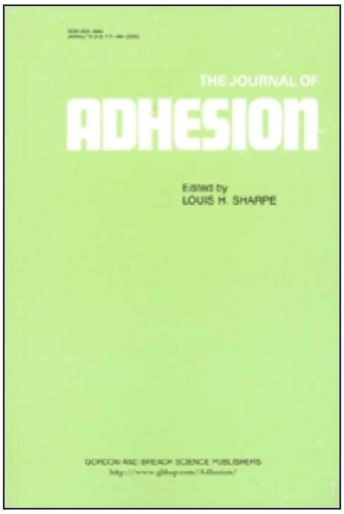

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Gan, L. M. , Ong, H. W. K. and Tan, T. L.(1984) 'Surface Treatment of Cold Rolled Steel by Phosphating', The Journal of Adhesion, 16: 3, 233 — 244
To link to this Article: DOI: 10.1080/00218468408074918
URL: http://dx.doi.org/10.1080/00218468408074918

J. Adhesion, 1984, Vol. 16, pp. 233–244
0021-8464/84/1603-0233 $18.50/0

Printed in the United Kingdom

Surface Treatment of Cold Rolled Steel by Phosphating

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(Received June 13, 1983; in final form July 23, 1983)

The effect of surface treatment on the kinetics of phosphating cold rolled steel (CRS) has been investigated. Scanning electron micrographs revealed different surface structures after chemical treatments. CRS etched with HCl gave the fastest rate as well as a higher weight of phasphate coating. A heated (oxidized) surface retarded the rate of phosphate deposition up to ten-fold. The strength of the phosphate layers deposited on CRS surfaces were calculated to be from 4.2 to 5.8×10^2 kN m^{-2}.

INTRODUCTION

Phosphating is widely used to give a protective layer on cold rolled steel and hence it is frequently a substrate for adhesives or sealants. As such it is required to withstand the typical stresses as are imposed in adhesives applications. These can be assessed by making the phosphated steel the substrate in a conventional lap-shear joint using a sealant polymer. A silicone rubber has been used in the work reported here.

A metal surface is, in fact, a metal oxide surface and its thickness and structure varies accordingly from metal to metal. There is a strong indication that the oxidation state of a metal in a metal oxide controls its surface charge characteristics[1]. The higher the oxides, the more acidic they are than the lower ones. Iron, for example, can be reduced from +3 to +2 valence state and this would alter the surface bonding characteristics materially[2]. Generally, commonly used surface pretreatment of metal tends to elevate the oxides to the highest valency state.

Corrosion involves a heterogeneous reaction[3] between a metal and its environment. The corrosion rate of a metal may be reduced effectively by interposing a coating between the metal and the corrodent.

Since any process which involves the deposition of a coating on a metal surface requires adequate surface pretreatment, the initial step is to provide a "clean" metal surface. That is, it is essential that oils, greases, waxes, weak oxide scale residues, mill scale and other contaminants[4] be removed before application of the zinc phosphate coating[5–8].

A typical phosphating reaction proceeds in a primary zinc phosphate/phosphoric acid system at elevated temperature; the primary phosphate is then converted into a tertiary zinc phosphate.

$$3Zn(H_2PO_4)_2 \rightleftharpoons Zn_3(PO_4)_2 + 4H_3PO_4 \qquad (1)$$

When a steel surface is dipped into the phosphating solution, it is attacked by the free phosphoric acid which liberates hydrogen and thus raises the pH of the solution, especially along the metal surface[9–10].

$$Fe + 2H_3PO_4 \rightarrow Fe(H_2PO_4)_2 + H_2 \qquad (2)$$

thus reaction (1) is driven to the right and the insoluble zinc phosphate precipitated on the steel substrate surface.

The overall reactions can be simplified as follows:

$$Fe + 3Zn(H_2PO_4) \rightarrow \underset{\substack{\downarrow \\ Zn_3(PO_4)_2\cdot 4H_2O \\ \text{(Hopeite)}}}{Zn_3(PO_4)_2} + Fe(H_2PO_4)_2 + 2H_3PO_4 + H_2$$

During the process of precipitation, the zinc phosphate is transformed into an insoluble hopeite with 4 water molecules.

In practice, phosphating by immersion involves a multi-stage process and it also gives rise to more problems mainly due to the nature and structure of the phosphate deposited. The growth of these phosphate layers requires a phosphate nucleation on the substrate surface and their subsequent lateral growth. Loukonis[10] suggested that the nucleation of first-stage crystals must grow to a size of sufficient surface area for the second-stage dendritic growth to be probable. These dendritic crystals grow in random direction and their branches could intertwine to the extent of enclosing cells of the phosphating solution. Thus further growth and/or dissolution of iron within the phosphate layer would occur.

This paper will attempt to examine the physical and geometric characteristics of cold rolled steel surfaces and their interactions with its phosphate coating. In particular, this paper is concerned with the surface structure, the reactivity of cold rolled steel and its oxide which are of practical importance.

EXPERIMENTAL

Pieces of cold rolled steel (CRS) of dimension 10.2 × 2.5 × 0.1 cm were degreased with toulene and acetone. They were then immersed in an alkaline bath (5% trisodium phosphate/1% Teepol solution) which was maintained at 80°C for a duration of 10 minutes. This was followed by a rinse with warm deionized water and dried at 90°C for 5 minutes. The "cleaned" specimens were stored in a desiccator.

The oxides present on the precleaned cold rolled steel were primarily those formed during the steel mill process. Such oxides were more or less uniform and of the order of 100 Å thick[10]. It is likely that both

TABLE I
Surface treatments of cold rolled steel

Adherend	Method of treatment		Remarks
1. As received	none		Dirty and oily
2. Degreased/ alkaline washed	10 min. at 80°C		
	trisodium phosphate	5%	Removed organic contaminants
	Teepol	1%	
	deionized water	94%	
3. Rusty	none		Ferrous/ferric oxides
4. Heated (oxidized)	Heated in furnace at 600°C for 2 hours		A denser mixed oxides layer
5. Acid etched (3% chromic acid)	1 min. at 30°C		Exposed grain boundaries
6. Acid etched (dilute HCl)	10 min. at 30°C Rinse in warm deionized water and dry for 10 min. at 90°C.		Removed rolling marks and further exposed grain boundaries.
7. Acid etched/ boiled (dilute HCl)	Similar treatment as in 6 plus immersion in boiling deionized water for 1 hour		Possible sealing of the surface oxides pores/ hydroxide formed

the low and high temperature iron oxides (α-Fe O and γ-Fe O) were present, and it is also likely that they were in hydrated form.

Degreased/alkaline washed CRS substrates were subjected to various and different surface treatments as shown in Table 1 prior to phosphating. After surface treatment, the weighed CRS substrate was immersed in a phosphating solution (5% Diverfos Z1 supplied by Diversey) for varying periods of time at 75°C. The phosphated surface was rinsed with cold deionized water and dried at 90°C for 24 hours. The final weight of the phosphated CRS was then recorded.

Preliminary examinations of these chemically treated and phosphated substrate surfaces were carried out with a optical microscope. The scanning electron microscope (Jeol 35 CF) was later employed for further investigation.

The strength of the phosphate layer as measured in a simple lap joint was determined by means of a silicone rubber sealant as shown in Figure 1. The length of the overlap was 2.0 × 2.5 cm and had a glue-line thickness of 0.1 mm. The pressure used for making these joints was approx. 2.2×10^3 kg/m^2.

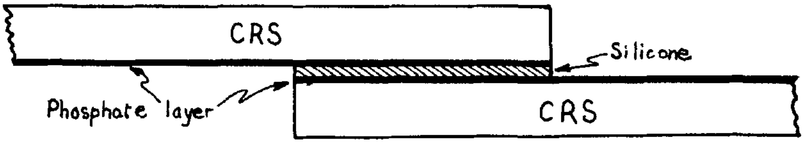

FIGURE 1 Arrangement of Single Lap-Shear Joint.

RESULTS

The scanning electron micrographs of Figures 2 to 7 revealed the different topographies of cold rolled steel surfaces after various chemical treatments. In the degreased/alkaline washed sample, a reasonably "clean" surface could be observed. It was free of adsorbed dust particles but contained the rolling marks typically found on rolled steel surfaces. In the rusty sample, as might be expected, a somewhat rougher surface could be observed. It was mainly of ferric and ferrous oxides which were randomly distributed throughout the surface. The heated (oxidized) sample gave a surface not quite like the rusty sample. The presence of the thermal cracks was quite apparent (see Figure 4).

Somewhat distinctive topographic features could be seen in the other

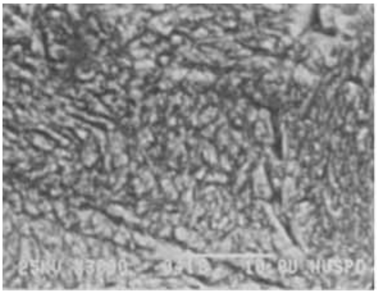

FIGURE 2 Degreased/alkaline washed CRS surface.

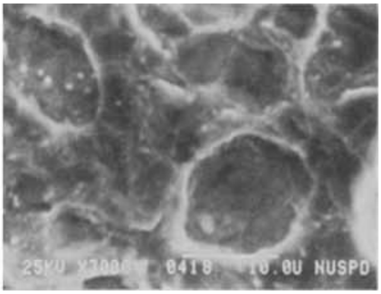

FIGURE 3 Rusty CRS surface.

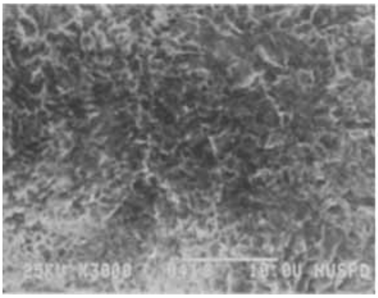

FIGURE 4 Heated (oxidized) CRS surface.

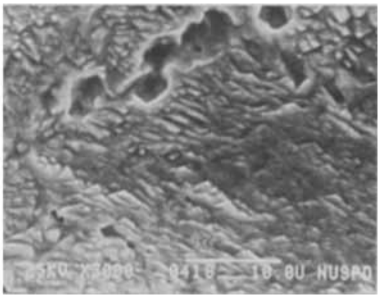

FIGURE 5 CRS surface etched with 3% chromic acid.

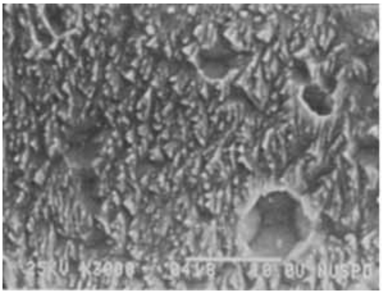

FIGURE 6 CRS surface etched with dilute hydrochloric acid.

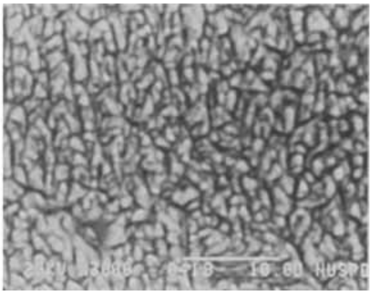

FIGURE 7 CRS surface etched with dilute hydrochloric acid and then boiled.

three samples. In the acid etched, to begin with, there was dissolution of the surface oxides and significant exposure of the grain boundaries. These two features likewise characterised the 3% chromic acid etched sample although the effect was on the whole less pronounced than in the dilute HCl etched sample. The most distinctive difference of all were the well-defined trenches and ridges seen in the acid etched/boiled sample. They might be due to hydroxide layer clusters.

It was preliminarily observed that phosphating of the dilute HCl etched CRS substrate at 75°C produced fast and maximum phosphate deposition and hence the subsequent work was done at that temperature.

A significant difference in coating weight was obtained for the treated CRS surface after phosphating and their respective kinetics are presented in Figure 8 and 9. In general, the rate of phosphate deposition

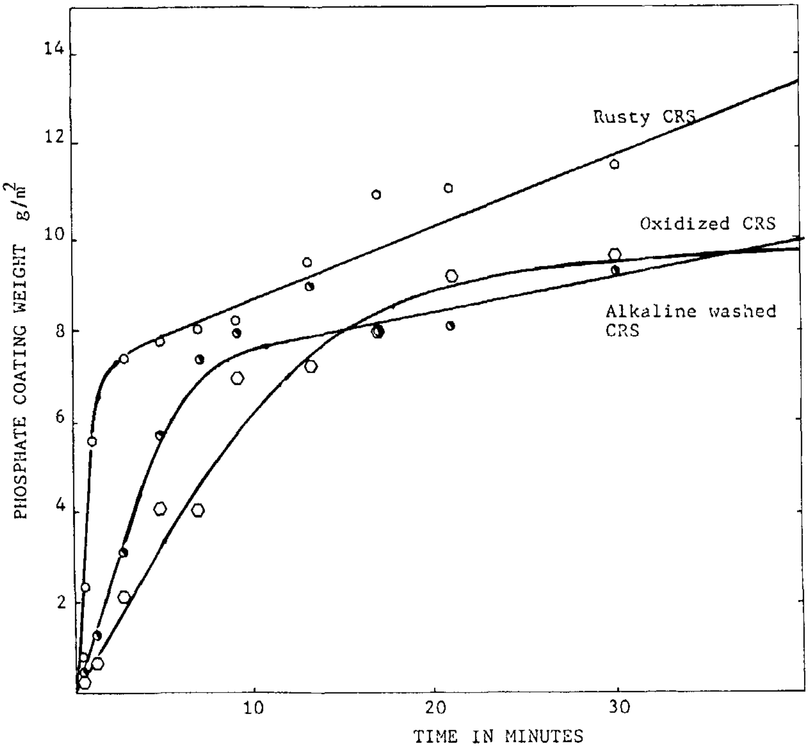

FIGURE 8 Kinetics of phosphating on oxidized CRS surfaces.

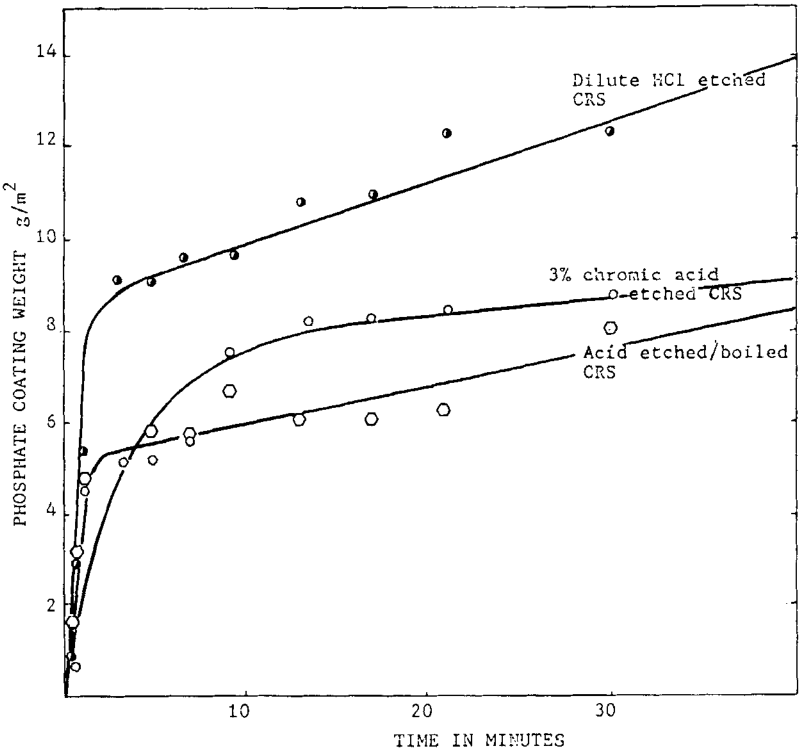

FIGURE 9 Kinetics of phosphating on acid-etched CRS surfaces.

proceeded rapidly in the first few minutes and subsequent deposition occurred at a much slower rate.

It is evident that the more emphasis should be placed on the earlier immersion up to the first 3 minutes. The different coating weight obtained in the early stage revealed the significant influence of the surface topography on phosphating. For example, the coating weight/area of the alkaline washed or heated (oxidized) surface was approximately one-fifth that of the rusty or acid etched surfaces after 30 seconds of immersion.

Unlike the others, the heated surface and alkaline washed surface also gave the curves of monotonically increasing coating weight *versus* time. Nucleation of the phosphate crystals at active sites (*i.e.*, edges, points, cracks, etched pits and grain boundaries) in both surfaces would be least due to their low surface nucleation densities. Fewer nucleation sites would be found on these two surfaces mainly because of their surface inactive oxide layers. In the case of heated surface, thermal stress cracks would promote initial nucleation of phosphate cyrstals and dendritic growth would proceed thereafter. However, oxidized surface could also retard the rate of phosphate deposition by as much as up to 10-fold in comparison with others. As for the alkaline washed surface, nucleation would depend on the rate at which "free" phosphoric acid dissolved the surface oxide and thus exposed the active grain boundaries.

In the other four samples, the rate of phosphate coating showed a pronounced change after the first few minutes. In these cases, it is envisaged that preferential nucleation would be at the less randomly distributed active sites and hence result in a non-uniform coating layer. Once the nucleation sites had been exhausted, there would be a transition to the dendritic growth which was manifested in the pronounced kink in the kinetic curves. Thereafter, the further dendritic growth proceeded smoothly.

The high coating weights were obtained with the rusty and dilute HCl etched surfaces. These surfaces were likely to contain the largest number of active sites which might arise from adsorbed contaminants, rough oxide particles, etched pits and exposed grain boundaries. They furnished the greatest possibilities for nucleations and subsequent dendritic growth. The growths of phosphate crystals are depicted in Figures 10 and 11 which show the differences in the deposited phosphate structures after varying periods of immersion.

TABLE II
Characteristics of phosphating on treated CRS surfaces.

Surface treatment	Apparent time for first-stage deposition (minutes)	Apparent rate of first-stage deposition (g/m^2 min.)	Coating Wt. after 30 minutes (g/m^2)
Dilute HCl etched	1	7.80	15.32
Rusty	1	6.10	11.57
Dilute HCl etched/boiled	1	4.50	7.98
3% chromic acid etched	3	1.58	8.73
Degreased/ alkaline washed	5	1.20	9.31
Heated (oxidized)	10	0.68	9.62

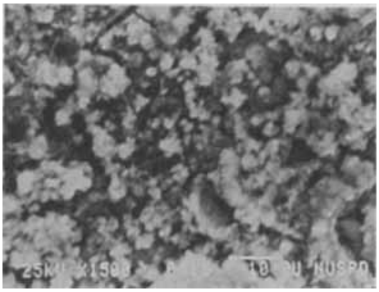

FIGURE 10 Phosphate crystals on HCl-etched CRS surface after 10 sec. immersion.

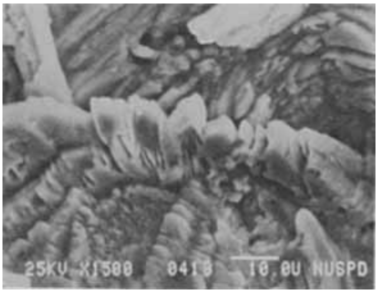

FIGURE 11 Phosphate crystals on HCl-etched CRS surface after 30 min. immersion.

In contrast, the HCl etched/boiled surface gave the lowest saturated coating weight. Its nucleations might be constrained to the well-defined trenches as well as ridges and they would not be as proliferate as on the other treated CRS surfaces.

Some of the characteristics of phosphating on the treated CRS surfaces are summarized in Table II. The results suggested strongly that the surface topography as well as the nature of the metal surface, surface oxides and hydroxides play an important role on the nucleation and the rate of phosphate coating. The effect which the oxide structure has on the phosphate coating is under investigation.

In an attempt to study the strength of the intertwined phosphate layers on treated CRS substrates, single lap joint of the phosphated samples were tested to destruction. The results of the lap-shear strength of phosphated CRS-silicone system are recorded in Table III. Adhesive failures prevailed in the unphosphated CRS substrate while failures within the phosphate layers were observed for all phosphated samples.

The strengths of these samples were always lower than those unphosphated ones.

The rusty surface with high coating weight, for example, exhibited the lowest strength while the alkaline washed sample with an average coating weight gave the highest. Three cases could be identified to produce high joint strength: namely, the alkaline washed, dilute HCl etched and heated (oxidized) surfaces. The apparent high strengths are attributed to the uniform nucleations and the subsequent dendritic phosphate growth intertwined to a greater extent than those of non-uniform growths.

As stated earlier, phosphate nucleation in the dilute HCl etched/boiled surface might be confined to the trenches as well as ridges and the lower strength could have resulted from its less entangled phosphate structures. As for the rough rusty surfaces, the phosphate nucleations would proceed unevenly and thus reduce the possibilities of further intertwined layers. This could account for the observed low strength. On the other hand, low tensile strength for chromic acid etched system could be due to less nucleation sites being generated as evidenced by low saturated coating weight.

As a whole, the strength of phosphate layer did not seem to vary significantly with immersion. It is estimated that the average strengths ranged from 4.2 to 5.8 × 10^2 kN/m^2 for the saturated phosphate coating.

TABLE III
Lap-shear strength of phosphated CRS-silicone sealant system.

Phosphating Immersion time (min)	Degreased surface	Rusty surface	Heated surface	Chromic acid etched surface	Dilute HCl	
					etched surface	etched/ boiled surface
	(Mean Lap-Shear Strength, 10^2 kN/m^2 ± S.D.)					
0	8.30 ±1.10	5.60 ±0.10	8.00 ±0.60	5.90 ±0.50	6.00 ±0.90	9.00 ±0.20
	Adhesive failure					
5	4.52 ±1.20	3.89 ±0.41	5.32 ±0.31	4.14 ±0.14	4.71 ±0.51	4.79 ±0.20
30	5.80 ±0.60	3.50 ±0.51	6.52 ±0.72	3.84 ±0.54	5.50 ±0.71	4.89 ±0.80
60	7.18 ±1.40	3.71 ±1.01	6.36 ±0.24	3.98 ±0.49	6.49 ±0.89	4.82 ±0.82
	Failure within phosphate layers					

The number of determinations for each value is 4.

DISCUSSION

In the surface treatment of CRS substrate, it is necessary to consider the nature and the formation of its surface oxide. The scanning electron micrographs revealed differences in surface topographies after the different prescribed surface treatments. An understanding of the surface oxide is important because it holds the phosphate crystals onto the surface. The continuous coating structure, which is an integral part of the surface, starts with the steel, building up through the oxide/phosphate layer to the zinc phosphate crystals.

Phosphating is an electrochemical process where the deposition/crystallisation of the phosphate coating takes place primarily at the localized cathodes on the metal surface. There must be active sites such as edges, points, cracks and grain boundaries on the metal surface for nucleation to start. The number of these nuclei (active sites) at the CRS surfaces can be varied by chemical treatments.

In the case of acid treatments, there is a greater tendency to expose the active sites on CRS surfaces and thus increase the phosphate deposition. This was reflected by the high rate of phosphate deposition and high saturated coating (Table II). On the other hand, the acid/boiled treatment would partially inactivate the substrate surface by forming hydroxide clusters. Consequently, phosphate deposition was more or less confined to its interstices resulting in lower deposition rate. In addition, it was found that the heated (oxidized) surface gave the lowest rate of deposition.

From the results obtained, it is concluded that the treatments which provided a rougher surface or/and more exposed grain boundaries conferred higher rate of phosphate deposition. However, the presence of oxides/hydroxides on CRS surfaces retarded the deposition rate. It is believed that the uniform nucleation of phosphate coating would promote greater intertwined phosphate structure which would yield higher strength. Further investigation on short time immersion is under way in order to establish the effect of surface topography upon the rate and the structure and strength of the phosphate coating.

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