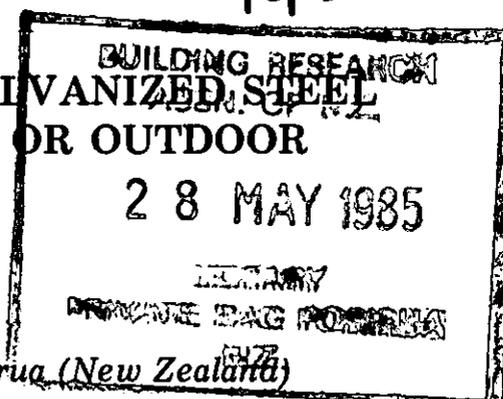B 09522 265

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ELECTRON SPECTROSCOPY OF CHROMATED GALVANIZED STEEL SHEET AFTER HEATING, IMMERSION IN WATER OR OUTDOOR WEATHERING

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Summary

Commercial chromate-passivated galvanized steel sheet specimens from five batches with different combinations of base metal thickness, zinc coating weight and zinc crystal size were subjected to heating at 80 °C for 100 h, immersion in distilled water for 24 h or exposure outdoors for 34 days. Changes in surface chemistry were assessed using X-ray photoelectron spectroscopy. The heating produced no discernible changes in chemistry, but the immersion and outdoor exposure specimens suffered marked loss of chromium from the passivating layer, and spectra indicated that zinc corrosion products were developing.

1. Introduction

The application of a thin chromium-containing coating to galvanized steel coil as it is manufactured has long been established as a means of protecting the surface against corrosion during storage. The mechanisms of protection by chromium-containing films have been described [1] as involving a general barrier coating, breaches in which are repaired as they form by reaction of chromium(VI) species held in the film. In an earlier paper [2] the application of X-ray electron spectroscopy (X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA)) to the study of such chromium-containing films was described. The metal surface beneath the film was apparently "invisible" to the electron spectrometer through the overlying film, implying the correctness of the manufacturer's claim (in the case studied) of a film thickness of 5 nm or less. The depth of surface analysis in ESCA is typically 0.5 - 2 nm [3] and as well as indicating which elements are present, the technique gives information on the oxidation states of the elements which occur. Because of the claimed protection mechanism, it is important to be able to assess accurately the relative amounts of the chromium oxidation states in the surface film. ESCA has a considerable potential applicability to such investigations.

An ESCA study is reported here which aimed to assess the way that the surfaces of chromated galvanized steel sheet specimens with a range of product parameters (sheet thickness, zinc crystal size etc.) respond to periods of heating, immersion in water or exposure outdoors.

There are reports of degradation of the ability of the chromium-containing film to protect the surface from corrosion after periods of heating, even below 100 °C [1, 4], and a study of acrylic latex paint adhesion to chromated galvanized steel showed reduced adhesion on heated specimens [5]. This study also demonstrated that there can be considerable variability in paint adhesion when chromated surfaces are painted under similar conditions using a model acrylic latex paint. This variability in adhesion, which might be regarded as reflecting variable surface chemistry, was found to be markedly lower if the specimen surface was exposed outdoors for 4 weeks before painting under equivalent conditions with the same paint. Knowledge of the response of chromated surfaces to immersion in water is obviously important since the major cause of degradation of galvanized surfaces during storage is trapping of water.

2. Experimental details

Five batches of chromated galvanized steel sheet were supplied by New Zealand Steel Ltd. with the product parameters shown in Table 1. The method of application and formulation of the passivating solution which is used to apply the chromium-containing coating at the end of the New Zealand Steel Ltd. production line is described by Prust and Glassman [6]. Care was taken in sample collection to ensure that panels were not handled with bare hands.

Specimens 25 mm × 10 mm in size were cut from two panels from each batch and heated at 80 °C for 100 h in a laboratory oven. Sections approximately 8 mm square were cut from each of these heated specimens for analysis (so that none of the edges of the heated specimen were included on the section to be analysed).

TABLE 1

Production parameters of galvanized steel batches as quoted by the manufacturer

Batch number	Total coated thickness (mm)	Zn coating mass (g m^{-2})	Zn crystal size description	Total Cr mass in surface film (mg m^{-2})
1	0.55	300	Regular	49
2	0.55	400	Regular	30
3	0.40	300	Minimized	32
4	0.40	400	Regular	35
5	0.40	400	Minimized	45

A second set of specimens 25 mm X 10 mm in size was cut from each of the ten panels and immersed in 50 ml distilled water in a 100 ml beaker so that the surface to be analysed was facing upwards (away from the beaker base). The beaker was left uncovered and unstirred in an office environment for 24 h, at the end of which time the specimens were removed and a section approximately 8 mm square was cut for analysis (again so that no cut edges exposed in solution were on the sections to be analysed).

A section was cut from one panel from each batch to form a 100 mm square panel which was exposed at 45° to the horizontal facing west (toward a busy road 60 m distant) approximately 3.5 m above ground level in Nottingham, Gt. Britain (52.580° N, 01.100° W). Exposure commenced on May 29, 1981, and samples for analysis were collected on June 15 (exposure, 17 days) and July 2 (exposure, 34 days). The sample racks were damaged between the two collection dates, resulting in loss of the longer-exposure specimens for batches 4 and 5. At all times, panels were handled only with gloved hands. Specimens approximately 8 mm square were collected at each date for ESCA examination.

The position of panel sections cut for environmental stressing was recorded for each panel, and sections approximately 8 mm square were cut from the panels adjacent to each of the areas removed for heating, immersion or exposure outdoors. These were regarded as "as-received" specimens, and they are referred to by this description in this paper.

The analysis was performed using a Vacuum Generators Ltd. ESCA-3 spectrometer. 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 with maximum (4 mm) slit width. The Cr 2p peak doublet coincides with a zinc Auger peak doublet in the spectrum generated by the aluminium source. The sample batch used previously [2] had a total chromium mass of 80 mg m^{-2} in its surface film, implying a much thicker chromium-containing layer than that found on the batches examined in this study (Table 1). Very little interference of this zinc Auger peak was found in the spectra of ref. 2, but there was significant interference in the present study, necessitating the use of both the aluminium and the magnesium sources. In the magnesium X-ray generated spectrum, the Zn 2p peak was often no more than a slight variation in the background line, while in the aluminium X-ray generated spectrum it was comparable in size with the chromium peak.

The usual spectrum collection method was to collect an aluminium X-ray generated low resolution survey spectrum to allow elements present to be identified, with subsequent detailed examination of selected peaks using the magnesium source if necessary. These detailed spectra were recorded onto punched paper tape, and a computer program was used to deconvolute overlapping peaks in the spectrum. The program assumes a

linear background and perfect gaussian peaks. The program was constrained to provide splitting of peaks only if the sum of squares for an $(n + 1)$-peak fit was less than 0.2 of the sum of squares for an n-peak fit.

Reported peak positions are referred to the Mo $3d_{5/2}$ at a binding energy of 228.0 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. The C 1s peak, usually used as a reference position, was also rejected because the carbon peak was expected to be one of those critically examined on the outdoor exposure specimens.

Although the spectrometer used is equipped with an AG2 ion gun, specimens were not subjected to depth profiling. Other work [2, 7] has previously demonstrated loss of chromium(VI) stability on the surface during bombardment with argon ions.

3. Results and discussion

3.1. Heated specimens

The difference between spectra of as-received and heated specimens was too small to be detected by this method. Tables 2 and 3 contain data found for these specimens; Table 2 includes the summary of the zinc and oxygen peak data for all the as-received specimens. The peak widths for zinc and oxygen on heated specimens were indistinguishable from as-received specimens. The designations Cr $2p_{3/2}$ and $Cr^{VI}(\%)$ in Table 3 disregard the zinc Auger contribution. This was done to permit comparison of peaks from single wide scale spectra.

No explanation of results reported [1, 4, 5] of the degradation of the protective ability of chromate coatings after heating emerges in this study. It is clear that chromium(VI) exists at similar levels on both as-received and heated surfaces, so that any loss of corrosion protection is not due to, for instance, a reduction process converting chromium(VI) to chromium(III). The variation in $Cr^{VI}(\%)$ in Table 3 between as-received and heated surfaces is non-uniform and analysis of variance shows no significant differences. Little significance should be attached to the precise values of $Cr^{VI}(\%)$ in Table 3 in view of the relatively small number of specimens from each batch which were examined and the possible involvement in peak area calculations by the zinc Auger peak. There appear to be no other chemical changes at the surface, and this suggests that some purely physical effect, perhaps cracking of the chromate coating, is responsible.

This hypothesis is strengthened by the way the Zn 3p:Zn 2p peak area ratio changes on heating, as shown in Table 3. Analysis of variance of these data shows a statistically significant difference in this factor across all batches. Though the effect appears at first sight most pronounced for batches 1 and 5, the statistical analysis does not show a specific batch effect. The way in which the ratio of these peak areas will alter when overlying films are altered is discussed in ref. 2. A reduction in the Zn 3p:Zn 2p ratio

TABLE 2

Peak characteristics[a] for zinc and oxygen on as-received and heated specimens in X-ray photoelectron spectra generated by an aluminium X-ray source (peak positions referred to Mo $3d_{5/2}$ at a binding energy of 228.0 eV)

Batch number	Number of specimens	Characteristics of as-received specimens				Characteristics of heated specimens[b]	
		$Zn\ 2p_{3/2}$		$O\ 1s$		$Zn\ 2p_{3/2}$	$O\ 1s$
		BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	BE (eV)	BE (eV)
1	8	1022.3 ± 0.1	2.16 ± 0.08	531.8 ± 0.1	2.91 ± 0.10	1022.2	531.7
2	8	1022.3 ± 0.1	2.11 ± 0.08	531.8 ± 0.2	2.87 ± 0.05	1022.4	531.8
3	8	1022.3 ± 0.2	2.16 ± 0.08	531.9 ± 0.1	2.91 ± 0.18	1022.3	531.8
4	8	1022.4 ± 0.2	2.16 ± 0.03	531.8 ± 0.4	2.84 ± 0.23	1022.1	531.8
5	7	1022.3 ± 0.2	2.07 ± 0.08	531.8 ± 0.2	2.98 ± 0.13	1022.1	531.7

[a]BE, binding energy; FWHM, full width at half-maximum height.
[b]Averaged over two specimens.

TABLE 3

Comparison of peak areas in X-ray photoelectron spectra generated using an aluminium source for as-received and heated specimens (each value is an average from two specimens)

Batch number	Cr^{VI} (%)[a]		$Cr\ 2p_{3/2}{:}Zn\ 2p_{3/2}$		$Zn\ 3p\ (total){:}Zn\ 2p_{3/2}$	
	As received	Heated	As received	Heated	As received	Heated
1	58.1	57.3	1.22	1.23	0.44	0.32
2	55.1	70.6	0.80	0.86	0.36	0.31
3	72.3	62.6	1.24	1.23	0.35	0.36
4	64.9	46.3	0.67	0.67	0.38	0.37
5	54.4	60.4	1.41	1.24	0.48	0.37

[a]Computed as follows: Cr^{VI}(%) = (area of peak near 580 eV)/(total area under spectrum at 575 - 582 eV).

is consistent with the increased escape of Zn 2p electrons that might occur if an overlying zinc-free film became cracked. This hypothesis would predict that the Cr:Zn ratio in Table 3 should also decrease on heating, but the statistical analysis suggests no significant differences. A contribution from the zinc Auger peak may be affecting this ratio.

3.2. Water-immersed specimens

Immersion of specimens in water for 24 h produced significant changes in spectra. The major changes are in the shape and size of the chromium peak. Table 4 shows chromium peak data for as-received and immersed specimens. The as-received data listed here are typical of those found throughout these experiments. The assignment of two chromium oxidation states at the surface 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 [8] for chromium peak positions in spectra of Cr_2O_3 and of $K_2Cr_2O_7$. The single peaks found by the computer for the specimens after immersion had good least-squares fits, but this may be of little significance. It will be observed for batches 1, 4 and 5 that the peak widths are considerably greater than those in the spectra of as-received specimens and that the peak positions for batches 2 and 4 after immersion are remote from those in the spectra of as-received specimens. The minimal values of the Cr:Zn ratio for most immersed batches in Table 5 show that the chromium peak areas are small. There is so little chromium left that partitioning between chromium(III) and chromium(VI) contributions to the peak cannot be done reliably.

TABLE 4

Comparison of Cr $2p_{3/2}$ peak parameters in X-ray photoelectron spectra generated by magnesium X-rays from specimens in the as-received state and after immersion (peak positions referred to Mo $3d_{5/2}$ at a binding energy of 228.0 eV; one specimen per entry in the table)

Batch number	As received		After immersion	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
1	577.3, 579.5	1.74, 3.21	578.3	4.47
2	578.1, 580.2	2.17, 2.19	575.9	3.93
3	578.1, 580.2	2.23, 2.04	578.1	3.06
4	577.8, 579.9	2.03, 1.74	575.8	6.20
5	577.4, 579.8	2.13, 1.74	578.4	4.97

Table 6 gives Zn $2p_{3/2}$ and O 1s peak data for the immersed specimens and values for the Zn 3p (total):Zn $2p_{3/2}$ peak area ratio on the immersed specimens. Microscopic examination of the immersed specimens revealed zinc corrosion product growth, and this is reflected in the depression of the

TABLE 5

Values for the area ratio Cr $2p_{3/2}$:Zn $2p_{3/2}$ for peaks in X-ray photoelectron spectra collected from chromated galvanized steel specimens as received, after immersion or after outdoor exposure (chromium data obtained using magnesium X-ray source; zinc data obtained using aluminium X-ray source; one specimen per entry in the table)

Batch number	Cr $2p_{3/2}$:Zn $2p_{3/2}$ after the following treatments			
	As received	Immersion for 24 h	Outdoors for 17 days	Outdoors for 34 days
1	1.01	0.17	0.28	0.11
2	0.56	0.04	0.19	0.07
3	0.45	0.12	0.15	0.10
4	0.21	0.03	0.13	—
5	0.51	0.04	0.18	—

TABLE 6

Characteristics and area ratios for zinc and oxygen peaks in X-ray photoelectron spectra generated by aluminium X-rays from samples immersed for 24 h (peak positions referred to Mo $3d_{5/2}$ at a binding energy of 228.0 eV; all results are averages from two spectra)

Batch number	Zn $2p_{3/2}$		O 1s		Zn 3p (total): Zn $2p_{3/2}$ area ratio
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)	
1	1022.4	2.37	531.8	2.84	0.31
2	1022.1	2.31	532.0	2.80	0.27
3	1022.1	2.31	531.9	2.74	0.29
4	1021.9	2.27	532.1	2.97	0.27
5	1022.4	2.23	531.7	2.93	0.35

Zn 3p:Zn 2p peak area ratio (Table 5) compared with as-received specimens (Table 3) and broadening of the Zn 2p peak (Table 6). There was no significant difference in oxygen peak parameters between as-received, heated and immersed specimens, however. This probably reflects a mixed oxide–hydroxide environment on each. The method cannot determine the metal with which the oxygen is associated (chromium or zinc). In this experimental method, oxygen in adsorbed films and in a molybdenum oxide film on the sample holder could also be contributing to the oxygen peak in the spectrum [2].

3.3. Outdoor-exposed specimens

Some similar effects to those on the water-immersed specimens were found on the samples exposed outdoors. The chromium(VI) fraction of the chromium-containing film was effectively lost within 17 days, and attrition of the chromium(III) residue was apparent after a second period of 17 days.

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Table 5 suggests that the initial attrition is less than that which occurs in 24 h of full immersion. Table 7 gives values for the ratio of Cr 2p and Zn 3p peak areas, both collected from magnesium-induced spectra of as-received and exposed specimens. These data provide confirmation of the trends of chromium loss shown in Table 5 (which uses the more artificial ratio of peak areas from differently sourced spectra).

Table 8 gives the chromium peak data for these outdoor-exposed specimens. There is a close similarity between the single chromium peak position here and the position of one of the peaks in the computer-split peak in the as-received specimen spectra (Table 8 should be compared with Table Table 4). Despite the broadening of the peaks in Table 8 compared with the computer-split peaks in Table 4, comparison of the spectral shapes suggested that the principal oxidation state present on the specimens exposed for 17 days was 3+, with perhaps a contribution (which cannot be quantified because it is so small) from the chromium(VI) which is contributing to the peak broadening.

TABLE 7

Values for the area ratio Cr $2p_{3/2}$:Zn 3p (total) for peaks in X-ray photo-electron spectra collected from chromated galvanized steel specimens as received and after exposure outdoors using a magnesium X-ray source (one specimen per entry in the table)

Batch number	Cr $2p_{3/2}$:Zn 3p (total) after the following treatments		
	As received	Exposure for 17 days	Exposure for 34 days
1	3.50	1.27	0.51
2	1.85	0.87	0.34
3	1.82	0.74	0.46
4	1.01	0.64	—
5	1.99	1.05	—

TABLE 8

Parameters for Cr $2p_{3/2}$ peaks in X-ray photoelectron spectra generated by magnesium X-rays from specimens after exposure outdoors (peak positions referred to Mo $3d_{5/2}$ at a binding energy of 228.0 eV; one specimen per entry in the table)

Batch number	Exposure for 17 days		Exposure for 34 days	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
1	578.0	3.46	578.2	3.76
2	578.5	2.96	578.2	3.36
3	578.1	2.70	578.4	2.88
4	578.0	4.09	—	—
5	577.9	2.81	—	—

Table 9 gives the zinc peak data for these outdoor-exposed specimens and Table 10 the oxygen peak data. (Assignment of split peaks as recorded in Table 10 is probably spurious but was made by the computer because the sum of squares for the two-peak fit was less than one-fifth that for a single peak. The best resolution of adjacent peaks to be expected of the spectrometer would be in excess of 1 eV.) The zinc and oxygen peak positions are moved significant distances in the spectra of the outdoor-exposed specimens compared with those in spectra from as-received specimens (Tables 9 and 10 should be compared with Table 2). This is apparently unlikely to be due to surface charging or similar effects in view of the relative constancy of the chromium peak position. Table 11 gives zinc peak ratio data. A value for the ratio tabulated here of 0.18 for a long-exposed galvanized surface (which might be expected to be totally covered by zinc corrosion product) is given in ref. 2. The values here show clear decreases from those in Table 3, reflecting loss of coverage by chromium-containing film.

TABLE 9

Parameters for Zn $2p_{3/2}$ peaks in X-ray photoelectron spectra generated using an aluminium X-ray source from chromated galvanized steel specimens exposed outdoors (peak positions related to Mo $3d_{5/2}$ at a binding energy of 228.0 eV; one specimen per entry in the table)

Batch number	Exposure for 17 days		Exposure for 34 days	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
1	1023.2	2.53	1023.2	2.54
2	1022.9	2.40	1022.9	2.59
3	1023.3	2.51	1023.2	2.48
4	1022.9	2.52	—	—
5	1022.8	2.45	—	—

TABLE 10

Parameters for O 1s peaks in X-ray photoelectron spectra generated using an aluminium X-ray source from chromated galvanized steel specimens exposed outdoors (peak positions related to Mo $3d_{5/2}$ at a binding energy of 228.0 eV; one specimen per entry in the table)

Batch number	Exposure for 17 days		Exposure for 34 days	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
1	532.6	2.88	532.5	2.74
2	532.3	2.91	532.3	2.84
3	532.7	2.82	532.6	2.68
4	532.2, 532.5	4.51, 2.48	—	—
5	532.1, 532.3	3.27, 1.96	—	—

TABLE 11

Values for the peak area ratio Zn 3p (total):Zn $2p_{3/2}$ in X-ray photoelectron spectra induced by an aluminium X-ray source from chromated galvanized steel specimens after outdoor exposure (one specimen per entry in the table)

Batch number	Exposure for 17 days	Exposure for 34 days
1	0.27	0.30
2	0.26	0.23
3	0.28	0.24
4	0.28	—
5	0.28	—

3.4. Other non-metal peaks

C 1s peaks on as-received specimens were usually analysed by the computer as single peaks lying at 285.0 ± 0.2 eV with respect to Mo $3d_{5/2}$ at 228.0 eV with an FWHM of approximately 2.4 eV. On immersed specimens the peak position remained the same, but the peak was broader (FWHM, 2.8 eV). The C 1s peak on specimens exposed outdoors was markedly asymmetric and was analysed as in Table 12. In general there was about 50% of the area under the peak at 284.2 - 284.6 eV.

TABLE 12

Parameters for C 1s peaks in X-ray photoelectron spectra generated using an aluminium source from specimens exposed outdoors (peak positions referred to Mo $3d_{5/2}$ at a binding energy of 228.0 eV; one specimen per entry in the table)

Batch number	Exposure for 17 days		Exposure for 34 days	
	BE (eV)	FWHM (eV)	BE (eV)	FWHM (eV)
1	284.2, 285.0, 286.5	1.74, 2.45, 4.74	284.5, 286.1	2.06, 3.92
2	284.6, 286.5	2.21, 4.27	284.4, 285.7	1.99, 4.02
3	284.7, 285.8	1.81, 2.48	284.4, 285.6, 286.5	1.76, 2.13, 5.02
4	284.6, 286.5	2.21, 4.69	—	—
5	284.4, 286.1	1.74, 4.79	—	—

Traces of sulphur and chlorine were also found on these specimens exposed outdoors. These elements had been absent on all other specimens examined. Insufficient detail was present in the spectra collected to allow precise identification of probable compounds present. Growth of corrosion products was visible to the naked eye on the specimens exposed for 34 days, and the peak area ratios for Cr 2p, Zn 2p and Zn 3p peaks (Tables 7 and 11) clearly point to diminishing islands of chromium-containing film surrounded

by a zinc corrosion product. The precise composition of the corrosion product is not clear. Sulphur, chlorine and carbon (in view of the asymmetry shown in Table 12) all appear to be involved, and in view of the changes in their peak positions oxygen and zinc are almost certainly involved as well. The broadening of the Zn 2p peak (Table 9) compared with that from as-received and immersed specimens is a further pointer to an increasingly heterogeneous environment of the zinc atoms. This emergence of corrosion product may be the basis for the observation [5] that paint adhesion to chromated galvanized steel sheet is less variable on a substrate weathered for 4 weeks than on a factory-fresh substrate.

3.5. Trace metals

The differences in intensity of peaks in XPS spectra from chromated and unchromated specimens which corresponded to aluminium and lead, which were known to be added to the zinc bath to control coating properties, were discussed in ref. 2. Both of these trace metals were also seen on some specimens in this study. In particular, batch 3 showed clear evidence of lead peaks in all except the specimens exposed for 34 days and aluminium traces on some specimens. However, both metals were unquantifiably small in concentration. Aluminium and lead were almost always undetectable on batches 1 and 2, while batches 4 and 5 had a variety of results in terms of the presence of these trace metals.

4. Conclusions

Heating of the chromated surface for 100 h at 80 °C causes no discernible changes in surface chemistry, and reported degradation of corrosion protection after such heating has to be related to a non-chemical effect, perhaps cracking of the chromium-containing film.

Immersion of the chromated galvanized steel surface in distilled water for 24 h results in marked loss of chromium from the film and the initial appearance of zinc corrosion products at the surface.

Exposure of the chromated surface outdoors for 34 days results in loss of the chromium(VI) fraction and most of the chromium(III) from the surface and the appearance of corrosion products which include traces of sulphur and chlorine from atmospheric pollutants.

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