

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

## Bonding of Vulcanized Elastomers for Underwater Use

D. Oldfield<sup>a</sup>; T. E. F. Symes<sup>a</sup>

<sup>a</sup> Materials Research Laboratory (MRL)-DSTO, Melbourne, Australia

**To cite this Article** Oldfield, D. and Symes, T. E. F.(1992) 'Bonding of Vulcanized Elastomers for Underwater Use', The Journal of Adhesion, 39: 2, 91 – 100

**To link to this Article:** DOI: 10.1080/00218469208026542

**URL:** <http://dx.doi.org/10.1080/00218469208026542>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*J. Adhesion*, 1992, Vol. 39, pp. 91–100  
Reprints available directly from the publisher  
Photocopying permitted by license only  
© 1992 Gordon and Breach Science Publishers S.A.  
Printed in the United States of America.

# Bonding of Vulcanized Elastomers for Underwater Use\*

D. OLDFIELD and T. E. F. SYMES

*Materials Research Laboratory (MRL)—DSTO, P.O. Box 50, Melbourne, 3032, Australia*

*(Received December 5, 1990; in final form August 13, 1991)*

Epoxy adhesives were used to produce strong and durable bonds between steel and four types of vulcanized elastomer. Chlorination of the elastomer surface prior to bonding and the use of an epoxy primer on the grit blasted steel surface gave the best results in laboratory trials as well as after tropical marine immersion for three years. A layer of natural rubber approximately 6 mm thick was found to be sufficient, if correctly bonded, to prevent completely the corrosion of mild steel during three years' immersion in tropical seawater. This system also performed well under dynamic flow conditions which were equivalent to a vessel travelling at a speed of 20 knots for 450,000 km.

**KEY WORDS** post-vulcanization bonding; elastomer/metal adhesion; elastomer/elastomer adhesion; elastomer surface treatment; marine immersion; epoxy adhesives.

## INTRODUCTION

One of the more demanding uses of adhesives is the bonding of acoustic coatings to submarine hulls to reduce the detectability of the submarine by active or passive sonar, as is evidenced by cases of anechoic tile loss from both Soviet<sup>1</sup> and Western<sup>2</sup> submarines. Effecting reliable adhesion of such tiles is particularly difficult, as there is little possibility of using adhesives which require either an elevated temperature or the application of pressure for curing, due to the large thermal mass of the substrate and the impracticability of putting a submarine into an autoclave. Hence an adhesive is required which will cure at ambient temperatures and low applied pressures to produce strong and durable bonds between vulcanized elastomers and steel surfaces.

In the past it has been difficult to obtain reliable and durable bonds between steel surfaces and vulcanized elastomers at ambient temperatures. We reported<sup>3</sup> an improved surface treatment for vulcanized elastomers which produced strong elastomer-to-elastomer bonds with a range of elastomers using a polyamide-cured epoxy adhesive. We concluded that chlorination of vulcanized elastomer surfaces with an organic chlorine donor, trichloroisocyanuric acid, produced strong, durable bonds with a simple epoxy adhesive. This paper complements that study by investigating the treatment that should be applied to steel surfaces to produce good elastomer-to-steel bonds which survive well in the marine environment.

---

\*One of a Collection of papers honoring John D. Venables, the recipient in February 1991 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

## EXPERIMENTAL

### Vulcanized Elastomers

The vulcanized elastomers used were prepared to the same formulations as in the previous paper.<sup>3</sup> They comprised bromobutyl rubber (ASTM designation—BIIR), natural rubber (NR), acrylonitrile-butadiene rubber, commonly known as nitrile rubber (NBR), and styrene-butadiene rubber (SBR). Each contained 70 parts by weight per hundred parts of rubber (phr) of N550 carbon black and the necessary antioxidants and compounding ingredients to produce good quality engineering vulcanizates.

### Vulcanizate Preparation

Compounding was performed in an internal mixer (200 mL effective capacity) and curing agents were added on a laboratory two roll mill (200 mm × 75 mm). The curing characteristics of each formulation were determined on a modified Monsanto LSD Rheometer and test sheets were moulded in a single cavity mould (250 mm × 250 mm × 6.35 mm) in an electrically heated press at 160°C for the time taken to reach 90 percent of the maximum torque measured in the Rheometer.

### Elastomer Surface Treatment

*Cyclisation*—the vulcanizate was immersed in concentrated sulfuric acid for one to two minutes then rinsed in distilled water and allowed to dry. The surface was flexed before bonding to induce the formation of fine cracks in the hardened surface layer. *Chlorination*—the vulcanizate surface was wiped successively with clean paper tissues moistened in ethyl acetate, trichloroisocyanuric acid (TCICA) in ethyl acetate (3% w/w) and finally acetone. The surface was allowed to dry for at least 4 hours before bonding and the discarded paper tissues soaked in TCICA were dampened with water before disposal to avoid spontaneous combustion as TCICA is a strong oxidizing agent.

### Steel Surface Treatment

Mild steel panels were vapour degreased with trichloroethylene, grit blasted with 60 mesh zircon sand and vapour degreased again. In some cases, as noted later, silanes were applied as 1% solutions in toluene to the panels which were allowed to stand in the laboratory for 24 hours to ensure hydrolysis of the silane. These silanes were: mercapto-functional,  $\gamma$ -mercaptopropyltrimethoxysilane, A-189, Union Carbide; amino-functional, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, Z-6020, Dow Corning; and epoxy-functional,  $\gamma$ -glycidoxypropyltrimethoxysilane, Z-6040, Dow Corning. In some cases, as also noted, a two-part epoxy primer, Epirez 123, Epirez Australia, was applied to the steel surface and allowed to cure.

### Adhesives

The following adhesives were used. Ingredients are expressed in parts by weight in parentheses, the supplier is shown for the first occurrence of the trade name, part (i) contains the epoxy resin and part (ii) contains the curing agents in each case.

Adhesive A—part (i), Epikote 828 (100), Epirez Australia; part (ii), Versamid 125 (100), A. C. Hatrick.

Adhesive B—part (i), Epikote 828 (100), epoxy-functional silane (2); part (ii), Versamid 125 (100).

Adhesive C—part (i), Araldite LC 139 (100), Ciba-Geigy; part (ii), Araldite LC 139 (100).

Adhesive D—part (i), Araldite K 273 (100); part (ii), Araldite K 273 (100).

Adhesive E—part (i), Araldite GY 250 (100), epoxy-functional silane (15); part (ii), Araldite LC 136 (64).

Adhesive F—part (i), Epikote 828 (100), silica filler, Aerosil 200 (8), Degussa, epoxy-functional silane, (2); part (ii), Ancamine MCA (55), Anchor Chemical, flexibilizer, LP3 polysulfide (50), Thiokol.

Adhesive G—part (i), Epikote 828 (100), silica filler, Aerosil 200 (8), epoxy-functional silane (2); part (ii), Ancamine TL (60), flexibilizer, LP3 polysulfide (50).

Adhesive H—part (i), Epikote 828 (100), silica filler, Aerosil 200 (8), epoxy-functional silane (2); part (ii), Ancamide 502 (20), Ancamine K 54 (5), flexibilizer, LP3 polysulfide (50).

### Peel Specimens

A bead of adhesive was applied to the long axis of a treated steel panel (150 mm × 75 mm × 2 mm) and a suitably treated elastomer strip (100 mm × 25 mm × 6.35 mm) was placed over the adhesive. An unbonded area (25 mm × 25 mm) was created at one end of the elastomer strip by masking with tape. A rectangular steel bar weighing about 500 g was placed on each specimen which was then allowed to stand at 20°C for at least 96 hours before testing. Adhesive thickness was typically about 0.125 mm and was assumed to be the same for all specimens. Specimens immersed in seawater were stored in screw capped glass jars in an oven at the desired temperature.

### NBR Specimens

A series of NBR specimens was prepared by bonding sheets of NBR, (150 mm × 75 mm × 6.35 mm) to cover completely each surface of prepared steel panels (150 mm × 75 mm × 2 mm). In addition to the epoxy primer, a chlorinated rubber primer, Bostik 9252, Bostik Ltd., and a metal primer, Chemlok 205, Lord Corp., normally used with vulcanization bonding systems were used. A polychloroprene (CR) “contact” adhesive, Boscoprene 2402, Bostik Ltd., normally used with the chlorinated rubber primer was evaluated as well.

### **Rotor Specimens**

NR slabs, (120 mm × 100 mm × 6.35 mm) were chlorinated and bonded to the convex primed surface of curved mild steel panels (150 mm × 150 mm × 2 mm, radius of curvature 0.6 m) with the desired adhesive. The panels were mounted on the outer vertical surface of a cylindrical rotor 1.2 m in diameter which was located in a large circular steel tank through which seawater was pumped at a rate of approximately 50 tonnes per day. The rotor facility was situated at HMA Dockyard, Williamstown, Victoria and seawater was pumped from the adjacent Hobsons Bay. The substantial pumping rate prevented the temperature of the seawater from rising above ambient when the rotor was in operation. The rotor was driven by a 15 kW geared electric motor so that the peripheral velocity of the rotor, at the surface where the panels were mounted, was about 20 knots. The inside surface of the tank was fitted with baffles to prevent the seawater in the tank rotating freely with the samples.

### **Marine Immersion Panels**

A NR slab, (250 mm × 125 mm × 6.35 mm) was chlorinated and bonded to one face of a treated mild steel panel (300 mm × 150 mm × 2 mm). Strips of the same material 2 mm thick were bonded to the same face so as to cover completely the steel surface and project about 10 mm beyond the edge of the panel. A sheet of commercial NBR or CR 2 mm thick was then bonded to the reverse face and to the projecting NR sheet, to form a complete rubber enclosure. Antifouling elastomer panels (125 mm × 125 mm × 2 mm) based on NBR were chlorinated and bonded to the NR slab using adhesive A.

The panels were immersed at a depth of 1 m below a raft at the North Barnard Islands, Queensland. The immersion site (17° 40'S, 146° 11'E) had an annual salinity range of 28 to 35.3 parts of sodium chloride per thousand and average annual seawater temperature range at a depth of 1 m of 23° to 31°C.

### **Peel Strength**

The elastomer adherends were trimmed to a width of 19 mm with a parallel bladed cutter and the mean force required to peel the adherend at an angle of 90° from the substrate was measured on an Instron 1026 tensile testing machine at a crosshead speed of 50 mm/min. A jig was used to ensure that the angle of peel remained at 90° throughout the measurements. Specimens which had been immersed in seawater were removed, the surface water was blotted off and the specimen was allowed to stand at 20°C for 48 hours before testing.

## **RESULTS AND DISCUSSION**

### **Elastomer to Steel Adhesion**

The increasing use of adhesively bonded structures in the aerospace industry has generated many reports<sup>4,5,6</sup> on the durability of such bonds. These studies, although

concentrating primarily on aircraft materials such as aluminum alloys, have also included some work on steel substrates. The durability in seawater of elastomer-to-metal bonds produced during vulcanization of the elastomer has also been reported.<sup>7</sup>

The aim of the present work was to establish the principles involved in producing durable bonds between vulcanized elastomers and steel surfaces using ambient temperature curing adhesives. A major objective was to determine how candidate adhesive systems performed during marine immersion over a period of years in tropical waters.

The variables studied were: elastomer type and surface treatment, steel surface treatment, adhesive formulation, and test specimen exposure conditions. The criterion for good bonding which was adopted was that failure should occur cohesively within the elastomer adherend, commonly referred to as rubber tear. Variations in measured peel strength of between 20 to 50 percent from the mean value have been noted by Cutts<sup>8</sup> as being typical for rubber-to-metal bonds. Hence the ability of an adhesive system to produce cohesive failure or rubber tear was regarded as more important than the absolute value of the peel strength. Cohesive failure in all the elastomers gave peel strengths in the range 5–22 kN/m whereas adhesive failures were in the range 0.2–2 kN/m. The locus of failure, rather than the absolute value of the peel strength, was therefore used in assessing the effects of the variables studied.

### **Elastomer Type and Surface Treatment**

Our previous work<sup>3</sup> showed that epoxy adhesive A had good water resistance and flexibility. Bonds between elastomeric adherends using such a system retained a large proportion of their bond strength even after 12 months immersion in seawater at 60°C provided that the adherends had been chlorinated before bonding.<sup>3</sup> This adhesive was used to prepare peel specimens from steel panels and four different elastomers, NR, BIIR, NBR and SBR. The elastomers used were typical of practical vulcanizates and moderate changes in compounding ingredients such as type and amount of carbon black or type of antioxidant would not be expected to lead to a different type of bond failure. Two different elastomer surface treatments were used on each elastomer, cyclisation or chlorination, and the adhesive was applied either directly to the grit blasted surface or over the epoxy primer. Additional specimens were prepared using adhesive B, which contained 1% of epoxy-functional silane, applied directly to the grit blasted steel surface. Peel tests were performed both before and after immersion of the specimens in seawater at 60°C for 1 month, thus producing a total of 48 different combinations. The elevated temperature immersion was intended to provide some assistance in ranking the durability of various surface treatments or adhesive systems. Peel tests, although particularly demanding, were seen as being relevant to the practical situation of elastomeric coatings bonded to submarine hulls.

The results, Table I, were similar to those for elastomer-to-elastomer adhesion,<sup>3</sup> with NR, NBR and SBR responding well to both cyclisation and chlorination. In contrast BIIR was only satisfactorily bonded after chlorination. The addition of

TABLE I  
Effect of elastomer type, elastomer surface treatment, and steel surface treatment

Elastomer type	Elastomer <sup>b</sup> surface treatment	Failure Locus <sup>a</sup>					
		Treatment on grit blasted steel surface/Adhesive used					
		Nil/A		Nil/B		Epoxy primer/A	
		Before <sup>c</sup>	After	Before	After	Before	After
NR	Cy	C	C	C	C	C	C
	Ch	C	A/S	C	C	C	C
BIIR	Cy	A/E		A/E		A/E	
	Ch	C	C	A/E	C	C	C
NBR	Cy	C	C	C	C	C	C
	Ch	C	A/S	C	C	C	C
SBR	Cy	C	A/S	C	A/S	C	C
	Ch	C	A/S	C	C	C	C

<sup>a</sup>Failure locus—C cohesive in elastomer, A/S between adhesive and steel, A/E between adhesive and elastomer.

<sup>b</sup>Cy—cyclisation, Ch—chlorination.

<sup>c</sup>Before and after immersion in seawater at 60°C for 1 month.

epoxy-functional silane to the adhesive, or an epoxy primer on the steel, was beneficial to durability. Epoxy-functional silanes had previously been found to increase the durability of bonds between epoxy adhesives and steel substrates.<sup>9</sup> All subsequent adherends were chlorinated, as described in the experimental section, as this was a generally applicable, simple and effective elastomer surface treatment. The epoxy primer was seen as a practical method to protect the freshly grit blasted steel surface until such time as the adhesive was subsequently applied. In a shipyard it may not always be possible to bond the rubber immediately to a freshly prepared surface, hence the use of a protective primer increases the flexibility of operations.

### Effect of Silanes

Three silanes with mercapto-, amino- or epoxy-functionality were applied as 1% solutions in toluene to grit blasted steel panels which were then allowed to stand in the laboratory for 24 hours to hydrolyse the silane. NR strips were then either bonded directly to the treated surface or bonded to the epoxy primer coated on to the treated surface. After immersion in seawater at 60°C for 1 month the adherends were either peeled without trimming or were trimmed to 19 mm width before peeling. Preliminary work had suggested that the act of trimming the 25 mm wide adherends sometimes produced cracks in the adhesive or primer which appeared to produce lower peel strengths. The only case where this occurred in this series was for those specimens with epoxy-functional silane and no epoxy primer, where rubber tear occurred for the untrimmed panels as opposed to adhesive/steel failure for the trimmed specimens, as shown in Table II. After immersion, failure at the adhesive/steel interface was observed for those specimens where the adhesive was applied directly over the mercapto- or amino-functional silane, whereas the specimens with adhesive directly over epoxy-functional silane or with epoxy primer over

TABLE II  
Effect of silane type on failure locus for NR/steel bonds

Silane on steel surface	Failure Locus <sup>a</sup>		
	Before <sup>b</sup>	After Immersion	
Mercapto-	A/S	A/S	(A/S)
Amino-	C	A/S	(A/S)
Epoxy-	C	C	(A/S)
Mercapto- + Epoxy primer	P/S	C	(C)
Amino- + Epoxy primer	C	C	(C)
Epoxy- + Epoxy primer	C	P/S	(P/S)

<sup>a</sup>Failure locus—C cohesive in elastomer, A/S between adhesive and steel, P/S between primer and steel, ( ) trimmed specimen.

<sup>b</sup>Before and after immersion in seawater at 60°C for 1 month.

the mercapto- or amino-functional silane retained strong elastomer tearing bonds. Use of epoxy-functional silane under the epoxy primer resulted in failure at the primer/steel interface after immersion.

### NBR Specimens

These test specimens consisted of NBR sheets, 6.35 mm thick, bonded all over both faces of the steel substrate so that only the edges of the steel panel were left exposed. Specimens were peeled after immersion in seawater at 60°C for 15 months or at 25°C for 39 months. The best performance was for adhesive A bonded to the epoxy primer, which gave rubber tearing bonds together with no corrosion of the steel substrate after either ageing period. A similar specimen with adhesive B, bonded to epoxy primer, showed rubber tear after 15 months at 60°C but primer/steel failure after 39 months at 25°C. Specimens prepared with either adhesive A or adhesive B, bonded to steel to which epoxy-functional silane had been applied gave adhesive/steel failures after both exposure periods.

Specimens prepared with either adhesives A or the CR adhesive to bond the NBR adherend to either a chlorinated rubber primer or a metal primer, identified in the Experimental section, all displayed cohesive primer failure when peeled after both immersion periods. There was no corrosion of the steel substrate in any of these specimens, even those which displayed cohesive failure in the primer or primer/steel failure when peeled.

### Marine Immersion Panels

A series of three different steel panels with all surfaces protected by bonded elastomer was immersed in tropical waters off North Queensland. One of each type of panel was withdrawn and tested after 1, 2 and 3 years. At the time the panels were prepared, the most promising system comprised an epoxy primer applied to the steel in conjunction with adhesive A used to bond the elastomeric adherends. This system performed better over three years immersion than alternative ones based on a chlorinated rubber primer on the steel and adhesive A or CR adhesive used to



bond the elastomer. Cohesive elastomer failure was found for the NR bonded to epoxy primer using adhesive A for panels immersed for 1, 2, and 3 years, whereas those panels with chlorinated rubber primer showed cohesive primer failure when epoxy adhesive A was used or adhesive/rubber failure when CR adhesive was used.

Antifouling elastomer sheets 2 mm thick, consisting of peroxide cured NBR containing tri-n-butyltin acrylate,<sup>10</sup> had been bonded to the exposed surfaces of the NR sheets to prevent growth of marine organisms during the immersion trial. The antifouling sheets showed cohesive failure when peeling from the underlying NR panel was attempted, even after 3 years' immersion, confirming the ability of adhesive A to resist the effects of marine immersion. The antifouling elastomer successfully prevented growth of barnacles and other macrofouling during the three years of the trial.

Kinloch<sup>5</sup> discussed the locus of failure in steel/epoxy/steel joints immersed in water where diffusion of water could occur along the bondline. The thermodynamic work of adhesion for an epoxy/steel interface changed from a large positive value in dry air to a large negative value when the interface was in water, which induced displacement of the adhesive from the steel surface by water. The effect was thus one of progressive encroachment of water into the joint with a change in failure mode from cohesive in the epoxy to interfacial failure at the steel surface. The rate of progression of the interfacial failure front was shown<sup>4</sup> to be approximately linear with time and to depend upon temperature with an activation energy of 32 kJ/mol.

When the elastomer was peeled from the marine immersion panels, water was found in the pocket around the edge of the panels due to incomplete bonding of the elastomer which overlapped the front and back of the panels and an area of interfacial failure between the epoxy primer and the steel substrate was observed progressing in from the edges of the panels. Under the 6.35 mm thick NR the distance of interfacial failure was found to be approximately 10, 20 and 30 mm in from the edges after 1, 2 and 3 years' immersion respectively, whereas under the 2 mm thick NBR on the rear face the corresponding distances were 30, 55 and 45 mm. The steel surfaces where interfacial failure had occurred were not corroded, even on the specimen immersed for 3 years.

The significance of this result is that it confirms that edge effects are important in underwater applications of bonded elastomers. If a structure can be designed to have no exposed underwater bond lines it would be expected to have a long lifetime, provided diffusion of water through the elastomer adherend was low. None of the panels, including those which were found to have very low peel strengths, showed lifting of the NR adherends even after 3 years' immersion. This reinforces the view that peel tests are a very severe way of evaluating bonding. A system which consistently performs well in peel testing would be expected to give excellent durability in the field, however, systems with apparently poor peel strength may in fact behave adequately in service, provided that they are not subjected to stress.

### **Rotor Panels**

This trial was intended to determine if water flow across a bonded elastomeric panel was likely to exacerbate adhesion problems. The bonded NR adherends, (120

mm × 100 mm × 6.35 mm thick), were not faired so that the leading edge would experience a significant hydrodynamic force which would tend to cause lifting of the adherend. The rotor facility<sup>11</sup> was designed to study the performance of underwater paints under dynamic flow conditions equivalent to a vessel speed of about 20 knots. The panels were attached to the rotor and immersed in seawater for a period of 22 months during which time the rotor was operating for a total of 507 days. This would be equivalent to a distance travelled at 20 knots of about 243,360 nautical miles (450,000 km) or roughly ten times around the world. None of the elastomer adherends became detached over this period and the best system, consisting of epoxy primer and adhesive A, showed no corrosion of the underlying steel substrate with mostly primer/steel failure and a small central area of rubber tear when the NR panel was peeled off. The measured peel strengths were all low (0.5–1 kN/m) as the failures were mostly interfacial at the steel surface, however the elastomer had not become detached in any case.

Slight corrosion, especially at the corners, was found under the NR panel after peeling a specimen which had epoxy-functional silane applied to the grit blasted steel under adhesive A. A similar result, with some pitting at the corners, was observed for a specimen with epoxy-functional silane on the steel under adhesive B, with the locus of failure being at the steel surface in both cases. Panels with the chlorinated rubber primer showed slight corrosion under the NR panel for both adhesive A and the CR adhesive and failure was at the primer/steel interface. A panel with the metal primer and adhesive A gave a similar result.

The flow of water across the panels was sufficient to cause significant erosion of the leading edge of the NR adherend and considerable erosion and corrosion of the steel panel where it was not protected by the elastomer. An earlier trial using commercial paint primers under adhesively bonded NR had resulted in rapid detachment of the elastomer due to cohesive primer failure.

Results from the rotor trial complemented those from the marine immersion under a moored raft, with a system consisting of the epoxy primer on the steel and adhesive A to bond the elastomer performing satisfactorily in both cases.

### Alternative Adhesive Systems

The polyamide-cured epoxy adhesive A used extensively in this work had been chosen on the basis of its simplicity and no attempt had been made to optimise the adhesive formulation. When dealing with the rough surfaces encountered on submarine hulls a thickened adhesive with gap-filling properties would have practical advantages. A series of specimens was prepared with NR adherends using thickened adhesives C to H, which included two commercial two-part systems C and D and others, E–H, which were based on systems reported as being particularly useful for underwater repairs to steel structures.<sup>12</sup> Epoxy-functional silane was incorporated into adhesives E (8.4%), F (0.9%), G (0.9%) and H (1.1%). The amounts of silane used were as suggested,<sup>12</sup> and it was of interest to see if the large amounts present in adhesive E would have any deleterious effect as the other amounts are more typical of general practice. These adhesives all produced rubber tearing bonds between steel and NR which retained their strength and locus of

failure on immersion in distilled water at 60°C for up to 200 days and which performed equally well bonded directly to grit blasted steel or to epoxy primer. The use of epoxy-functional silane on the steel under the epoxy primer did not confer any additional benefit and, in fact, produced steel/primer failure for adhesive E which contained the large amount of epoxy-functional silane. This was the only specimen which did not fail cohesively in the elastomer. Specimens using the two commercial adhesives, C and D, over epoxy primer, which were immersed for 1500 days (4.1 years) in distilled water at 60°C, still produced rubber tear when peeled after this time.

## CONCLUSIONS

The durability of epoxy adhesive bonds between steel substrates and vulcanized elastomers depends largely on preventing access of water to the adhesive bondline. The most promising systems, for use where the bonded elastomer would be immersed in seawater for long periods of time, consist of an epoxy primer on the steel, chlorination of the vulcanized elastomer surface and an epoxy adhesive with a water resistant curing system. Diffusion of water along the steel/epoxy interface produces progressive interfacial failure which can only be retarded in a practical situation by designing to minimise the occurrence of exposed bondlines. Bonding rubber cover strips over bondlines should be beneficial as bonds between two rubber surfaces appear to be resistant to the effects of marine immersion.

Corrosion of mild steel panels immersed in tropical seawater for three years was completely prevented by bonding a 6.35 mm thick NR sheet to the steel using an epoxy adhesive over an epoxy primer on the steel surface. This adhesive/primer system also performed well under dynamic seawater flow conditions, achieving an equivalent distance of 450,000 km at 20 knots without bond failure.

## Acknowledgments

Thanks are due to B. E. Woods, M. Troy and M. Cutler for experimental assistance and to P. J. Jackson, R. Zugno and A. Camilleri for compounding, moulding and testing the elastomers.

## References

1. *Jane's Defence Weekly*, 765 (1987).
2. *Jane's Defence Weekly*, 18 (1989).
3. D. Oldfield and T. E. F. Symes, *J. Adhesion*, **16**, 77 (1983).
4. R. A. Gledhill and A. J. Kinloch, *J. Adhesion*, **6**, 315 (1974).
5. A. J. Kinloch, *J. Adhesion*, **10**, 193 (1979).
6. J. Comyn, D. M. Brewis, R. J. A. Shalash and J. L. Tegg, in *Adhesion 3*, K. W. Allen, Ed. (Applied Science, London, 1979), p. 13.
7. A. Stevenson, *Int. J. Adhesion and Adhesives*, **5**, 81 (1985).
8. E. Cutts, in *Developments in Adhesives-2*, A. J. Kinloch, Ed. (Applied Science, London, 1981), Chap. 10.
9. M. Gettings and A. J. Kinloch, *J. Mat. Sci.*, **12**, 2511 (1977).
10. P. Dunn and D. Oldfield, *Rubber Industry*, **9**, 34 (1975).
11. J. H. Bishop, *Oil Col. Chem. Assoc. Proc. News*, **19**, (12) 81 (1985).
12. M. R. Bowditch, *British Patent*, 1598431 (1981).