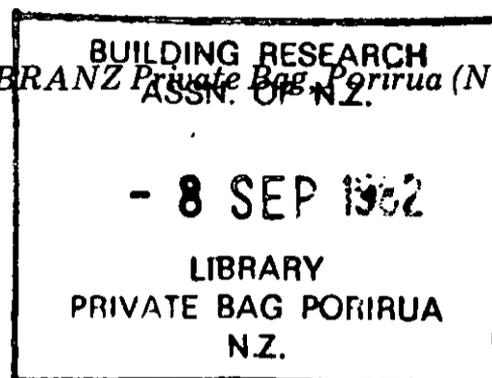# ELECTRON SPECTROSCOPY OF CHROMATED GALVANIZED STEEL SURFACES

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Summary

A commercial chromate-passivated galvanized steel sheet was investigated by X-ray photoelectron spectroscopy. The study was begun because earlier work had suggested that surface reactions during painting seemed highly variable but the results do not indicate a specific cause for this. The chromium-containing film was found to be slightly variable in thickness (although below 5 nm) and to contain approximately 60% of its chromium in the chromium(VI) oxidation state. Comparison of spectra from unchromated and chromated specimens suggested that the chromating mechanism appeared to include removal of aluminium and lead from the surface. These metals appeared to be surface segregated on unchromated specimens. The chromating solution included perchlorate and fluoride ions and it is postulated that the fluoride ion has removed the trace metals in a complexing reaction. No entrapment of these foreign anions in the chromating film was detected. A binding energy of 1022.6 ± 0.2 eV for Zn $2p_{3/2}$ in zinc chromate is postulated.

1. Introduction

The application of thin chromium-containing passivating films to galvanized steel articles has long been established as a means of protecting the surface against corrosion during storage. The method of film production has also been known for many years to affect significantly the behaviour of the film in service [1]. It has been shown recently that different passivating solutions yield quite different film compositions when applied to galvanized steel surfaces [2]. Even when the same passivating solution composition is used, however, variations in adhesion of paint films (which might be regarded as a function of surface chemistry) can be shown to be wide [3]. Several factors, including metal reactions with paint constituents, have been suggested previously as possible reasons for the difficulty in obtaining satisfactory paint adhesion to galvanized steel. It is difficult to visualize how unoxidized metal

could exist at a surface which had been exposed to warm chromic acid solution (as had been the experience of the panels used in ref. 3). An electron spectroscopy study was therefore planned which would examine surfaces for variations in surface chemistry across a single batch of chromated galvanized steel sheet.

The particular benefits of applying electron spectroscopy to the study of this system are the ability of the technique to analyse the outermost surface layers (which form the site of paint adhesion, corrosion and other surface reactions) and to assess the chemical state of elements as well as indicating their presence. An unsuccessful attempt had earlier been made [3] to apply scanning electron microscopy (SEM)–energy-dispersive analysis of X-rays (EDAX) techniques to analysis for chromium on the surface. This failed because the depth analysed was too great. Electron spectroscopy techniques such as electron spectroscopy for chemical analysis (ESCA) examine the outermost 2 - 10 nm, while SEM–EDAX averages over the outer micron [4]. The masses of chromium-containing coatings applied to coil-galvanized steel strip as the last process in the coating line are typically of the order of 20 - 40 mg m^{-2} according to the manufacturers. If a density of the film of 5.2 kg m^{-3} is assumed (based on the density of Cr_2O_3 [5]), the film thickness will be less than 10 nm. Thus, ESCA studies might be expected to be very useful in providing evidence on the film composition.

Extensive reports of electron spectroscopy studies of chromate films on aluminium are available (e.g. refs. 6 - 8) but very few such investigations on galvanized steel substrates have been reported.

2. Experimental details

Panels cut from a single width of chromated galvanized steel coil 1200 mm wide were supplied by New Zealand Steel Ltd. The materials and methods used for application of the chromium-containing coating by this company are subject to a U.S. Patent [9] and use a bath which contains 10 - 30 (g CrO_3) l^{-1}, 0.5 - 0.85 (g ClO_4^-) l^{-1} and 0.1 - 0.27 (g F^-) l^{-1} at a pH of about 1.0. The sheet parameters were as follows: total coated thickness, 0.55 mm; zinc crystal type, minimized spangle; zinc coating mass, 300 g m^{-2}. Care was taken during panel collection that fingermarking did not occur. Specimens approximately 8 mm square were cut from these panels for surface analysis, with no further surface treatment. Specimen distribution across the width of the production coil is shown in Fig. 1.

A Vacuum Generator ESCA-III spectrometer was used for the analysis. Vacuum in the analysis chamber was maintained below 10^{-8} Torr for all analyses. Specimens were held between molybdenum foils on the sample transfer probe with a 4 mm square window cut in the top foil so that cut edges of the specimen were hidden from the X-ray beam. The Al Kα X-ray source was operated at 10 kV and 10 mA and the magnesium source at 8 kV and 20 mA. The analyser energy was 50 V at the maximum (4 mm) slit width.
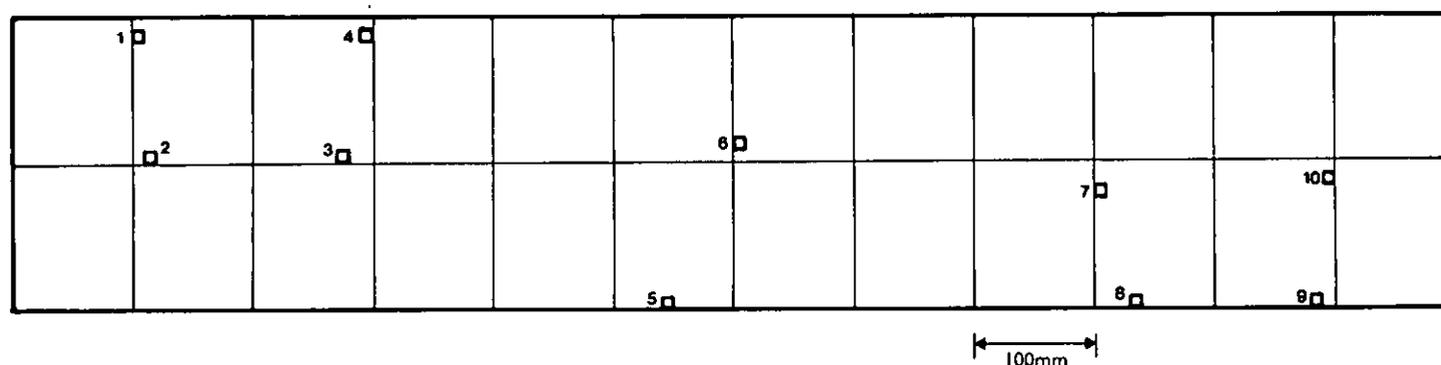
Fig. 1. Positions from where specimens were taken for electron spectroscopy (the numbers are those used in Tables 1 - 3).

A low-resolution survey spectrum was collected from each specimen, so that all elements present at the surface could be identified. Selected peaks from each element were then examined in more detail. These detailed spectra were recorded onto punched paper tape and a computer program was used to deconvolute overlapping peaks in the spectra. The program assumes a linear background and perfect gaussian peaks.

Reported peak positions are referred to C 1s at a binding energy of 285 eV. Consideration was given to using the Au $4f_{7/2}$ peak as the reference position but this was rejected because of interference of the Au $4f_{5/2}$ peak with the Zn 3p peak.

Although this spectrometer is equipped with an AG2 ion gun, depth profiling on specimens was not attempted after trials showed that this treatment produced significant alteration in the Cr 2p peak shape. As shown in Fig. 2, 60 s of sputtering at 80 μA effectively removed the part of the chromium peak assigned to chromium(VI). Reduction of chromium(VI) to chromium(III) during electron spectroscopy has been reported previously [6, 10]. The few specimens which were given a light argon ion sputtering (less than 5 s) gave chromium peak area enhancement compared with all peaks except molybdenum. (It seems logical that the molybdenum peak should increase markedly in intensity in view of the considerable area of molybdenum exposed to the sputtering beam.) Loss of this chance to improve the signal intensity was accepted, however, in order to try to preserve specimen surface integrity. Similarly, chromium peaks were recorded as soon as possible after switching on the X-ray source.

Two unchromated specimens from batches with otherwise similar production parameters from the same source were examined under the same spectrometer conditions. These were cleaned before placing in the spectrometer by thorough swabbing with acetone. These specimens were submitted to 60 s of argon ion sputtering after the as-received spectra had been collected and the spectra of the sputtered surface were then collected.

A specimen from a batch with similar production parameters which had been exposed outdoors for 3 years, and so had developed a coating of zinc oxides and other compounds, was also examined under the same spectrometer conditions, with no surface cleaning before examination. The pri-
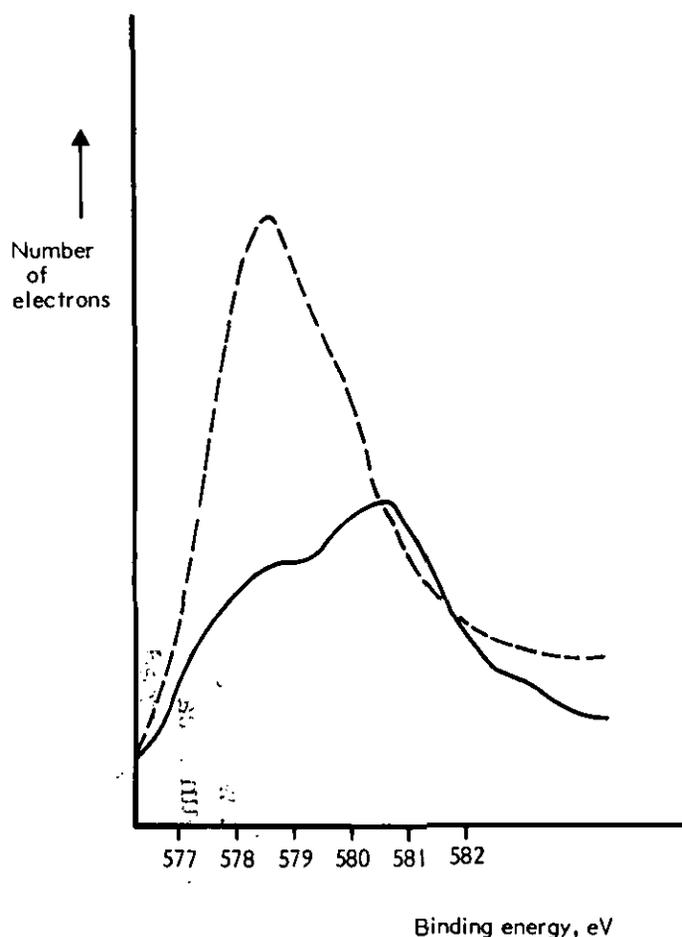
mary aim with this specimen was to obtain data on relative sizes of zinc peaks.

3. Results

Data on Cr 2p$_{3/2}$ peaks and zinc Auger peaks collected from chromated surfaces using the magnesium X-ray source for spectrum generation are summarized in Table 1. The assignment of two oxidation states in the Cr 2p$_{3/2}$ peak is based on the computer analysis performed, in which the computer is simply told to fit two peaks to the data. The peak separation which has resulted is in good agreement with the results of Helmer [11] for spectra of Cr$_2$O$_3^{2-}$ and K$_2$Cr$_2$O$_7$. The summary (mean and standard deviation) of the data of Table 1 shows fairly high uniformity across the sheet.

The data on the Zn 2p$_{3/2}$ and O 1s peaks, collected on the same specimens, using the aluminium X-ray source are summarized in Table 2. The Zn 2p$_{3/2}$ peak was almost undetectable on some specimens in the spectrum generated by the magnesium source and yet was of comparable size with the chromium peaks in the spectrum generated by the aluminium source.

TABLE 1

Peak positions and parameters in the X-ray photoelectron spectra generated by a magnesium X-ray source from chromated galvanized steel surfaces

Specimen position	Zn Auger BE (eV)	Cr $2p_{3/2}$ components[a]				Ratio of peak 2 area to total Cr peak area (%)
		Peak 1		Peak 2		
		BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	
1	908.4	578.0	1.92	580.1	2.61	62
2	908.4	577.9	1.74	580.1	2.35	60
3	908.6	577.8	2.16	580.1	2.23	53
4	908.1	578.1	2.03	580.2	2.00	53
5	908.1	577.8	1.82	580.1	2.34	66
6	907.8	577.4	1.76	579.7	2.32	65
7	907.8	577.7	2.00	580.4	2.45	57
8	908.3	578.5	1.93	580.2	2.27	55
9	907.9	578.0	2.25	580.3	2.13	53
10	908.2	577.9	1.84	580.1	2.45	61
Mean	908.2	577.8	1.95	580.1	2.32	58.5
Standard deviation	0.3	0.2	0.16	0.2	0.16	4.7

Peak positions referred to C 1s at a binding energy of 285.0 eV; BE, binding energy; FWHM, full width at half-maximum peak height.
[a]Splitting of peak as indicated by computer analysis.

TABLE 2

Peak parameters in the X-ray photoelectron spectra generated by an aluminium X-ray source from chromated galvanized steel surfaces

Specimen position	O 1s		Zn $2p_{3/2}$		Trace metals present
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	
1	532.2	2.93	1022.9	2.11	Al
2	532.1	2.87	1022.7	2.25	—
3	532.1	2.93	1022.5	2.05	—
4	532.1	2.98	1022.7	2.14	—
5	531.8	3.20	1022.6	2.19	—
6	531.4	2.93	1022.1	2.18	—
7	532.2	2.92	1022.6	2.37	Pb
8	532.5	3.07	1023.0	2.08	Al
9	532.0	3.06	1022.6	2.16	—
10	532.0	3.08	1022.7	2.22	Al
Mean	532.0	3.02	1022.6	2.18	
Standard deviation	0.3	0.11	0:2	0.09	

Peak positions referred to C 1s at a binding energy of 285.0 eV.

TABLE 3

Relative area data for peaks in spectra collected from chromated galvanized steel surfaces

Specimen position	$Zn\ 2p_{3/2}$: $Zn\ Auger$	$Zn\ 2p_{3/2}$: $Zn(3p_{3/2} + 3p_{1/2})$	$Zn\ 2p_{3/2}$: $Cr\ 2p_{3/2}$ (total)
1	5.78	2.24	1.95
2	9.31	4.81	2.17
3	4.06	3.57	1.16
4	2.29	2.38	1.08
5	5.20	2.97	1.76
6	4.45	3.48	2.43
7	8.56	3.44	2.28
8	5.68	3.07	1.84
9	6.00	3.02	2.16
10	7.03	3.18	2.11
Mean	5.84	3.22	1.89
Standard deviation	1.98	0.68	0.43

Zinc Auger and Cr $2p_{3/2}$ data from magnesium X-ray source; other peaks from aluminium X-ray source.

Unfortunately, in the spectrum from the aluminium sources the Cr $2p_{3/2}$ peak lies on top of the zinc Auger peak whose parameters are listed in Table 1. Table 3 lists the ratios of the Zn $2p_{3/2}$ peak area to some of the other measured peaks: it is clear from this that there is no stable ratio of the Zn $2p_{3/2}$ peak area to the area under this zinc Auger peak and so the slightly artificial ratio involving the Cr $2p_{3/2}$ peak area from the magnesium source spectrum has been used to avoid the unquantifiable errors which would arise owing to the zinc Auger peak area if this peak in the aluminium source spectrum is used.

Traces of aluminium and lead were found on a few of the chromated specimens, as shown in Table 2. The peaks found were always too small to allow reliable area comparison with the zinc peaks; in fact, unless these trace metals were specifically sought in the spectrum, the spectrum would normally have been regarded as perhaps having a slight background variation in the regions corresponding to these elements.

Both lead and aluminium were present in significant amounts on the unchromated minimized spangle surfaces examined. The data found for peaks in the spectra from these specimens are summarized in Table 4.

Table 5 shows the peak parameters for the specimen exposed for a lengthy period outdoors. (The peak shifts compared with the other tables may reflect the presence of other compounds or may simply be due to charging of the surface, which is a more loosely bound layer than on the fresh samples.)

TABLE 4

Peak parameters in the X-ray photoelectron spectra generated from unchromated galvanized steel specimens before and after sputtering, using an aluminium X-ray source

	55ZM300		40ZM300	
	As received	After sputtering	As received	After sputtering
Zn 2p$_{3/2}$				
BE (eV)	1022.8	1022.4	1022.9	1022.2
FWHM (eV)	2.39	2.60	2.28	2.21
Area	24310	74200	8222	46110
Pb 4f$_{7/2}$				
BE (eV)	138.5	Absent	139.2	139.4
FWHM (eV)	2.16		2.77	2.35
Area	820		6417	2700
Al 2s$_{1/2}$				
BE (eV)	119.4	120.2	119.8	120.1
FWHM (eV)	2.61	2.54	2.77	2.64
Area	2080	2409	2268	2267

Peak positions referred to C 1s at a binding energy of 285.0 eV.

TABLE 5

Peak parameters in the X-ray photoelectron spectrum generated from a weathered galvanized steel surface using an aluminium X-ray source

Peak	BE (eV)	FWHM (eV)	Area
Zn 2p$_{3/2}$	1025.1	2.59	42090
Zn(3p$_{3/2}$ + 3p$_{1/2}$)	92.1	3.17 ⎫	7675
	95.2	3.30 ⎭	
Zn Auger	905.7	5.53	7046

Peak positions referred to C 1s at 285.0 eV.

4. Discussion

Approximately 60% of the total chromium on the examined surface was in the chromium(VI) oxidation state. This value, which is fairly uniform across the surface, exceeds considerably the only previously published value (approximately 33% [2]) found for the ratio of chromium(VI) to total chromium reported from an electron spectroscopy study of a chromate film on a zinc substrate. It is also higher than those reported from studies of chromate films on aluminium (0% [6], approximately 33% [7] and 25% - 30% [8]). The difference may be attributed to the different modes of film formation used to produce the chromate coating. Williams [12] surveyed reports on mechanisms of this formation over zinc substrates and drew atten-

TABLE 6

Relative amounts (at.%) of metals at the surface of unchromated galvanized steel specimens (from Table 4)

	55ZM300		40ZM300	
	As received	After sputtering	As received	After sputtering
Zn	77	91	38	83
Al	20	9	32	12
Pb	3	0	30	5

tion to the apparently large increase in film build-up if anions such as sulphate were present. Bishop et al. [2] used such anions in solution although it is not clear what the chromium-containing film weight was over the surface. The films used in the present work are at the lowest end of the coating weights discussed by Williams [12].

No non-chromium anions were found trapped in films on the surfaces examined. This also contrasts with other studies using zinc and aluminium substrates for chromium-containing films [2, 6, 8]. While it is possible that the film thickness in the present study is so small that it is simply unable to trap detectable quantities of fluoride or perchlorate anions (both of which are present in the chromating solution [9]), this is regarded as improbable. The chromium peaks are of sufficient intensity that if these anions were included in the same proportion as the bulk solution they would be fairly easily identified.

Aluminium and lead were usually absent from the chromated surface. This may be an indication that the role of the fluoride ions is to complex these metals and to remove them from the surface. The amounts (at.%) of the metals in the unchromated surfaces are shown in Table 6. These have been calculated using the following assumptions.

(1) The ratio of sensitivities of detection of Al 2s to Zn $2p_{3/2}$ is 0.3. (Literature values for this ratio range from 0.3 [13] to less than 0.1 [4]. If the assumed value is in error, it will underestimate the amount of aluminium present.)

(2) The ratio of sensitivities of detection of Zn 2p to Pb $4f_{7/2}$ is 1 [14].

The additions of lead and aluminium to the galvanizing bath in a continuous galvanizing line are customarily of the order of a few tenths of a per cent. Thus, surface segregation of these metals appears to have occurred on the examined unchromated specimens. (This phenomenon has been observed on a series of other specimens examined in the course of this research programme, the results from which have not been reported.) Removal of trace metals from galvanized steel strip during painting pretreatments has been reported previously from an Auger electron spectroscopy study [15]. In the present study, the aluminium level has been reduced during chromating to a value (say less than 3 at.%) which is too low to measure in the system used here. The reduction is not simply a peak suppression phenomenon by the

coating across the surface; the Zn 3p signal, which appears in the same region of the spectrum as the Al 2s signal, is of comparable sizes on as-received specimens of both chromated and unchromated material.

The absence of the Zn 2p peak from the spectrum collected using the magnesium X-ray source might be attributable to three causes: (1) the lower intensity of electron emission after excitation by magnesium X-rays than by aluminium X-rays [14]; (2) absorption of emitted electrons by an adsorbed layer of gas and water molecules at the surface (because this layer has not been sputtered away); (3) absorption of emitted electrons by the chromium-containing film, which requires the assumption that this film is zinc free.

Two further findings support the third assumption. The first is that the Cr $2p_{3/2}$ peak area increased relative to that of Zn $2p_{3/2}$ when a short sputtering was performed on a chromated specimen (although both peaks increased in area). Since ejected Zn 2p electrons are of lower energy (by approximately 450 eV) than ejected Cr 2p electrons, the Zn 2p electrons should be retarded more than Cr 2p electrons if they originate in the same plane. If, however, only a percentage of a film thickness overlying the zinc is removed by sputtering, while all that overlying the chromium is removed, the result would be predicted to be that observed. The second supporting finding is the depressed value of the Zn 2p to Zn 3p peak area ratio on the fresh specimens (where respectively chromium-containing film and trace metal segregation appear to overlie the zinc) compared with that found on the long-exposed specimen (compare Tables 3 and 5).

If this hypothesis of a zinc-free chromium-containing film is correct, an estimate can be made of the film thickness. It may be predicted, in view of other studies (e.g. ref. 16), that the escape depth of Zn 2p electrons with a kinetic energy of 465 eV (i.e. in the aluminium-generated spectrum) will not be greater than 1 nm and may be rather less than this. Since the sampling depth (i.e. the source of 95% of detected electrons) is approximately three times the escape depth [17] it seems valid to claim a probable average film thickness of not more than 3 nm. This would be consistent with the mass of the deposited film claimed by the manufacturer, as discussed in the Introduction to this paper.

The variability in ratios of peak areas on the chromated specimens (Table 1) is suggested to be due to variations in the chromate film thickness. These variations may not always be attributable to production processes; for example, movement of panels against each other during transport would be expected to contribute to local thinning of the film. The variability shown is not likely to be unusual for sheet surfaces which need to be given surface coatings.

The Zn 2p peak appears to be in quite a constant position in chromated specimen spectra (Table 2), and this position seems similar to that found on the unchromated surface (Table 4) (although there is some movement toward lower binding energies after sputtering of unchromated surfaces). Schon [18] claimed that it was not possible to resolve the positions of the Zn 2p peak for zinc metal and zinc oxide but others [19] have managed

to show discrete positions for zinc compounds, depending on the anion.

It is postulated that the value of 1022.6 ± 0.2 eV for Zn $2p_{3/2}$ in Table 2 is that for zinc chromate (which does not appear to have been published previously). The previous reports have suggested positions for the Zn 2p peak at 1020.4 eV for metallic zinc and for the zinc salts between 1023.3 eV (iodide) and 1026.0 eV (fluoride) (referred to C 1s at 285.0 eV). In these compounds, the Zn $2p_{3/2}$ peak width was 2.4 ± 0.1 eV (which is rather broader than that reported here). In view of the apparent removal of aluminium and lead from the surface during chromating it must be expected that the zinc surface has been oxidized. This is supported by the position of the zinc Auger peak which agrees reasonably with those quoted for zinc(II) [18, 20].

It does not appear to be safe to draw firm conclusions regarding the state of the oxygen atoms in the surface film from the results reported here. The peak is in the correct position to correspond to a transition metal—OH bond [21] and is much closer to Cr^{III}—OH than to Cr^{III}—oxide reported positions [22]. It also agrees reasonably with positions for oxygen in for example $Na_2Cr_2O_7$ [23]. It is, however, impossible to discount the chance of contributions from adsorbed gases or water vapour, or perhaps from oxide films on the molybdenum holder (although the Mo—O peak position separation does not resemble those quoted from MoO_2 or MoO_3 [24]).

The results presented here do not indicate a clear reason for paint adhesion variations across the width of the coil. There is a suggestion that the thickness of the chromium-containing film changes haphazardly across the surface but this is as close to a possible reason as emerges. Even in instances where the film appears to be thinnest (*i.e.* high ratios of Zn 2p to other peaks in Table 3) a fairly constant ratio of chromium(VI) to total chromium still remains.

5. Conclusions

The chromated galvanized steel sheet studied had a chromium-containing film of variable thickness, less than 5 nm thick, across the 1200 mm width of the galvanized steel coil. The film contained approximately 60% of its chromium in the chromium(VI) oxidation state and this was quite uniform across the surface. Previous reports of chromium(VI) reduction during study by electron spectroscopy were confirmed.

The film did not contain zinc ions but probably overlaid an oxidized zinc surface. The chromating mechanism appeared to include removal of aluminium and lead from the surface. These metals were surface segregated on comparable unchromated surfaces from the same supplier.

Professor J. S. L. Leach for provision of research facilities and to Dr. P. J. Boden and Dr. P. A. Brook for discussions regarding aspects of the work. Dr. Brook wrote the computer program used for data analysis.

The supply of specimens by New Zealand Steel Ltd. is acknowledged.

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