JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 457–464

Coloured coatings on aluminium produced by varying the duration of a.c. electrolysis treatment. II. Thick coatings

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Received 4 April 1978

Durable anodized coatings having various colours were developed on aluminium by employing a 'three baths–three processes' system, in which electrolyses were conducted in three different baths. The first used either d.c. or a pulse sequence in a single acid, the second d.c. in a mixture of H_3PO_4 and H_2SO_4 and the third a.c. in an electrolyte containing boric acid, metal salt and an amine.

1. Introduction

For the colouring of aluminium, the anodized coating can be obtained by electrolyzing in a bath containing either a single acid or mixtures of acids in a 'one bath–one process' system. The coatings obtained from some single acid baths, such as sulphuric acid, oxalic acid, etc., have excellent durability and its thickness is controlled by the electrolysis duration. While the coatings from some single acid baths, such as phosphoric acid, are thick enough for exterior use (e.g. architectural purposes), the electrolytic processes are very difficult to control.

In electrolytic colouring, the 'one bath–one process' and 'two baths–two processes' systems have been reported. However, the former is not practical since the coating has a low thickness and the colours developed are not reproducible. One of the methods employed in the latter process is known as the usual method [1–7] and another method has been reported by the present authors [8]. In the usual method [1–7], the major component of the first and second electrolytes is sulphuric acid and a nickel salt respectively, and the coatings are thick enough to be used for exterior purposes providing anodizing is performed at a relatively high current density in the first electrolysis. However, colourful coatings have not been obtained. On the other hand, the major component of the first and second electrolytes in the method proposed previously by the present authors [8] is phosphoric acid and boric acid plus nickel salt, respectively, and the coating obtained is is of a thickness which is not durable enough for exterior use. However, the coating develops colours depending on the duration of the second electrolysis.

The present paper describes the anodized coating on aluminium using the new 'three baths–three processes' system, in which an additional electrolysis in an acid bath was conducted prior to the 'two baths–two processes', in order to produce a thick coating which is durable enough to be applicable for exterior use. This was achieved by controlling the voltage or current density of both first and second electrolyses. Various colours were obtained, dependent on the duration of the third electrolysis.

2. Experimental

Aluminium plates used in the present investigation had a purity of more than 99·0% (Japanese Industrial Standard A 1100) and a thickness of 1·0 mm.

Procedures for the preparation of the anodized coating on the aluminium were similar to those employed in a previous paper [8], although an additional electrolysis pre-treatment was used in the present experiments prior to the 'two baths–two processes'.

Post-treatment of the coating was generally not carried out. However, sealing with boiling

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water and/or coating with a clear acrylic-resin paint by dipping were carried out for some samples.

The thickness of the anodized coating obtained was measured with a high frequency eddy current thickness meter (AD-602 R, EMEC Co., Ltd) [9].

Measurement of the colour difference scale, *L*, *a* and *b*, and observation of the microstructures of the coating were carried out in the manner described in a previous report [8].

Weather resistance of the anodized coating was measured with an ultra-violet weather meter (WE-SH-2C, Suga Test Instrument Co., Ltd) [10]. Samples of the coating which had been exposed in an atmosphere maintained at a temperature of 63° C ± 5° C and a humidity of 52% for periods of 100 and 300 h, were observed, and its colour-fastness assessed using the colour-scale meter.

Furthermore, the sample of the deposits only, prepared by dissolving the coating with H_3PO_4 + H_2CrO_4, was leached with 1 : 4 HNO_3 solution and after removing the aluminium, the leached solution was evaporated down to 25 ml. A known amount of this solution was taken into a separating funnel and 2·0 ml of 1 wt% ethyl alcohol solution of dimethylglyoxim and 3·0 ml of 10 wt% sodium citrate solution were added. After adjusting the pH of the solution to a value higher than 7·5 with concentrated NH_4OH, 1 ml of chloroform was added. The nickel was extracted into the chloroform layer by shaking the funnel. The separated chloroform phase was dehydrated by passing through sodium sulphate and the dehydrated sample solution was poured into a glass cell (10 x 10 x 30 mm). The nickel content in the sample solution was analysed with a photoelectric spectrophotometer (Type 6, Hirama Scientific Co., Ltd) using a wavelength of 360 nm.

3. Results and discussion

From the 'two baths–two processes', described previously [8], a coating whose colour could be controlled was observed to develop. However, the coating (~ 0·7 μm) was not thick enough to be durable for exterior use. To improve the durability, attempts have been made to increase the thickness of the coating, without losing the colour quality, by employing the 'three baths–three processes' system.

From the preliminary experiments, some combinations of electrolyte composition and electrolysis conditions were found to yield a durable coating also having a variety of colours.

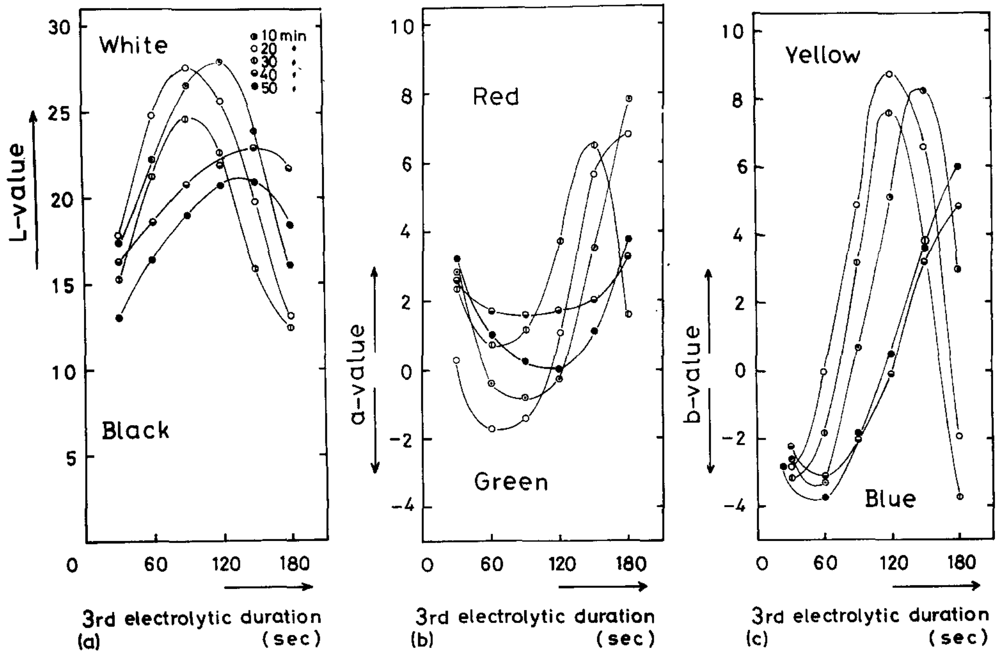

Fig. 1. Plots of the third electrolysis time against the colour difference scale: (a) *L*, (b) *a* and (c) *b*, of the anodized coating, for different durations of the second electrolysis.

Table 1. Conditions of anodizing

		Electrolyte			*Electrolysis*				
Test	*Number*	*Formulation* ($g\,l^{-1}$)		*pH*	*Order*	*Waveform*	*Voltage* (V)	*Current density* ($A\,dm^{-2}$)	*Duration* (min)
A	1	$(COOH)_2$	35	1 <	1st	d.c.	30–50	1–1·3	30–50
	2	H_3PO_4 H_2SO_4	30 1	1 <	2nd	d.c.	10–30	0·02–0·15	10–50
	3	$Ni(CH_3COO)_2$ H_3BO_3 $(HOCH_2CH_2)_2NH$	20–50 30–60 5–30	5·5 ~ 7·5	3rd	a.c.†	8–17	0·2–0·4	1/6–1/2*
B	1	H_2SO_4	150	1 <	1st	d.c.	15–18	0·8–1·2	30–90
	2	H_3PO_4 H_2SO_4	30 1	1 <	2nd	d.c.	10–30	0·02–0·15	10–50 (2–45)
	3	$Ni(CH_3COO)_2$ H_3BO_3 $(HOCH_2CH_2)_2NH$	20–50 30–60 5–30	5·5 ~ 7·5	3rd	a.c.†	8–17	0·2–0·4	1/6–1/2*
C	1	H_2SO_4	150	1 <	1st	pulse‡	20–40 (peak)	2·5–6·0 (average)	30
	2	H_3PO_4 H_2SO_4	30 1	1 <	2nd	d.c.	10–30	0·02–0·15	30–60
	3	$Ni(CH_3COO)_2$ H_3BO_3 $(HOCH_2CH_2)_2NH$	20–50 30–60 5–30	5·5 ~ 7·5	3rd	a.c.†	8–17	0·2–0·4	1/6–1/2*

* for each electrolytic cycle
† frequency, < 200 Hz
‡ frequency, 200 Hz

These are shown in Table 1; the first bath is a solution of sulphuric or oxalic acid, the second contains phosphoric and sulphuric acids, and the third boric acid, nickel salt and an amine.

The thickness of the coating obtained from tests A, B and C in Table 1 was in the range 9–11 μm, when the electrolysis was carried out for 30 min at 22° C, and 50, 15 or 35 V. After the second electrolysis in each test at the same bath temperature and 25–30 V for 30 min the value was $\sim 1\ \mu$m. However, the thickness of the coating obtained in the first electrolysis from the 'two baths–two processes' system at 22° C for 30–60 min at 30 V was 1–3 μm.

Considering the chemical formulations and pH value shown in Table 1, the third electrolysis is not expected to dissolve the coating formed in the first and the second electrolyses. From these observations, it is clear that the 'three baths–three processes' system gives a much thicker coating than the coating produced by the 'two baths–two processes' system.

The plots of the colour difference scales, *L*, *a* and *b*, of the coating obtained from test B versus the third electrolysis duration using the bath of $30\,g\,l^{-1}$ $Ni(CH_3COO)_2$ + $30\,g\,l^{-1}$ H_3BO_3 + $10\,g\,l^{-1}$ $(HOCH_2CH_2)_2NH$ are shown in Fig. 1 for various durations of the second electrolysis. The coatings can be classified into two groups: those prepared by electrolysis for the shorter durations (10, 20 and 30 min) and for longer durations (40 and 50 min). The colours of the coatings from both groups gradually get darker after $\sim$ 120 s in the third electrolysis. The colours of the coatings

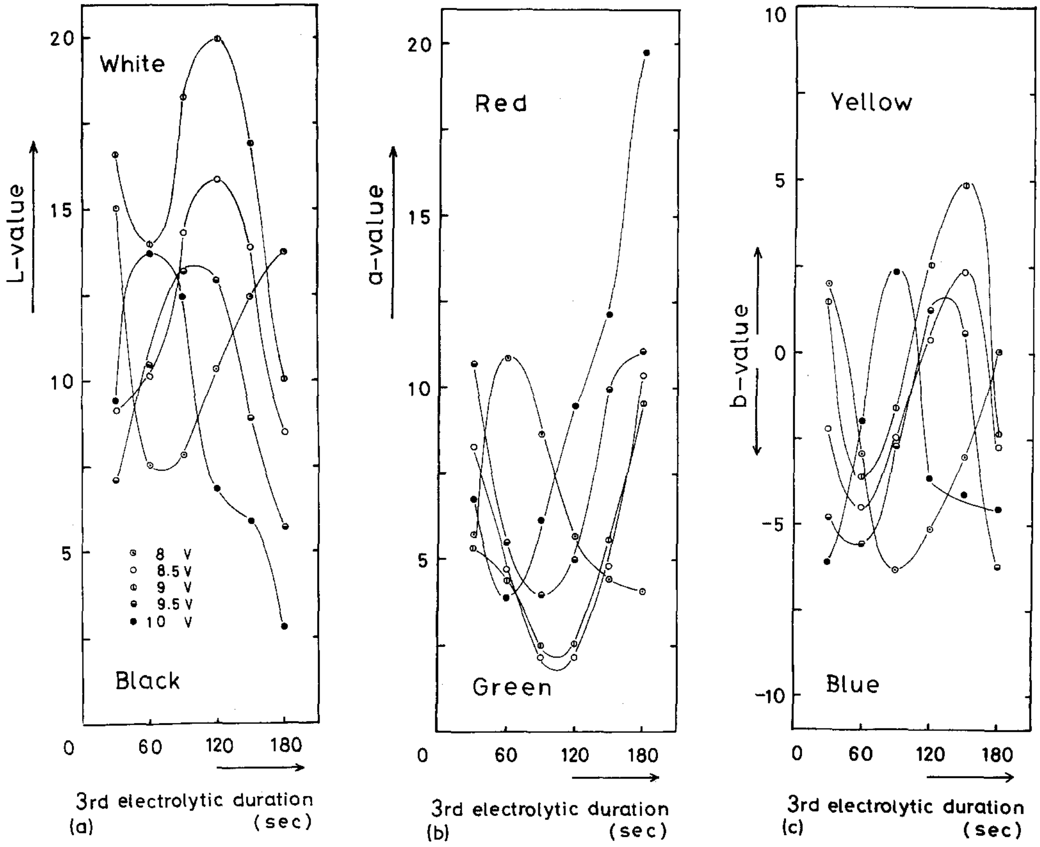

Fig. 2. Plots of the third electrolysis duration against the colour difference scale: (a) L, (b) a and (c) b, of the anodized coating, for different voltages of the third electrolysis.

obtained from the former group were observed visually to vary during the electrolysis as follows:

brown → reddish purple → bluish purple →
blue → yellow → orange → red → indigo →
green → pale green → dark brown → brown.

Fig. 2 shows plots of L, a and b of the coating versus the duration of the third electrolysis, for different voltages of the third electrolysis. The variation of the colours of the coatings obtained at 8·5, 9·0 and 9·5 V are almost the same as those for the shorter duration group.

The plots of L, a and b against the third electrolysis duration for the coating obtained after 30 min pre-treatment in the second electrolysis in Fig. 1a–c is reproduced in Fig. 3a–c, respectively. The curve for the deposit prepared by dissolving the coating with $H_3PO_4 + H_2CrO_4$ is also shown. The curves for the coating and those for the deposits have almost inverse gradients. Visually observed colours of the coating and those of the deposits are shown in Table 2.

Micrographs of the samples, prepared in the second electrolysis in 30 g l^{-1} H_3PO_4 + 1 g l^{-1} H_2SO_4 at 22° C, 25 V, 0·08 A dm^{-2}, after a first

Table 2. Visually observed colours of the coating and the deposits

Material		*Duration of 3rd electrolysis*
Coating	*Deposit*	(s)
bluish grey	pale brown	30
pale bluish grey	brown	60
pale brown	blue	90
orange	sky blue	120
red	pale green	150
greenish blue	bluish yellow	180
dark brown	dark brown	210

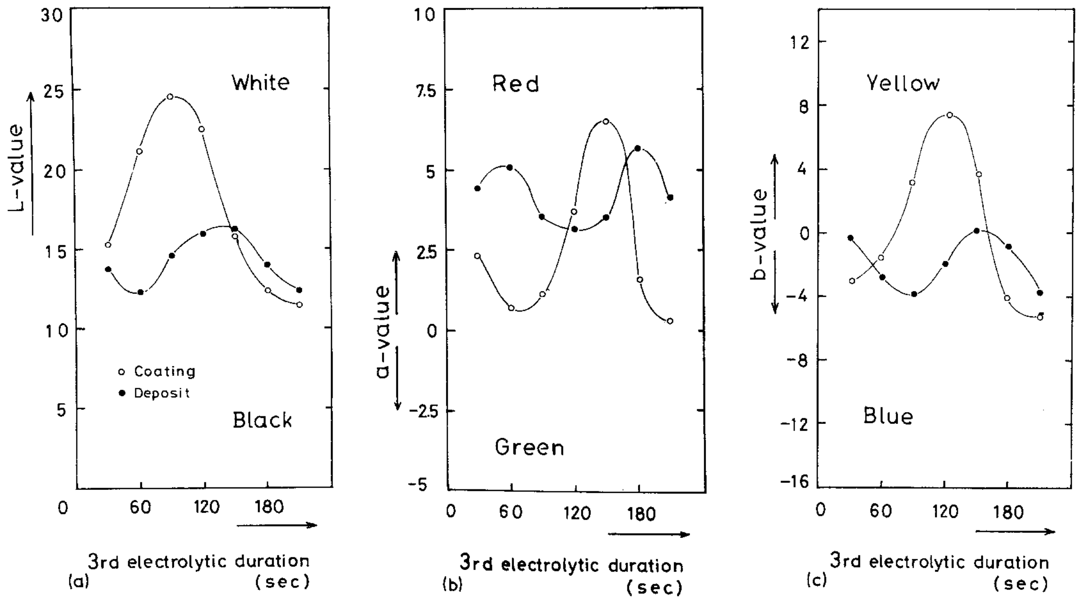

Fig. 3. Plots of the third electrolysis duration against the colour difference scale: (a) L, (b) a and (c) b, of the anodized coating obtained by pre-treatment for 30 min in the second electrolysis, and that of the deposits.

electrolysis in 150 g l^{-1} H_2SO_4 at 22° C, 15 V, 1·0 A dm^{-2} for 30 min were obtained. Fig. 4a shows the surface just after the first electrolysis, and Fig. 4b and c show the surface after the second electrolysis for a duration of 20 and 40 min, respectively. In Fig. 4a no remarkable change is observed and rolling lines are evident. In Fig. 4b, pore widening seems to have started, although the rolling lines are still evident. In Fig. 4c the rolling lines have disappeared and a rugged surface has formed, presumably by pore widening.

Fig. 5 illustrates a sectional view of the coating obtained by the treatment of the sample for Fig. 4 but after the third electrolysis in the bath of 30 g l^{-1} $Ni(CH_3COO)_2$ + 30 g l^{-1} H_3BO_3 + 10 g l^{-1} $(HOCH_2CH_2)_2NH$ at room temperature, 9 V, 0·2 A dm^{-2}. Fig. 5a–c show the view after 30, 90 and 150 s for the third electrolysis, respectively. As can be seen, the coating contains double layers, i.e. an outer and an inner film, and the latter is shown with an arrow in the photograph. The pores in the outer layer are formed by the first electrolysis and those in the inside layer by the second electrolysis at the bottom of the original pores which had been formed by the previous electrolysis. As the third electrolysis proceeds,

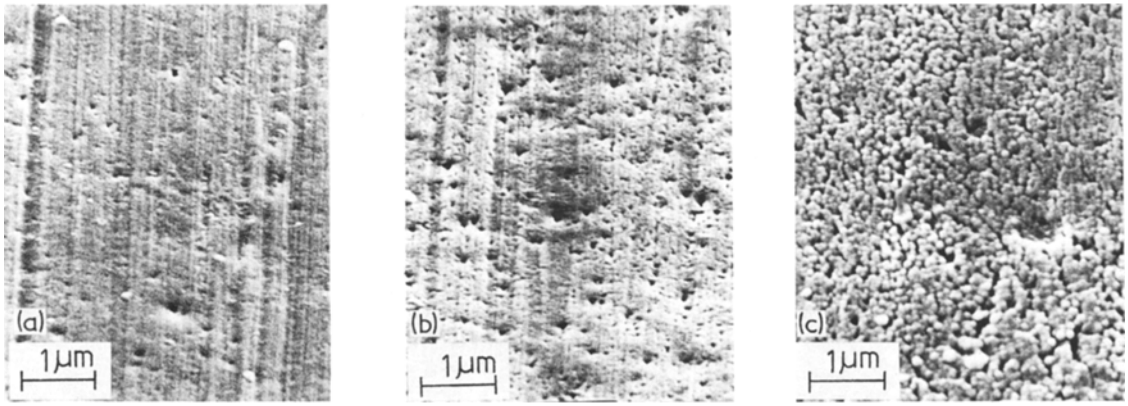

Fig. 4. Surface of the anodized coating after the second electrolysis: (a) 0 min, (b) 20 min, (c) 40 min.

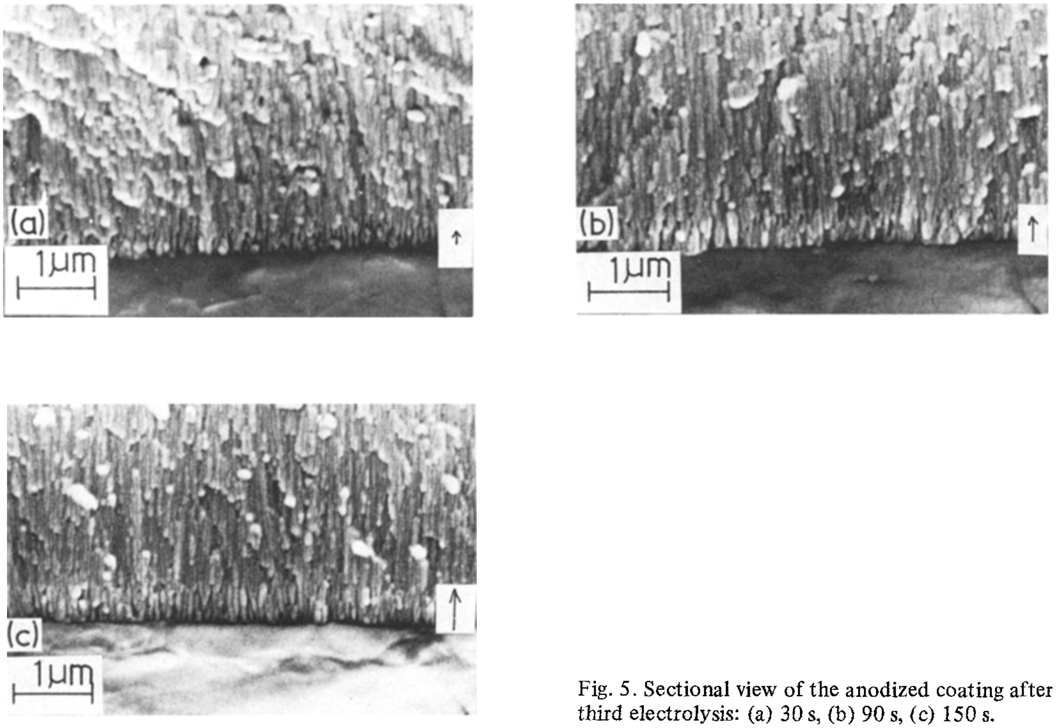

Fig. 5. Sectional view of the anodized coating after the third electrolysis: (a) 30 s, (b) 90 s, (c) 150 s.

filling in the inside layer progresses but is barely evident in the photographs, on which the filled pores appear whitish and unfilled pores blackish. Changes in pore size after the second electrolysis and after a certain duration of the third electrolysis can hardly be seen comparing the pore size in each layer on the photographs. Although no identifications were made, the deposits are assumed to be metallic nickel, together with nickel compounds, as verified in the previous report [8].

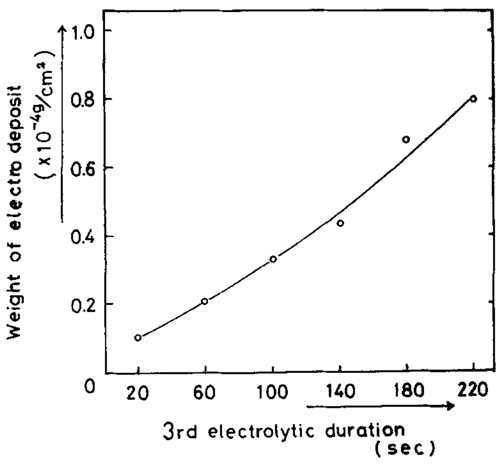

Fig. 6. Plots of the third electrolysis duration against the weight of nickel in the deposits.

The relationship between the weight of the nickel in the deposits and the duration of the third electrolysis was investigated. As Fig. 6 indicates, the weight of the deposits increases almost linearly with the increase of the electrolysis duration. In the case of the deposits obtained by the usual method, the weight of the nickel is reported to increase rapidly within the first 10 min duration and then increase only gradually [11]. Furthermore, the weight of the nickel in the present investigation is far less than that obtained in the usual method. These differences are probably due to the different mechanisms of deposition.

The weather resistance of the multicoloured coating, obtained under the same condition as the sample for the curve of 30 min duration of the second electrolysis, was examined and the results are shown in Fig. 7. Plots of the colour difference scale against the third electrolysis duration for the samples before and after a 100 h test showed almost the same trend. However, a considerable difference is observed for the plots of the unexposed sample and that of the sample exposed for

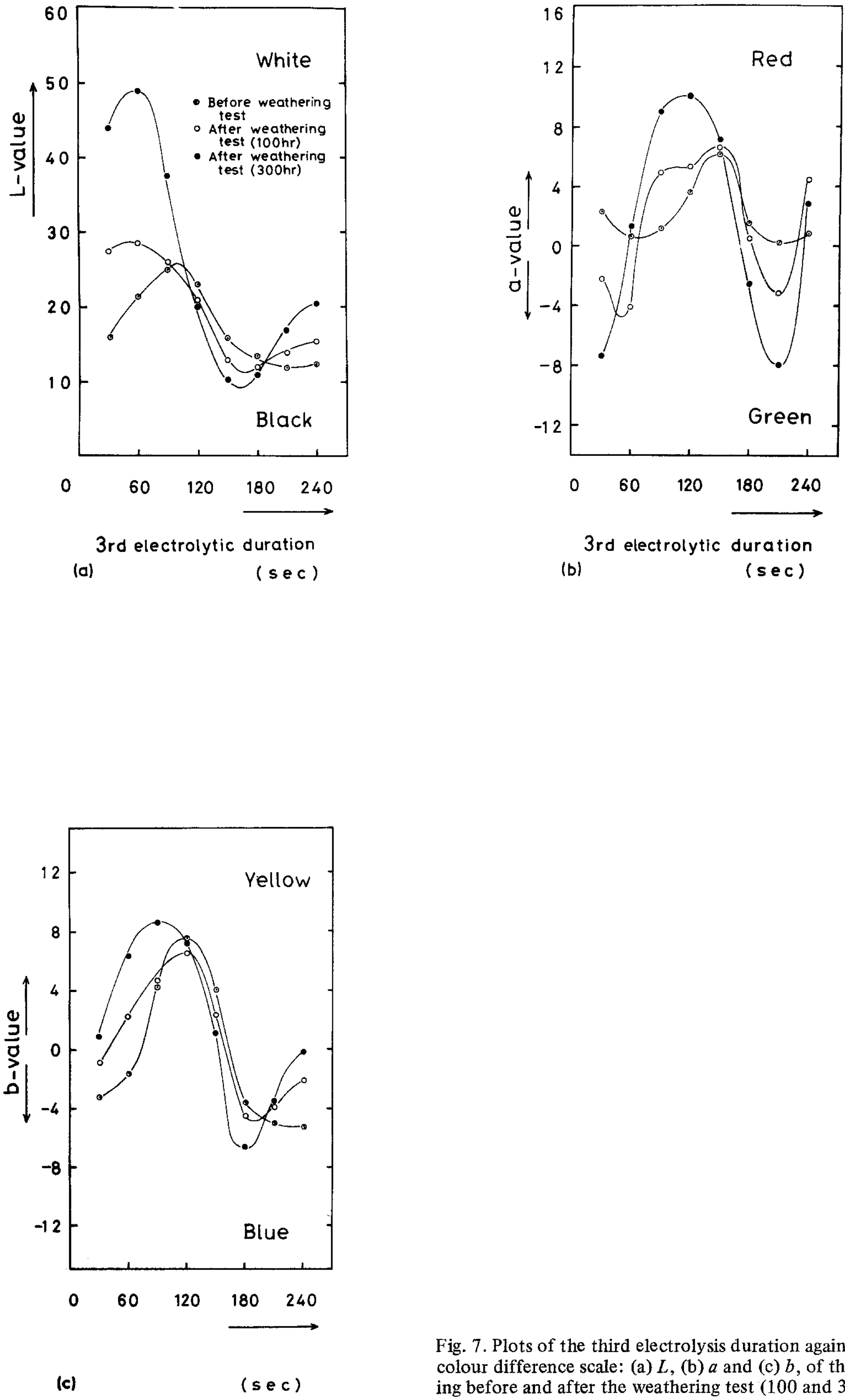

Fig. 7. Plots of the third electrolysis duration against the colour difference scale: (a) L, (b) a and (c) b, of the coating before and after the weathering test (100 and 300 h).

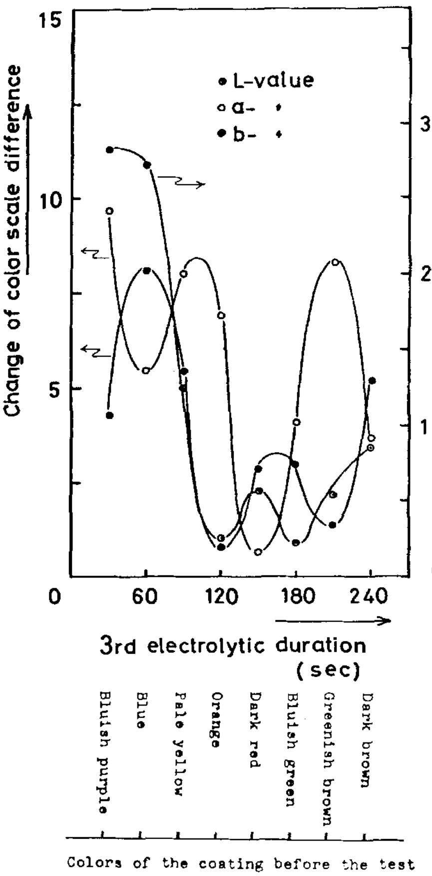

Fig. 8. Plots of the third electrolysis duration against the change in the colour difference scale, *L*, *a* and *b* of the anodized coating before and after 300 h weathering test.

300 h. Slight fading of the colours was recognised by visual observation for the samples of 100 and 300 h exposure. The degree of the fading is not uniform, and it seems to be dependent on the original colour of the coating, i.e. the colours before the exposure. In order to indicate this fading, changes in the values of *L*, *a* and *b* for the samples before and after 300 h exposure were plotted against the duration of the third electrolysis. This is shown in Fig. 8, below the abscissa axis on which the visually observed colours are also presented. The figure indicates that the coating with colours of dark red, greenish blue and dark brown appears to fade less than the other colours.

Taking into consideration the fact that the above-mentioned results were for the coating which had not been post-treated, the post-treatment of the coating obtained in the present method would be expected to be applicable for exterior use.

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