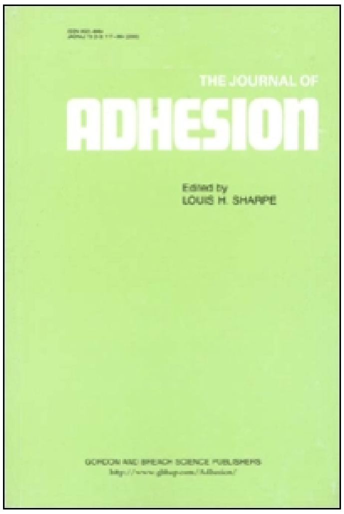

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Bonding of Natural Rubber to Steel: Surface Roughness and Interlayer Structure*

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This paper is concerned with two aspects of the adhesion produced by the vulcanisation bonding of a simple natural rubber (N.R.) compound to mild steel. Adhesion was measured using a 45° peel test.

When the N.R. was bonded, using a proprietary bonding agent (Chemlok 205/220), to "smooth" steel (acid etched) or to "rough" steel (phosphated) high values of peel energy ($\geq 4.5\,\mathrm{kJm^{-2}}$), and good environmental resistance to water were obtained, with failure cohesive largely within the rubber. The highest values of peel energy ($\approx 7.5\,\mathrm{kJm^{-2}}$) were associated with a phosphated surface which consisted of plate-like crystals which directed the stresses away from the substrate in a way which produced a failure surface within the rubber which showed extensive tearing and cracking.

The nature of the layer formed in the interfacial region by interaction between bonding system and rubber was investigated using a chlorinated rubber as a "model compound" representing the adhesive and uncompounded N.R. to represent the rubber. When a blend of the two was heated in air at 150°C, evidence was found of a solid state chemical reaction in which carbonyl groups were incorporated into the blend which became visually homogeneous. Further evidence points to the relevance of this change to adhesion in rubber-to-metal bonding.

Keywords: Rubber-to-metal bonding; peel test; surface roughness; phosphating

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*One of a Collection of papers honoring F. James Boerio, the recipient in February, 1999 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

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INTRODUCTION

A significant stimulus to the study of adhesion is that it provides the combination of interesting scientific challenges with work of undoubted practical relevance. A good example of this is the study of rubber bonding. Rubber is an important and engineering material, the range of application of which can be extended by bonding it to other materials. Bonding of rubber to metal is essential in applications in civil engineering such as bridge bearings, and in the automobile industry in engine mounts and suspension units [1, 2]. This is an area, along with many others, to which Jim Boerio has made significant contributions. He has made studies of commercial rubber bonding systems and has recently developed new primer systems for rubber bonding based on plasma-polymerised acetylene [3–5]. It may be appropriate, then, that this paper which addresses some fundamental aspects of adhesion *via* a study of rubber-to-metal bonding should form a part of a collection of papers honouring Jim Boerio.

A widely-used rubber-to-metal bonding technique is "in vulcanisation" bonding [6]. Here the metal is pretreated, typically by degreasing and phosphating or grit blasting, prior to the application of a primer layer, followed by an adhesive layer. The metal is then inserted in an appropriate mould and the rubber compound is moulded around it and heated to vulcanise *in situ*. Although this is a viable technological process, many theoretical aspects of its mode of action are not well-understood [7, 8]. For example, how critical is the roughness of the substrate surface for obtaining good bonding? do interdiffusion and chemical interaction between the bonding agent layers and the rubber play an essential rôle in adhesion?

The influence of roughness and of interdiffusion on adhesion are subjects of wide relevance within contemporary research in adhesion science [9–13] and their study within the context of rubber-to-metal bonding might be expected to throw light onto the broader field. In this paper, work will be discussed which relates adhesion to (i) the influence of surface topography and (ii) the nature of the polymer layer formed at the substrate interface. The context of the investigation is that of typical rubber to metal bonding procedures.

Influence of Substrate Topography

Mild steel with different surface pretreatments was chosen, and a commercial bonding system was applied to its surface. Adhesion specimens were made by injection moulding a simple natural rubber compound against prepared steel sheets and curing *in situ*.

Most pretreatments commercially used for steel prior to in vulcanisation bonding involve surface roughening by grit blasting or phosphating. The surfaces produced by both methods vary enormously, according to the operating parameters chosen [14–19]. In this work we contrasted the effects of two different phosphating processes, which produced rough coatings of different composition and topography [20], with that of a simple acid etch producing a relatively smooth surface.

Measurement of Adhesion

The peel test was selected for measurement of adhesion, as it gives an adhesion fracture energy which can, in principle, be analysed into component energies associated with different energy loss processes, giving an insight into different mechanisms contributing to the overall adhesion [7, 21]. After peeling, the fracture surfaces are in convenient form for analysis by microscopy and surface analytical techniques.

A simple energy balance analysis shows that for peeling a flexible strip (width b, thickness h) at an angle, θ, from a rigid substrate the force applied, F, is related to the peel energy (per unit area), P, by

$$P = (F/b)\ (\lambda - \cos\theta) - W_\lambda h \qquad (1)$$

where λ is the extension ratio (extended length/original length) of the freed strip, and W_λ is the strain energy density (strain energy per unit volume) expended in stretching the freed strip, whether elastically or plastically, to extension ratio λ [21, 22].

Peel tests were conducted over a range of rates and angles. As the peel angle is increased, the calculated peel energy, for a standard substrate, increased from 5 kJm^{-2} at 30° to 30 kJm^{-2} at 90° [23]. The failure mode was in all cases cohesive within the rubber. At 90°

there were noticeable ridges on the surface perpendicular to the peel direction and a marked tearing back into the rubber tab [24, 25]. The peel trace exhibited slip-stick behaviour which could be correlated with the failure pattern observed. At low peel angles, however, a smooth, thin rubber layer was left on the substrate, and the peel load was relatively steady. For these reasons we have adopted a 45° peel angle as standard for the work reported in this paper.

The Nature of the Layer Formed in the Interfacial Region

An important aspect of the bonding process is the interaction between a compounded rubber and the adhesive. As Boerio *et al.*, have reported [26], both components of the proprietary bonding system are complex formulations, with chlorinated rubber being a significant component of the adhesive. Because of the complexity of these systems we have undertaken a study of relatively simple model systems in order to try to understand the nature of the changes that occur during rubber-to-metal bonding and their relationship to adhesion. We have, therefore, studied the interaction between masticated natural rubber (N.R.) and chlorinated natural rubber, using microscopy, supplemented by infrared spectroscopy, DSC and NMR.

EXPERIMENTAL DETAILS

Materials

Mild steel – B.S. 6323, pt. 6 CEW 2BK, thickness 3 mm.

Natural rubber: Standard Malaysian Rubber Latex Grade SMR L.

Chemlok 205 and 220 bonding system manufactured by Henkel.

Chlorinated rubber: Pergut S20 (Bayer, M_n $3.9 \times 104\,\mathrm{g\,mol}^{-1}$, polydispersity 1.8).

Rubber Compounds

A simple natural rubber compound was selected for this work, and was prepared in two stages in a laboratory Banbury internal mixer. Further details are given in Ref. [23].

TABLE I Rubber compounds used (Composition expressed as parts by weight)

Ingredient	*Black 1A*	*Delayed cure*
SMR L	100	100
Zinc oxide	5	5
Stearic acid	2	4
N220 carbon black	30	30
Sulphur	1.5	1.5
CBS	1.5	1.5
Vulcatard A	–	10

This compound is designated "Black 1A". Some experiments were done with a similar compound containing a retarding agent to delay the cure. The formulations of both compounds are shown in Table I.

Pretreatment of Steel

The steel was cut into coupons 120 mm long by 40 mm wide. Three different pretreatments were used.

Phosphate 1

This was a commercial phosphating process, undertaken under factory conditions. Its essential features were as follows:

(i) degrease, alkali derust, rinse in cold water, 20°C;
(ii) rinse conditioning stage (deposits titanium compound);
(iii) phosphating bath zinc, nickel and manganese phosphate, nitrate accelerator;
(iv) cold water rinse, hot demineralised water rinse, dry in hot air.

Phosphate 2

This treatment, based on the work of Ong [27], was done in the laboratory.

(i) Degrease in boiling industrial methylated spirit and dry *in vacuo*;
(ii) immerse for 20 min at 65°C to 75°C in a phosphating solution consisting of ZnO (2.25 g,), $NaNO_3$ (2.0 g), 85% phosphoric acid (5 cm^3) and water (330 cm^3);
(iii) immerse in ultrasonic bath of distilled water for 2 minutes;
(iv) wash with water and industrial methylated spirit and dry *in vacuo*.

Acid etch

(i) Degrease in 1,1,1-trichloroethane;
(ii) immerse for 30 sec in 6M hydrochloric acid, prepared by diluting the concentrated acid (12M) with an equal volume of water;
(iii) rinse in distilled water, dry on Whatman's No.1 filter paper.

Bonding of Rubber

The peel test pieces were prepared by compression moulding.

First the Chemlok 205 and 220 bonding system was applied by painting onto the pretreated steel surface. The test pieces were placed in the mould at 150°C and the rubber compound was moulded against the steel surface under a load of 50 tons on a 11 inch diameter ram. The compound was cured at 150°C for 20 min.: this was equivalent to the time measured on a Monsanto MDR2000E rheometer for the rubber to reach its optimum state of cure (T_{MAX}). Further details are given in Ref. [23].

Peel Testing

The peel tests [23] were carried out on an Instron 1122 test machine at a crosshead speed of 50 mm/min. with a peel angle of 45°.

The extension ratio and the strain energy density required for Eq. (1) were determined from auxiliary tensile tests in which stress and extension ratio were measured.

Characterisation of Materials and Failure Surfaces

A range of physical techniques were used. Details of the apparatus are given.

SEM/EPMA: Jeol 6310.
XPS: Vacuum Generators ESCA Lab Mark II.
XRD: Philips PW2273/20 X-ray tube used with Philips PW1877 PC-APD version 3.5b diffraction software.
IR: Perkin Elmer 1710.

NATURE OF STEEL SURFACES AND OF THE BONDING AGENT

The two principal topics of this paper are the influence on adhesion of (i) substrate surface roughness and (ii) the interaction of the bonding agent with the rubber. Before these can be discussed it is necessary to discuss the characteristics of the surfaces produced and of the bonding agents employed.

Characterisation of Pretreated Steel Surfaces

Phosphated Steel

Phosphating of steel produces a range of different compounds with different chemical nature and physical form according to the conditions employed [19]. Two phosphates which are often present are phosphophyllite, $Zn_2Fe(PO_4)_2 \cdot 4H_2O$, and hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$. Manganese may also be incorporated as $Zn_2(Fe,Mn)(PO_4)_2 \cdot 4H_2O$. In order to establish which chemical compounds were produced, the surfaces were characterisation by XPS and X-ray diffraction, supplemented by reflection-absorption infra-red spectroscopy. Table II and Figures 1 and 2 compare the results with what would be expected from phosphophyllite and hopeite. The topography was studied by scanning electron microscopy (Figs. 3(a) and (b)).

The commercially-produced *Phosphate 1* is complex. The presence of phosphophyllite as a major component is indicated is indicated by the X-ray diffraction pattern, but the XPS showed some manganese to

TABLE II X-ray photoelectron spectroscopy of phosphated steels

	Elemental ratio measured			
	Zn/P	*O/P*	*Fe/Zn*	*C/O*
Found				
*Phosphate 1	0.2	4.1	4	0.2
Phosphate 2	1.7	5.7	0.1	0.5
Expected				
Phosphophyllite $Zn_2Fe(PO_4)_2 \cdot 4H_2O$	1	6	0.5	0
Hopeite – $Zn_3(PO_4)_2 \cdot 4H_2O$	1.5	6		0

* Also some Mn found.

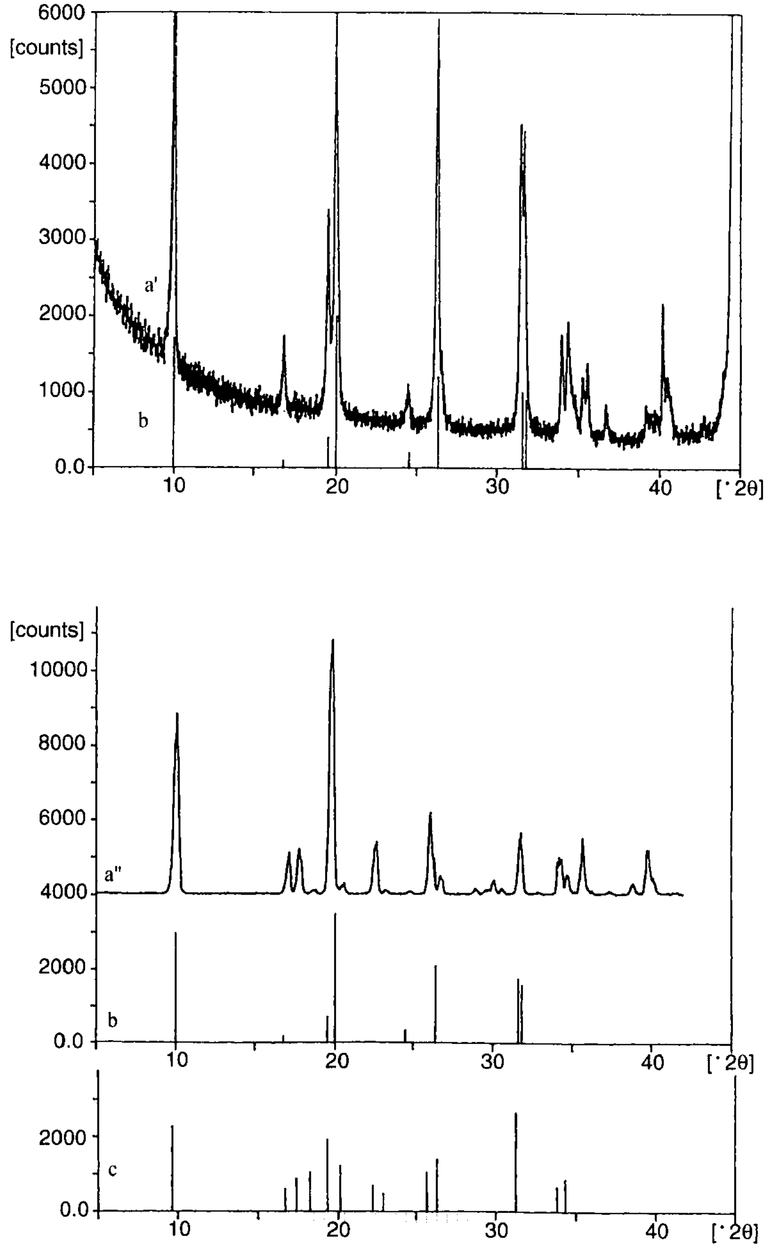

FIGURE 1 X-ray diffraction of phosphated steels: (a′) Phosphate 1, (a″) Phosphate 2, (b) phosphophyllite, (c) hoepite.

be present. This may be in the form of $Zn_2(Fe,Mn)(PO_4)_2 \cdot 4H_2O$ which has a similar X-ray diffraction pattern to phosphophyllite. The appearance in the SEM was of nodular crystals 3 to 5 μm in size.

The results for *Phosphate 2*, produced in the laboratory, are relatively easy to interpret. The surface is mainly hopeite. There is evidence of a small amount of phosphophyllite; the X-ray results suggest about 3%. This treatment produced plate-like crystals with dimensions 20–30 μm.

Acid etch

This treatment produced an oxidised steel. XPS indicated some silicon ($Si/C = 0.05$) and a small amount of chlorine ($Cl/C < 0.01$) in the surface regions. The SEM (Fig. 3(c)) revealed shallow etch pits, but the surface was much less rough than either of the phosphated surfaces.

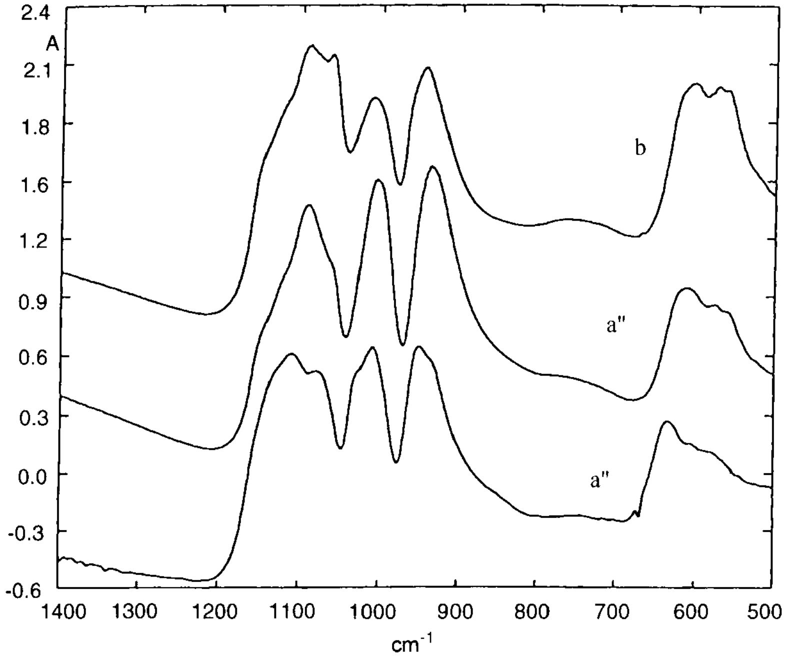

FIGURE 2 Infra-red spectra of phosphated steels (a′) Phosphate 1, (a″) Phosphate 2, (b) $Zn_3(PO_4)_2 \cdot 2H_2O$.

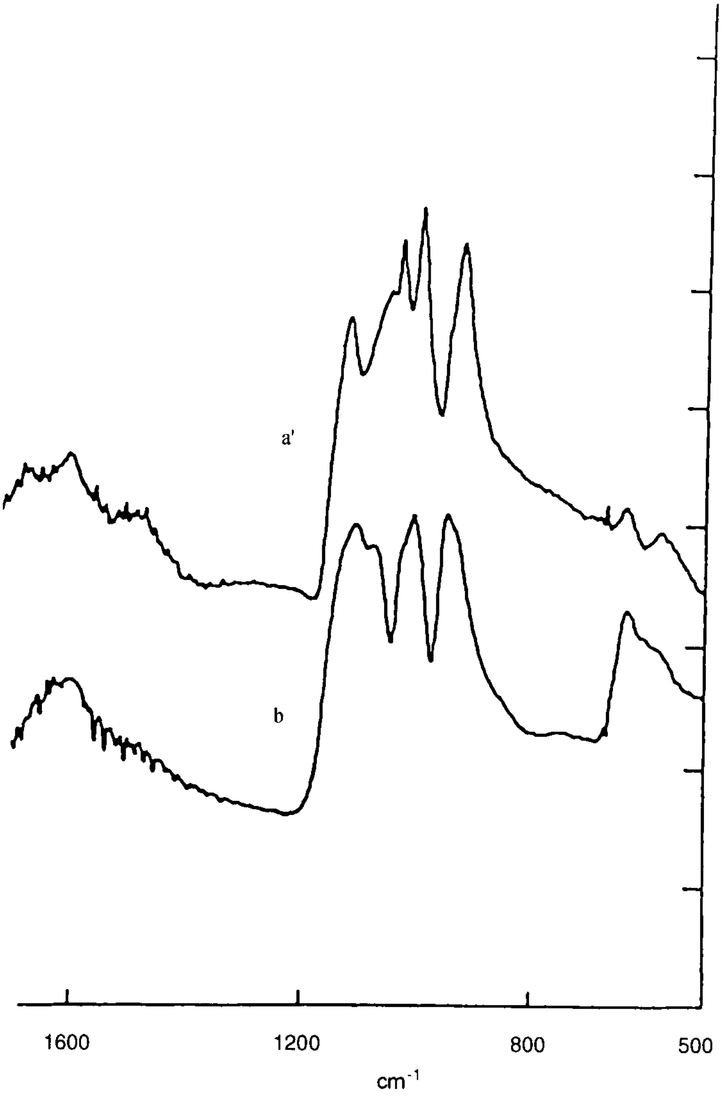

FIGURE 2 (Continued).

Characterisation of Bonding Agent

The composition of the Chemlok 205/220 adhesive system employed in this work is not published by the manufacturer. However, reference to the patent and scientific literature [2, 7, 8, 28–32] suggests that the 205 primer comprises chlorinated rubber (probably chlorinated polyisoprene), epoxy resins and metal oxides (zinc and titanium). The

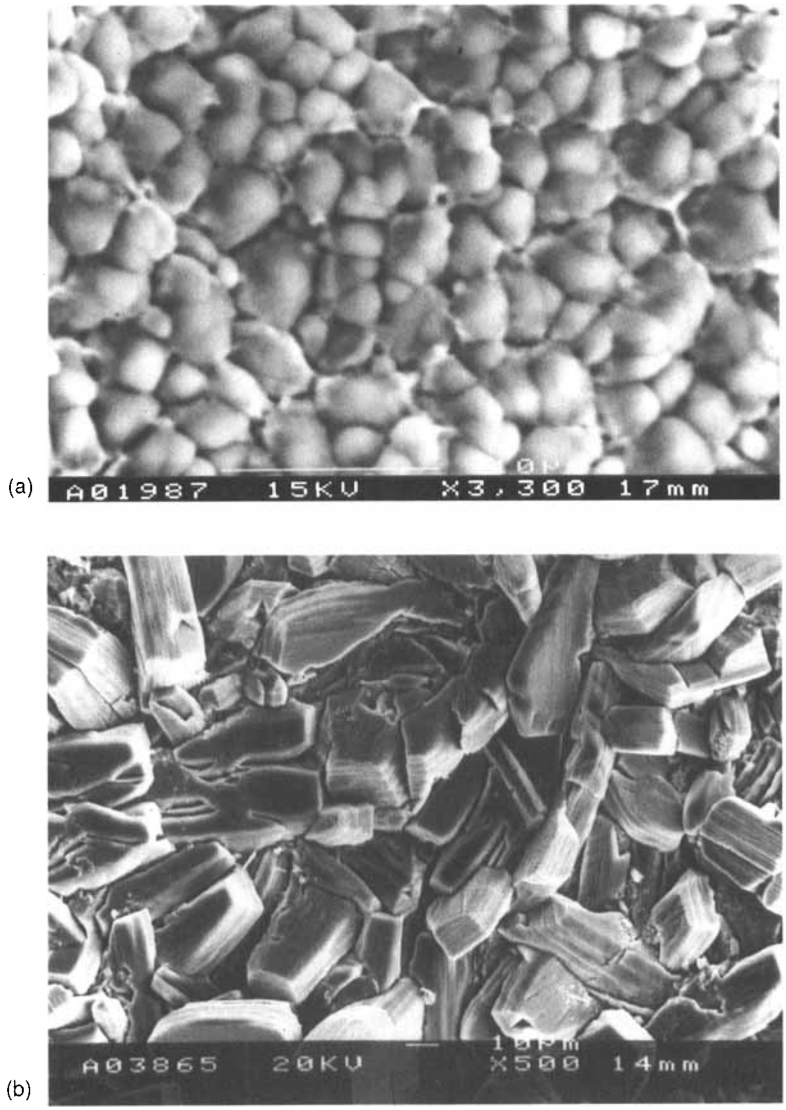

FIGURE 3 Scanning electron micrographs of treated steel surfaces. (a) Phosphate 1, (b) Phosphate 2, (c) Acid etch.

(c)

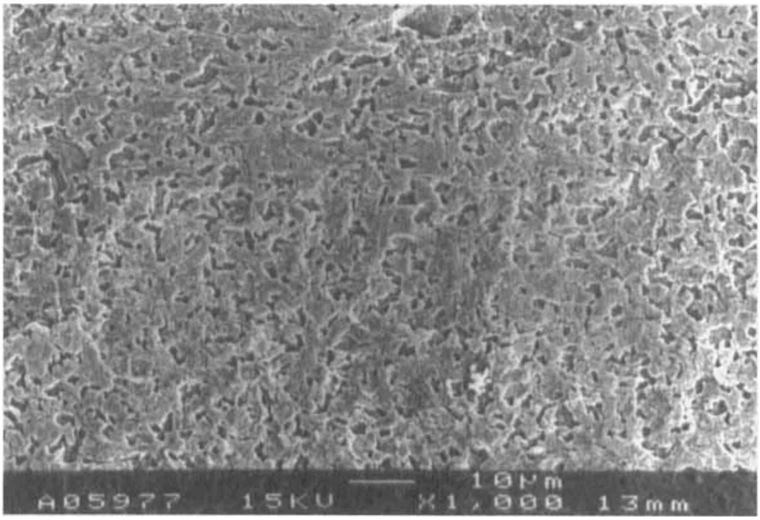

FIGURE 3 (Continued).

TABLE III Summary of the results of analysis of Chemlock 205/220 bonding system

Component	*Composition*	*Experimental techniques*
Primer: Chemlock 205	ZnO, TiO_2, a chlorinated polymer (M_n 1.6×10^5 g mol^{-1}) and an unidentified residue, soluble in alcohol, which contains aromatic and aliphatic functionalities. XPS: C, O, Cl and traces of Na and Zn.	XRD, XPS, EPMA, IR, NMR, GPC.
Adhesive Chemlock 220	Crystalline and amorphous components. Probably chlorinated rubber. Aromatic and aliphatic functionalities. XPS: Br, O, C and Cl.	NMR, XRD, IR, XPS.

220 topcoat (adhesive) may contain chlorinated rubbers, carbon black and a crosslinking agent (sulphur and possibly a dinitroso-containing moiety).

The two components of the adhesive system were investigated by a number of analytical techniques which, broadly speaking, confirmed the indications obtained from the literature. The results are summarised in Table III.

ADHESION TO TREATED STEEL

The peel energies for steel with the three different surface treatments are shown in Table IV. The results are interesting as the adhesion obtained when the elaborate commercial phosphating treatment (Phosphate 1) is used appears no better than that obtained with a simple acid etch. Although the mean peel energy for Phosphate 2 is the highest, the scatter is large and it is not possible to say from these results that differences in surface treatment exert any significant influence on the peel energy.

In many bonding systems surface pretreatment is used, not so much to improve the initial adhesion as to improve the bond durability in a humid environment. Good durability would usually be a requirement for rubber-to-metal bonds in service. A simple water immersion test was, therefore, undertaken. The results (Tab. V) show that all three surface treatments performed well, with little or no deterioration being observed in periods up to two months. Of course, differences might emerge in a more aggressive environment or over longer exposure times. Indeed, a small amount of attack was evident at the edge of one or two of the etched steel samples, suggesting that at longer immersion times the adhesion would fall off.

The obvious conclusion to be drawn from the results of Tables IV and V is that high rubber-to-steel adhesion can be obtained independently of producing a conspicuously rough substrate surface. It would be tempting further to conclude that surface roughness had no influence on the adhesive fracture energy of these bonds. However, a careful examination of the modes of failure, especially for "Phosphate 2", shows that certain differences of surface topography do influence the fracture energy.

TABLE IV Adhesion of natural rubber compound 1A to steel: effect of steel surface pretreatment. Peel energies ($kJ/m^2 \equiv N/mm$); Peel angle 45° and crosshead speed 50 mm/min

Substrate	*No. of peels*	*Peel energy*[#] *kJ/m*^{2}
Acid etched	6	4.93 ± 0
Phosphate 1	4	4.39 ± 0.41
Phosphate 2	4	5.93 ± 2.68

[#] With 95% confidence limits.

TABLE V Adhesion of natural rubber compound 1A to steel: effect of immersion in water at ambient temperature. Peel energies ($kJ/m^2 \equiv N/mm$); Peel angle 45° and crosshead speed 50 mm/min

Immersion time (days)	*No. of peels*	*Peel energy*[#] kJ/m^2
Acid etched		
0	6	4.93 ± 0
7	3	4.99 ± 1.20
15	4	5.39 ± 0.41
21	4	5.38 ± 0.11
58	4	4.99 ± 0.40
Phosphate 1		
0	4	4.39 ± 0.41
14	4	4.39 ± 0.60
38	4	4.35 ± 0.73
Phosphate 2		
0	4	5.93 ± 2.68
45	4	5.62 ± 3.19
46	4	5.33 ± 2.16

[#] With 95% confidence limits.

Modes of Failure

Acid etch and Phosphate 1

The failure surfaces were examined microscopically. The acid-etched steel and Phosphate 1 steel gave broadly similar peel energies and failure morphologies. The failure surfaces were grey-black in colour and smooth to the naked eye, but at 40 x magnification they appeared slightly textured. Failure appeared cohesive within the rubber, some distance (perhaps hundreds of microns) from the substrate surface.

Phosphate 2

It is clear from the results of Table V that there is much wider variability in peel energy for these surfaces. When the individual results are examined, it becomes apparent that the distribution is bimodal, some peel energies being around $4.5\,kJ/m^2$, others much higher around $8\,kJ/m^2$. Moreover, the two groups exhibit different failure modes.

Both peeled surfaces of the samples failing at *lower energy* were speckled in appearance. Under the microscope the substrate showed a grey-black rippled rubber surface, the "specks" consisting of deep holes going down perhaps to the steel itself. In some of the holes phosphate crystals could be seen. The rubber counter-surface was complementary, the "speckles" here being crystals standing proud of the grey rubber surface.

The Phosphate 2 specimens failing at *higher energy* showed a quite different fracture morphology. To the naked eye the surfaces were uniform dark grey-black except that there were a number of thin, light coloured arcs reaching from the edges of the peeled material, in some instances up to quarter of the width peeled, Figure 4. They were convex towards the end at which peeling was started.

Microscopic examination and EPMA showed that the arcs consisted of regions where most of the phosphate coating had been pulled away from the substrate and was standing proud of the surface of the peeled rubber strip to which it was still adhering.

Most of the fracture area of these specimens comprised the areas appearing dark grey to the naked eye. Much of this region consisted of

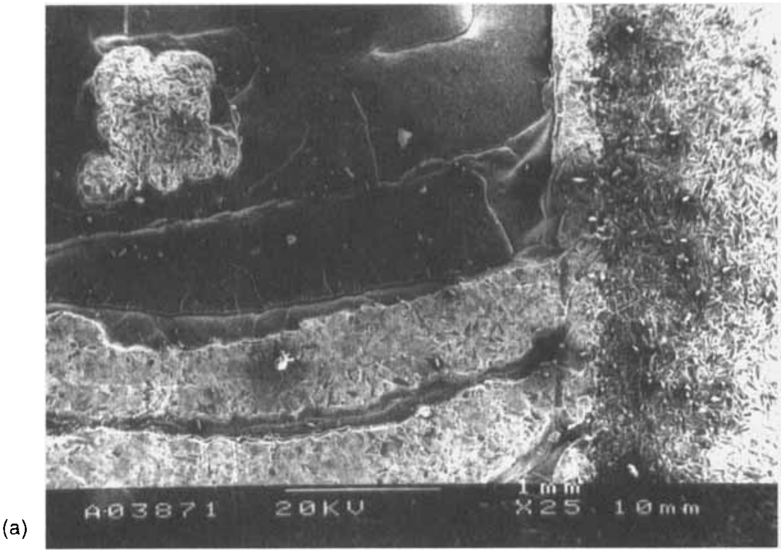

FIGURE 4 Scanning electron micrographs of the surfaces of (a) the substrate and (b) the rubber produced after peeling natural rubber compound 1A from steel with *lower coating weight* "Phosphate 2" treatment. Peel front advances from bottom to top.

(b)

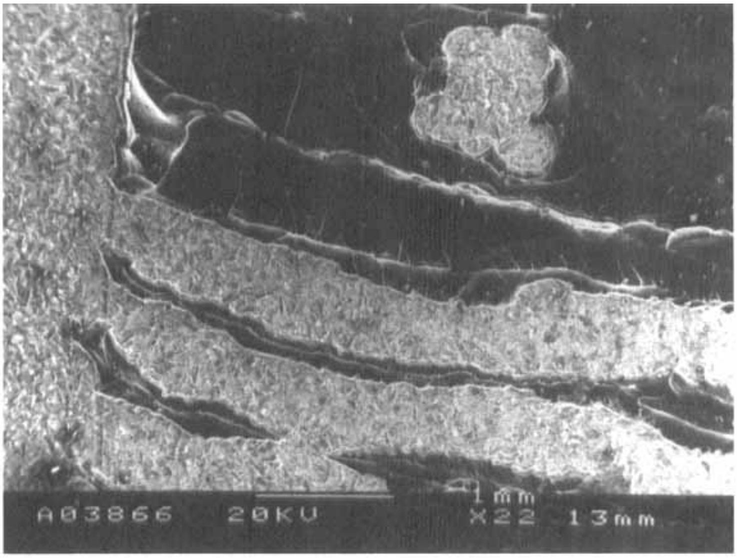

FIGURE 4 (Continued).

a succession of ridges roughly parallel to the peel direction, shown schematically in Figure 5. The ridges were decidedly asymmetrical. On the substrate, the side facing down the direction of peel was nearly vertical; the other side was much less steep. The region in between the ridges was often quite short.

On the peeled rubber strip, complementary features were observed, the previous "inter-ridge" regions now corresponding to plateaux between ridges (Fig. 5). The less-steep ridge gradient now faced down the peel direction. At the roots of the vertical face of the ridges (which faced up towards the start of the peel) were cracks going perpendicularly into the rubber.

Microscopic examination of the phosphated steel itself in areas against which rubber had not been moulded showed that the "speckled" failure surfaces were associated with large phosphate crystals, some platelike sticking up at various angles from the surface. The phosphate crystals on the specimens displaying the arcs were much finer. This distinction is shown by the differences in coating weight between the two types of specimen summarised in Table VI.

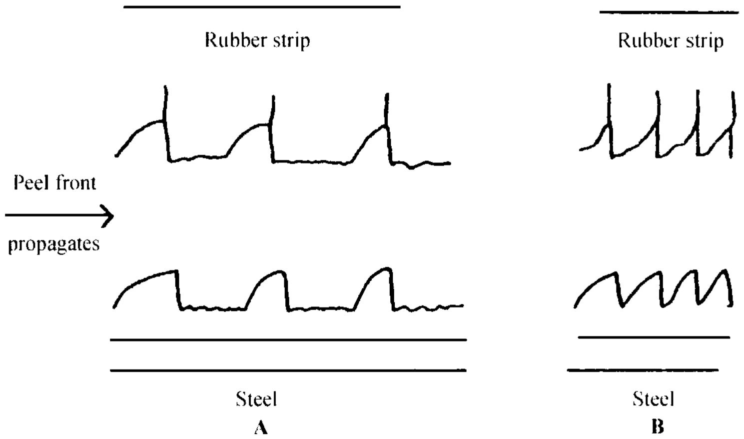

FIGURE 5 Diagram showing the formation of ridges and tears formed on the failure surfaces when peeling rubber from steel with *lower coating weight* "Phosphate 2" treatment. (*Often the inter-ridge distance is small giving B rather than A.*)

TABLE VI Adhesion of natural rubber compound 1A to steel with "Phosphate 2" treatment. Effect of water immersion at ambient temperature classified according to failure mode. (Peel angle 45° and crosshead speed 50 mm/min)

Phosphate coating weight, g/m²	*Peel energy# kJ/m²*	*Failure mode*
No exposure		
16.6	**5.8**	**rubber + short arcs**
25.2	4.54	speckled
18	5.03	speckled
16.5	**8.33**	**rubber + short arcs**
Mean#	5.93 ± 2.68	
45 days in water		
25.4	5.08	speckled
21.4	4.21	speckled
12.2	**8.58**	**rubber + short arcs**
25.3	4.62	speckled
Mean#	5.62 ± 3.19	
46 days in water		
21.6	4.62	speckled
13.3	**7.37**	**rubber + short arcs**
23.2	4.62	speckled
16.1	4.71	speckled
Mean#	5.33 ± 2.16	
Means# of results above, according to failure mode:		
14.7 ± 3.6	**7.52 ± 2.00**	**rubber + short arcs**
22.0 ± 2.9	4.68 ± 0.23	speckled

With 95% confidence limits.

Surface Treatment and Peel Energy

The following relationship is suggested. Both *acid etching* and *Phosphate 1* treatment produce a surface that the bonding agent can easily wet and adsorb onto. When the rubber is moulded, a strong bond forms so that the peel forces concentrate close to the interface leading to cohesive failure in the rubber near the interface. The peel energy represents the energy associated with producing a relatively smooth fracture surface and with deforming a relatively small volume of rubber near the substrate during peeling.

The *Phosphate 2* surfaces are much rougher and the platelike crystals tend to arrest the peel propagation locally causing a build up of stress which deforms a larger volume of rubber: on fracture, some of this strain energy is dissipated viscoelastically, some of it is dissipated in producing the much rougher surfaces involving the ridges and cracks observed. The high stress may be sufficient to initiate failure, from time to time, of the phosphate coating itself. If this occurs the stored strain energy is sufficient to drive the crack down the stress gradient to the edge of the peeling strip. This is the origin of the arcs of detached phosphate. The fracture energy for these samples would seem to be limited by that of the phosphate coating.

If the phosphate coating is too thick it becomes cohesively weaker, limiting the energy that can be stored and dissipated by fracture of the rubber. This is the situation where the speckled fracture morphology is observed. Fracture of small regions of phosphate occur, but the stored strain energy is not great enough to drive them very far, so they remain as isolated regions.

The adhesion to all these treated steel surfaces is high. The large loads that are transmitted from the peeling rubber strip to the steel substrate have to be transmitted *via* the bonding agent layer at the interface. What are the characteristics of this layer which are associated with its effectiveness in bonding?

THE NATURE OF THE LAYER FORMED IN THE INTERFACIAL REGION

As was discussed above, both components of the bonding system are complex formulations. Our own analysis, summarised in Table III, has confirmed literature [26] reports that a significant component of the adhesive is chlorinated rubber together with natural rubber, *cis*-1,4-polyisoprene. We, therefore, decided to use these two components as a simple model system to study interactions which might occur in the interfacial regions during bonding and to relate the findings to the adhesion obtained.

Thin films of the chlorinated rubber and natural rubber were prepared by dissolving the materials in xylene, and casting solutions onto glass, allowing the solvent to evaporate, followed by drying *in vacuo*. In order to simulate the vulcanisation process, some of the films were heated at 150°C for various periods of time. Full details are given in Refs. [33] and [34].

The thermal behaviour of solvent-cast films of chlorinated natural rubber, masticated natural rubber and a 1 : 1 w/w blend (2% w/v in xylene) of these two polymers was studied using differential scanning calorimetry (DSC), infrared spectroscopy, nuclear magnetic spectroscopy (NMR) and scanning electron microscopy (SEM). The results support the following conclusions [33, 34]. When a natural rubber-chlorinated rubber blend is heated in air at the vulcanisation temperature, some type of accelerated chemical oxidation occurs which does not occur in the component homopolymers. The resulting heated material no longer contains rubber-like polyisoprene units. This reaction is associated with a change in phase structure from a heterogeneous mixture to what appears visually to be homogeneous material (Fig. 6).

Relevance to Adhesion

Further evidence points to the relevance of this change to adhesion in rubber-to-metal bonding. This has been obtained by measuring the peel strength of adhesive bonds produced using the model compounds in the place of proprietary bonding agents. In order to allow adequate time for the N.R.-chlorinated rubber reaction to occur, the rubber compound used in these experiments was modified by addition of a retarding agent (Tab. I). As ancillary stress-strain results were not available for this rubber, the results in Table VII are shown as peel force (F/b in Eq. (1)), rather than as peel energies (P).

Enhanced adhesion obtained when the blend was used as a bonding agent, compared with results using either primer alone or primer plus

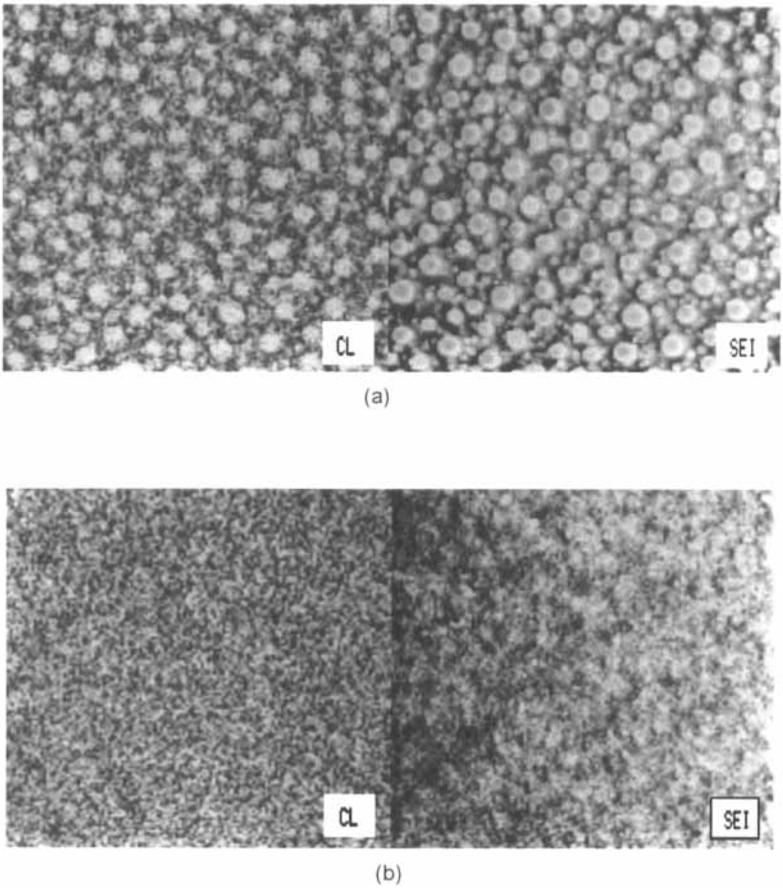

FIGURE 6 Electron probe microanalysis (EPMA) of blend of natural rubber and chlorinated rubber deposited on glass from xylene. Secondary electron image (SEI) and chlorine distribution (a) before and (b) after heating in air for 30 min at 170°C.

TABLE VII Adhesion of a "delayed cure" natural rubber compound to phosphated steel ("Phosphate 1") coated with various bonding systems

Coating	*No. of peels*	*Peel force*[#] *N mm*$^{-1}$
Chemlok 211/220	6	15.7 ± 1.1
Chemlok 211 (primer)	6	1.7 ± 0.1
Chemlok 211/Pergut S20	6	2.3 ± 0.4
Chemlok 211/Blend (natural rubber and chlorinated rubber)	6	4.0 ± 0.2

[#] With 95% confidence limits.

chlorinated rubber, suggest the significance of the interaction between the two components of the blend during formation of effective bonds. While these results are indicative, rather than conclusive, they do point to the importance of compatibility between components in the interfacial regions of rubber-to-metal adhesive bonds.

As discussed in the previous section on "Characterisation of Bonding Agent", the commercial Chemlok system contains many components absent from the "model" bonding agents. It is not surprising, then, that the full commercial product gives much higher adhesion than any of the model systems.

CONCLUSIONS

When a simple natural rubber compound was "in vulcanisation" bonded to steel using a proprietary bonding agent, good adhesion and good bond durability in an aqueous environment were obtained with different steel pretreatments. The layer formed by the bonding agent is capable of transmitting high loads between the rubber and the steel.

It is interesting that two phosphating processes, producing rough surfaces of different characteristics, and an acid etch, producing a relatively-smooth oxidised surface, all performed well under laboratory conditions. This suggests that high rubber-to-steel adhesion can be obtained independently of producing a conspicuously rough substrate surface.

Although the mode of failure was dominantly cohesive within the rubber, one of the pretreatments clearly showed that substrate surface topography can influence both the failure path and the peel energy. This treatment was Phosphate 2, which produced plate-like crystals. At low coating weights when the crystals were relatively small, they directed the stresses away from the substrate in a way which involved large volumes of rubber in deformation and produced a failure surface within the rubber which showed extensive tearing and cracking. Some fracture of the phosphate crystals themselves may occur, and this sets a limit on the peel energy obtainable.

In order to investigate the nature layer formed by interaction between bonding system and rubber in the interfacial region, a model compound, consisting of chlorinated natural rubber blended with natural rubber, was used. It was found that a solid state chemical reaction between components occurs under bonding conditions, leading to homogenisation of the blend. Results of experiments using the model compound blend as a substitute for the top coat (adhesive) layer of the proprietary bonding system suggest that such a reaction may play a part in the formation of effective rubber-to-steel bonds.

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