derived from the relative positions of the two dissimilar metals in the galvanic series.

All testpieces were immersed in a large excess (35 litres) of synthetic sea water, prepared in accordance with the ASTM standard.<sup>3</sup> All trace heavy elements were included as provided for in the standard. The water pH was measured initially as 8.2. The initial oxygen content was 8 ( $\pm$  1) mg/l.

After various exposure times, testpieces were removed from the sea water tanks and evaluated for the extent of any bond failure. This evaluation consisted in removing the testpiece from its restraining jig and pulling to failure on a Zwick 1740 universal test machine. The shear modulus, stress and strain at break was recorded, and then all bond surfaces were mapped to provide an accurate record of the area of bond failure. These measurements enable the results to be plotted in terms of failure penetration

depth, % area of bond failure, and stored elastic energy required to cause failure. In this paper, the results are discussed primarily in terms of the failure penetration depth. This was taken as the average of the maximum penetration depths of bond failure over each of the four bonded surfaces.

## RESULTS

### The effect of high cathodic potentials

The highest potential was provided by means of the system illustrated in Figure 2, namely using a Zinc sacrificial anode in combination with carbon steel/rubber testpieces. This produced a measured cathodic potential of 1040–1070 mV at the testpiece surface (with reference to a Ag/AgCl reference electrode). There then resulted fairly rapid bond failure at all temperatures tested but no corrosion of the carbon steel. Figure 3 shows typical failure surfaces from these tests. Each failure surface consists of three regions. There is a lower black region where failure occurred through the rubber. This region was asymmetrically located because in simple shear bond failure was always observed to initiate at the leading edge. This is the point where local shear or surface tensile strains in the elastomer are a maximum. Adjacent to the region of

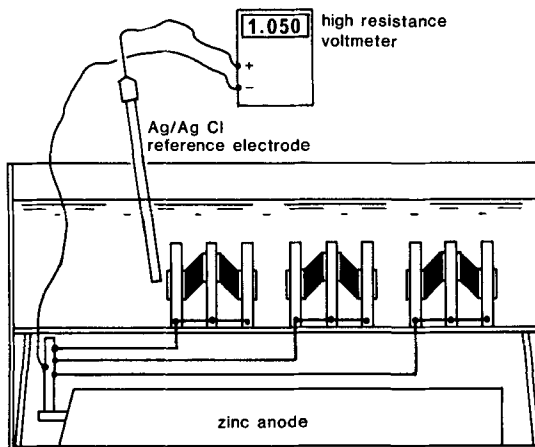
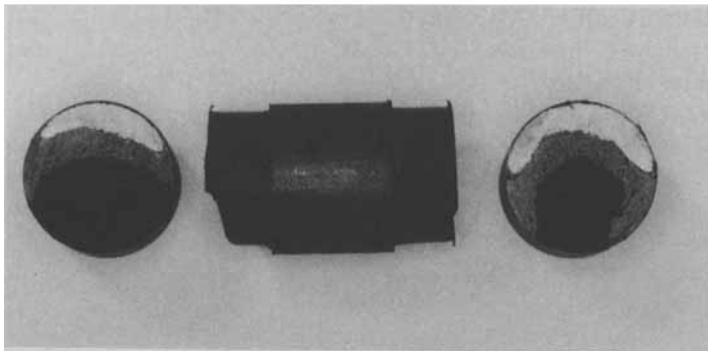
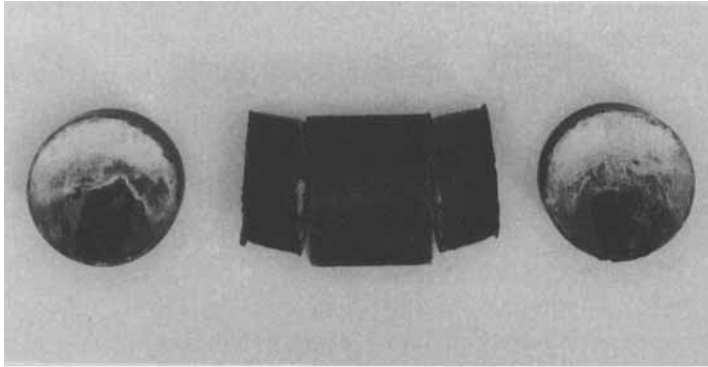


FIGURE 2 Test arrangement for tests at high cathodic potentials.

**(a) 45° C****(b) 3° C**

**FIGURE 3** Typical bond failure surfaces (a) sea water exposure at 3°C (b) sea water exposure at 45°C.

rubber failure is a grey region where the failure locus was predominantly at the bond between the metal and the primer coating. Small rubber particles were, however, left adhering to the steel in places in this region. The bond failure seen here occurred only as a result of the pull to failure test. The uppermost failure region in the photographs of Figure 3 shows a powder deposit. This was a bluish colour for tests at 3°C and a cream white colour for tests at 45°C. The colour was intermediate at 23°C. Chemical analysis showed the blue-white deposit to contain predominantly magnesium (Mg) with lesser amounts of S, Cl, Ca, Fe and Zn while

the cream-white deposit was predominantly Zinc (Zn) with lesser amounts of S, Ca, Mg, S and Cl. All of these elements were constituents of the sea water used in the experiments. These deposits formed on the steel surface after bond failure had occurred. The deposits were observed to increase in thickness until, after about 200 days of sea water exposure, they filled the gap opened between rubber and metal by bond failure. Similar deposits also occurred on all other exposed electrically connected steel surfaces and were, of course, an indication that the cathodic protection provided by the sacrificial zinc anodes was working correctly.

When determining any change in adhesive bond strength (interfacial failure energy), it is important to know if there was any change in the cohesive strength of the rubber. Clearly, if the rubber strength decreased during a test then the area of bond failure could be anomalously lower than would be the case if the rubber strength remained constant. To investigate this point, the energy required to cause fracture was measured by integrating the force/deflection curve from the shear pull to failure test. This energy was then divided by the total rubber volume to derive a characteristic stored energy density,  $W$ , at fracture. In the absence of bond failure,  $W$  can be used to characterise the critical tearing energy of the rubber—and indeed then yields a value comparable with results from standard tear tests. With an area of bond failure, however, the fracture geometry is more complicated, although the same approach can be used. It is sufficient for present purposes to describe the results empirically. Figure 4 shows the stored energy density plotted against sea water exposure time for each testpiece with a cathodic potential of 1050 mV (the largest areas of bond failure). The root exposure time, in fact, correlated with area of bond failure—the latter acting as a starter crack for subsequent cohesive fracture through the rubber. As a control experiment, a set of new dry testpieces were cut at the bond to various depths—simulating the full range of bond failure depths observed. The geometry of bond failure was also simulated. These testpieces failed at identical failure energies,  $W$ , to the testpieces that had exhibited bond failure, following sea water exposure for up to 2 years. This shows clearly that there was *no* significant change in rubber strength during the tests. The failure penetration depths are thus entirely representative of changes in adhesive bond strength.



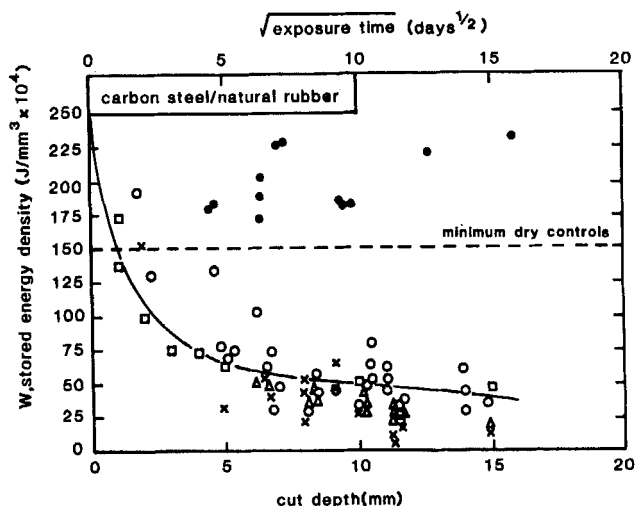


FIGURE 4 Stored elastic energy at failure vs bond exposure time @ 1050 mV  $\Delta$  3°C,  $\circ$  23°C,  $\times$  45°C; vs bond exposure time—zero potential  $\bullet$  all temps; vs cut depth—dry control testpieces  $\square$ .

The characteristic stages of the bond failure process are illustrated in Figure 5, where bond failure penetration depth has been plotted against the square root of seawater exposure time. If diffusion processes are involved, then a linear relation between penetration depth and  $(\text{time})^{1/2}$  would be expected from classical theory.

The first stage was a time lag observed before any bond failure could be measured (*i.e.* less than 0.5 mm failure penetration depth). This "induction period" increased with decreasing potential and decreasing temperature. The second stage was a period of increasing penetration of bond failure into the testpiece as an approximately linear function of the square root of exposure time. This enabled a failure penetration rate to be defined for each test condition. Finally, there was an approach to an "equilibrium" depth of bond failure. For the testpiece design used, the maximum possible depth was 15 mm (assuming some asymmetry). In a number of cases the equilibrium failure penetration depth was found to be considerably less than 15 mm.

Additional tests were performed to investigate the effect of lower

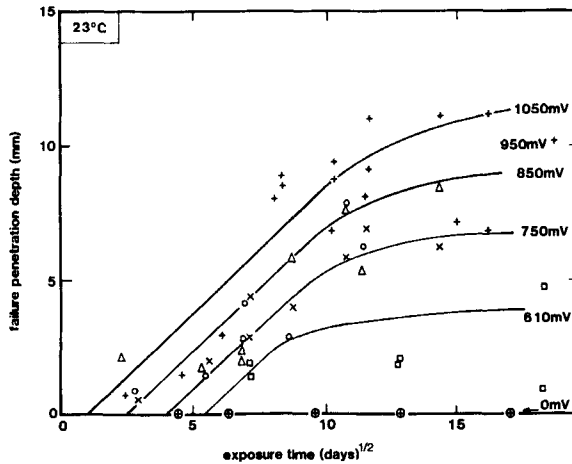


FIGURE 5 Penetration depth of bond failure vs root seawater exposure time 1050 mV,  $\Delta$  950 mV,  $\circ$  850 mV,  $\times$  750 mV,  $\oplus$  0 mV. All tests at 23°C. All NR/carbon steel testpieces.

potential differences on carbon steel testpieces than was possible using zinc anodes. For this purpose, a potentiostatic arrangement was installed which supplied a constant impressed current at a chosen potential difference. A series of platinum electrodes were installed and connected to a current source to provide constant cathodic potentials of 0.95 V, 0.85 V, 0.75 V and 0.61 V at the bond edge of the carbon steel testpieces. The same general test method was used as described for the experiments with zinc anodes. Separate sea water tanks were used for each different cathodic potential. All test with impressed currents were performed at 23°C. The results are shown in Figure 5.

Substantial delamination was observed after long sea water exposure periods in all cases. No steel corrosion was observed with cathodic potentials of 950 mV or 850 mV, although some was observed after long periods with 750 mV and more with 610 mV. There were now no thick powder deposits on exposed steel surfaces. There were again no changes in modulus or energy at break that could not be attributed to the geometrical changes caused by bond failure—*i.e.* no changes in the rubber itself.

There was a progressive increase in induction period as the level

of imposed cathodic potential was reduced—from 1 day at 1050 mV to 30 days at 610 mV. After the induction period was completed and bond failure began to be observed, the failure penetration rates were, however, the same for all potentials as far as could be ascertained within the limits of experimental error. This rate was  $1.0 (\pm 2) \text{ mm}/(\text{day})^{1/2}$ . After very long exposure periods (up to 3 years), the penetration depth approached an equilibrium value which increased from 4 mm at 610 mV to the maximum possible ( $\geq 12.5 \text{ mm}$ ) at 1050 mV. These results are summarised in Table II. Identical testpieces exposed to sea water in the same restraining jigs (Figure 1(b)) but without electrical connection to a potentiostat or to a dissimilar metal (*i.e.* 0 mV) showed no bond failure whatsoever—even after more than 3 years sea water exposure.

#### **The effect of dissimilar metals in contact**

Testpieces using metal parts of Inconel, two types of titanium and stainless steel were exposed to seawater at 3°C, 23°C, and 45°C in separate tanks. The testpieces were strained to 100% shear in the holding jigs shown in Figure 1(b). These holding jigs were all fabricated from carbon steel. The system was not electrochemically inert for the Inconel, stainless steel or titanium testpieces, and the possibility existed of electrochemical interactions between the dissimilar metals in contact—throughout the seawater exposure period. The outer surfaces of the holding jigs were initially painted with a chlorinated rubber coating to prevent gross corrosion of the carbon steel. However, this only lasted about 1 year and after this some corrosion of the holding jigs could be observed with a layer of corrosion product over the floor of the test tank. Carbon steel testpieces were also mounted in the carbon steel holding jigs and electrically connected to a large block of zinc to create a known cathodic potential of 1050 mV.

The full set of results are shown in Figure 6, where the failure penetration depth has been plotted against the root seawater exposure period for all electrochemical conditions and all temperatures. Again (*cf* Figure 5) there was a definite time lag or induction period before any bond failure could be observed. This time lag increased with decreasing temperature and decreasing cathodic potential. The dissimilar metal combination showing the largest

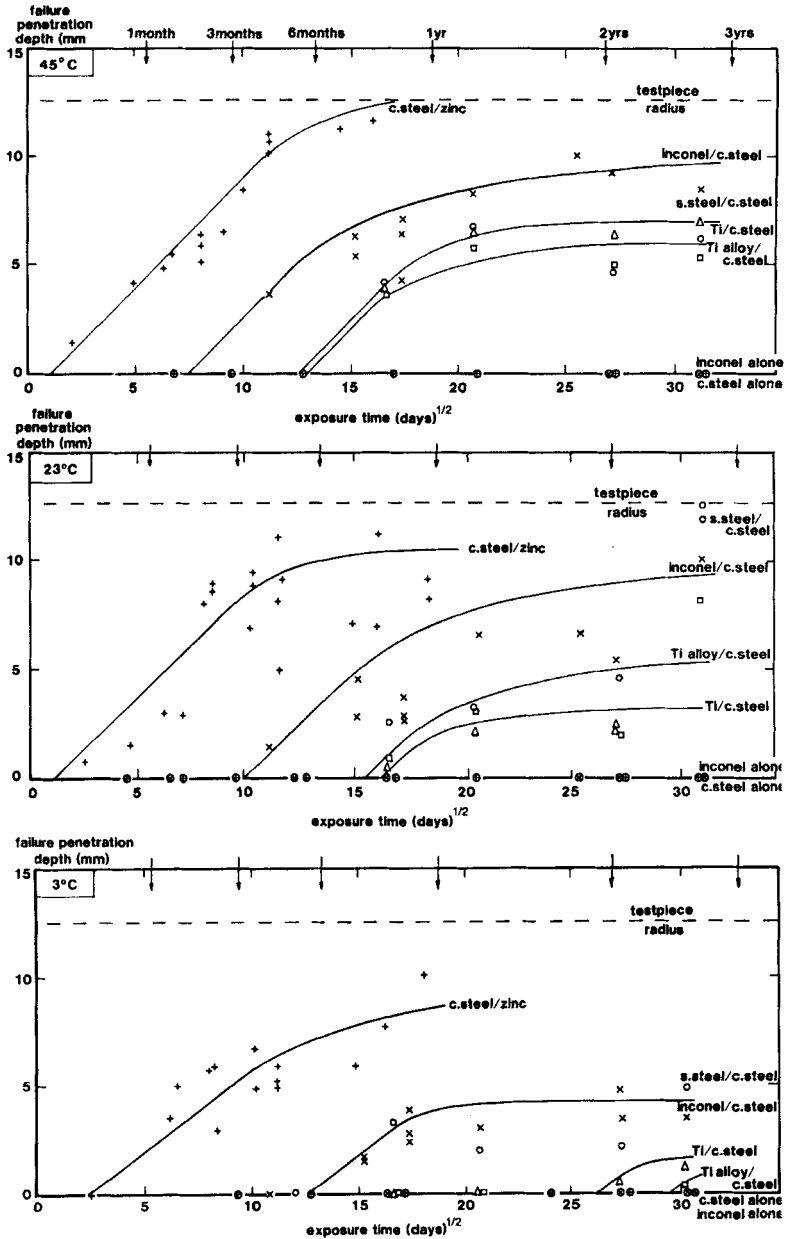


FIGURE 6 Penetration depth of bond failure vs root seawater exposure time (a) 3°C (b) 23°C (c) 45°C. + carbon steel/zinc; O stainless steel/carbon steel; x inconel/carbon steel; Δ pure titanium/carbon steel; U titanium alloy/carbon steel; ⊕ carbon steel alone; ⊗ inconel alone.

cathodic potential was carbon steel/zinc, at 1050 mV. The exact values of the local potentials caused by the other metallic combinations were not known, but would be considerably less than 1 V. The measured rates of failure penetration were all  $1.0 (\pm 0.2) \text{ mm}/(\text{day})^{1/2}$  within experimental error—for all temperatures and all electrochemical conditions. It is possible that there were small differences in rate with temperature, but experimental precision does not permit this to be stated. There appeared to be an approach to a final “equilibrium” depth of bond failure in all cases. This increased with increasing temperature and increasing cathodic potential. These results are summarised in Table III below. It is interesting that the most striking differences are all in induction period—which increased with decreasing temperature or decreasing potential.

### Effect of elastomer strain

The asymmetric appearance of the region of bond failure in Figure 3 suggested that elastomer strain may influence the bond failure penetration depth. To investigate this possibility, a series of experiments was performed using different elastomer strains. Twelve carbon steel testpieces were exposed to seawater with a cathodic potential of 1050 mV but zero elastomer strain. A further set of similar testpieces was subjected to 25% compression strain in the holding jigs shown in Figure 1(c). The results of these tests, which were all performed at 23°C are shown in Figure 7.

TABLE III  
Summary of bond failure penetration depths for different combinations of dissimilar metals during seawater exposure at 3°C, 23°C, and 45°C

Condition	Induction period (days)			Maximum penetration depth (mm)		
	3°C	23°C	45°C	3°C	23°C	45°C
C. steel/Zn	5.8	1.1	0.8	10	11	15
Inconel/c. steel	151	96	53	5	11	10
S. steel/c. steel	151	96	53	5	10	7
Ti/c. steel	676	262	154	>2	6	7
Ti alloy/c. steel	864	237	164	>1	4	6
Inconel alone	>1000	>1000	>1000	0	0	0
C. steel alone	>1000	>1000	>1000	0	0	0

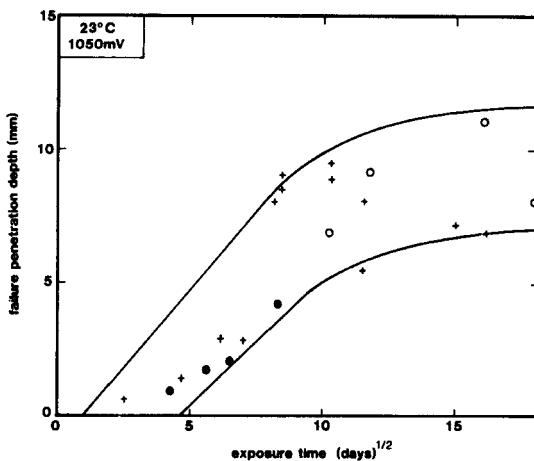


FIGURE 7 Effect of elastomer strain on bond durability. + 100% shear strain; ○ zero strain; ● 25% compressive strain.

All of these different strain conditions did show bond failure. Within experimental error, there was no difference whatsoever in induction period, failure rate or final bond failure penetration depth between any of the different elastomer strains applied during testpiece exposure. This leads to the conclusion that elastomer strain has no effect on bond durability. The presence of local shear strain does not accelerate bond failure, neither does the presence of a compressive strain retard it.

## DISCUSSION AND CONCLUSIONS

Electrochemical potentials have been found to play a dominant role in limiting rubber/metal bond durability. The behaviour is the reverse of normal corrosion activity in the sense that bond failure occurs when rubber is bonded to the more noble metal that is relatively protected from corrosion. In corrosion studies of metals, it has been found<sup>4</sup> that it is not just the relative position of the metals in the galvanic series that determines corrosion activity, but also their polarisation behaviour. Polarisation effects can lead to a breakdown of the metal oxide structure which later on creates the

possibility of, for example, pitting corrosion on stainless steels in seawater. In the present case, it is possible that some change occurs to the metal oxide surface during the induction period before any bond failure is observed. Thereafter, the rate of failure may be determined simply by a reaction rate—possibly influenced by the rate of diffusion of electrolyte through the metal primer layer.

When two dissimilar metals are in electrical and electrolytic contact, the difference in electrochemical potential between them will cause electron flow. Corrosion of the more noble metal is usually decreased and that of the more active metal is increased. It is normally considered<sup>4</sup> that any electrochemical reaction can be divided into oxidation and reduction reactions and that there can be no net accumulation of electric charge during such reaction. From this, the evolution of hydrogen at the cathode (more noble metal) is likely. It is possible that this evolution of molecular hydrogen enters into an adverse reaction with the primer coating on the metal, such that the bond integrity is destroyed.

There was no evidence of the evolution of hydrogen gas during the tests. The physics of the adhesive bond formed between the interfaces metal/primer/bonding agent/rubber is not well understood at any of these interfaces. The extremely strong and durable nature of the bonds even after prolonged exposure to moisture (in the absence of electrochemical reactions) makes it unlikely that they simply involve secondary intermolecular forces. On the other hand they do possess some features (*e.g.* rapid dissolution in the presence of certain selected solvents) that make it unlikely that they are all primary chemical bonds. It is possible that some form of ionic bonding contributes to perhaps the normal secondary intermolecular bonding thought to occur for other adhesive systems. Such bonds may be relatively more susceptible to disruption by electron flow and electrochemical activity.

These experiments lead to the conclusion that it is *only* in the presence of electrochemical activity that these rubber/metal bonds fail. In electrochemically inert conditions rubber/metal bonds have been found to be completely stable, even after 3 years seawater exposure and significant water absorption by the rubber.

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