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# *Coloured coatings on aluminium produced by varying the duration of a.c. electrolysis treatment I. Thin coatings*

K. WADA, T. HATANO, K. UCHIDA

*National Institute for Researches in Inorganic Materials, Namiki, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan*

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Variously coloured coatings on aluminium were obtained by varying the duration of the a.c. electrolysis in a bath containing $H_3BO_3$, $Ni(CH_3COO)_2$ and $(HOCH_2CH_2)_2NH$, after an initial d.c. pretreatment in a mixture of $H_3PO_4$ and $H_2SO_4$. Electron-optical observation of the microstructure reveals that many tiny columns grow on the outer layer of the anodic film and the column consists of fine nickel particles, together with amorphous material.

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## 1. Introduction

It is generally known that porous coatings are formed on aluminium by anodizing in acid baths. The outer layer contains fine cylindrical parallel-sided pores, perpendicular to the macroscopic surface of the aluminium and the barrier layer which separates the porous layer from the aluminium [1, 2].

As Sheasby and Cooke [3] described in a historical review of the electrolytic colouring of the aluminium, Caboni [4] originally tried to colour by immersing aluminium and its coating in solutions of copper, nickel, or silver salts in order to deposit the appropriate metal in the pores by applying alternating current (a.c.). In 1963, Asada [5–7] investigated the fundamentals of the process and considerably extended the range of metal salts which could be used for colouring, to include the salts of selenium, magnesium, vanadium, gold and zinc. Since then, numerous methods for colouring have been described in the patent literature [8–10]. However, most of the methods yield rather simple colours, e.g. amber, bronze, and black, depending on the metal salts employed [11–13]. Coatings possessing various colours have not been obtained by merely increasing the electrolysis time without changing the formulation of the electrolyte. According to the recent patent applied for by Asada [14], yellow, gold, bronze and black finishes can be achieved without changing the salts. However, the coating obtained does not show shades of bright colours.

The present paper demonstrates a new process to obtain multicoloured anodized coatings which produce shades of red, through to violet, to black on aluminium by varying the electrolysis time.

## 2. Experimental

Aluminium foils of 99·8% purity and thickness of 0·1 mm were used for the experiments. Prior to anodizing, the foil was degreased by wiping with trichloroethylene in order to avoid losing the brightness of the original surface.

Anodizing was conducted in the preliminary experiments by employing various electrolytic conditions, most of which are shown in Table 1. It can be seen in Table 1 that anodic film colouring was attained with three systems: (a) One bath–one process, i.e. electrolysis was carried out in a bath applying a.c. only; (b) one bath–two processes, i.e. electrolysis in a bath applying direct current (d.c.) first, then a.c. in the same bath; (c) two baths–two processes, i.e. electrolysis by applying either d.c. or a.c. in one bath, followed by a second a.c. electrolysis in a different bath.

The chemicals used as electrolytes were reagent grade and the electrolyses were undertaken in a bath maintained in the temperature range 15–30° C utilizing aluminium as the working electrode and a carbon plate as a counter electrode. In the

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*Table 1. Conditions of anodic oxidation and colours developed*

| | | Electrolyte | | | Electrolysis | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *System* | *Test* | *No.* | *Formulation* ($g\,l^{-1}$) | *pH* | *Order* | *Wave form* | *Voltage* (V) | *Current density* ($A\,dm^{-2}$) | *Duration* (min) | *Colour developed with increasing electrolytic duration* |
| One bath–one process | A | – | $H_3PO_4$ 20–60 | > 1 | – | a.c. | 30–50 | 0·9–1·6 | 5–60 | pale red, light yellowish green, pale green |
| | B | – | $H_3PO_4$ 20–60<br>$H_2SO_4$ 0·5–1<br>$H_3BO_3$ 30–60<br>$Ni(CH_3COO)_2$ 20–50<br>$(HOCH_2CH_2)_2NH$ 5–30 | > 3 | – | a.c. | 10–50 | 0·8–1·2 | 2–30 | blue, dark blue, yellowish green, green yellow, orange, purple |
| one bath–two processes | C | – | $H_3PO_4$ 20–60<br>$H_2SO_4$ 0·5–1<br>$H_3BO_3$ 30–60<br>$Ni(CH_3COO)_2$ 20–50<br>$(HOCH_2CH_2)_2NH$ 5–30 | > 3 | 1st | d.c. | 5–50 | 0·04–0·2 | 10–90 | pale blue, light yellowish green, yellowish green, green, pale purple, pale brown, reddish brown |
| | | | | | 2nd | a.c. | 10–20 | 0·2–0·5 | 2–10 | |
| two baths–two processes | D | 1 | $H_3PO_4$ 20–60<br>$H_2SO_4$ 0·5–1 | > 1 | 1st | a.c. | 10–30 | 0·8–1·2 | 5–60 | dark brown, reddish purple, bluish purple, blue, yellow, orange, red, green, yellowish green, blackish brown, black |
| | | 2 | $H_3BO_3$ 30–60<br>$Ni(CH_3COO)_2$ 5–30<br>$(HOCH_2CH_2)_2NH$ 5–30 | 6–8 | 2nd | a.c. | 10–20 | 0·5–0·8 | 0·5–10 | |
| | E | 1 | $H_3PO_4$ 20–60<br>$H_2SO_4$ 0·5–1 | > 1 | 1st | d.c. | 5–50 | 0·04–0·2 | 2–60 | brown, reddish purple, bluish purple, blue, yellow, orange, red, green, yellowish green, chocolate, indigo, dark blue, dark green, black |
| | | 2 | $H_3BO_3$ 30–60<br>$Ni(CH_3COO)_2$ 20–50<br>$(HOCH_2CH_2)_2NH$ 5–30 | 6–8 | 2nd | a.c. | 10–20 | 0·2–0·5 | 0·5–5 | |

first electrolysis, the submerged area ratio of the two electrodes was 1 : 1.

In order to determine the effect of the duration of the second electrolysis on the development of the colour of the coating, a pair of electrodes was immersed in the bath initially and after conducting the electrolysis for a fixed period, the aluminium electrode was raised ~ 20 mm and again the electrolysis was conducted under conditions identical to those in the previous run. This electrolytic cycle was repeated more than ten times for each foil.

The colour difference scale, *L*, *a* and *b* for the colours of the coating was measured with a 'Colour and Colour $\Delta E$ Computer' (Suga Test Instrument Co., Ltd) [15].

The effect of humidity on the change in the colours of the coating was examined in a glass column (100 mm diameter), the top of which was open to air. The column was filled with steam produced by heating water in the closed bottom of the column with an electric heater; the humidity at the position where the anodized sample was suspended inside the column was measured by a psychrometer near that position.

The surface of the coating was observed with a scanning electron microscope (JSM-50, Japan Electron Laboratory Co., Ltd) and the deposits formed at the bottom of the pores in the anodized coating were examined with an electron microscope (HU-11D, Hitachi, Ltd).

To identify the colours of the deposits at the bottom of the pores, samples were prepared by dissolving the coating with a mixture of $H_3PO_4$ and $H_2CrO_4$ at ~ 99° C for ~ 5 min.

## 3. Results and discussion

The results of the experiments shown in Table 1 suggested that the system two baths–two processes was promising. Therefore, the present paper reports on the anodized coating from the system in test E. The following data were obtained from the experiments conducted in the first and second electrolyses, the first applying d.c. in the bath of $30\,g\,l^{-1}\,H_3PO_4 + 1\,g\,l^{-1}\,H_2SO_4$ and the second applying a.c. in $30\,g\,l^{-1}\,H_3BO_3 + 30\,g\,l^{-1}Ni(CH_3COO)_2 + 10\,g\,l^{-1}(HOCH_2CH_2)_2NH$. During the d.c. electrolysis a barrier layer containing pores forms on the aluminium surface [2]; the a.c. electrolysis produces the deposits at the bottom of the pores. The system produces anodized coatings having various colours dependent on the a.c. electrolysis time.

Under identical conditions of d.c. electrolysis, substitution of either $H_2SO_4$ or oxalic acid for $H_3PO_4 + H_2SO_4$, and various metal salts for nickel acetate also yields multicolours. The latter is shown in Table 2. The formulations containing stannous sulphate or cobalt sulphate gave shades similar to those in test E.

The typical change of shade of the coating obtained by increasing the duration of a.c. electrolysis is shown in Fig. 1a,* which was taken from the direction normal to the base of the coating. Fig. 1b was taken obliquely (~ 45°). It can be seen in the photographs that the shade of the colours of the coating varies continually with the a.c. electrolysis time and finally ends up black. The photographs indicate that the colours depend on the direction of observation and it seems that the colour of any area in Fig. 1a and that of the corresponding area in Fig. 1b are complementary for each colour.

According to Miyata and Kujirai [16], hygroscopicity of the coating increases with decreasing thickness of the coating, and the water-retaining power of the coating increases at a humidity higher than 60%. In the present work, the original colour of the coating changed when the absorbed water content was higher than 60%. This phenomenon was observed for a longer period of time in an atmosphere of alcohol or acetone. When the coating had dried, the coating again showed the original colours. This phenomenon was very reproducible.

Figs. 2a–c show the plots of the colour difference scale, *L* (white–black), *a* (red–green) and *b* (yellow–blue), for the colour of the coating as a function of the a.c. electrolysis time at the optimum voltage (10–25 V). The samples were pretreated at different d.c. voltages for 30 min.

*Table 2. Formulations of the electrolytes in which various metal salts are substituted for the nickel salt in system 5 of Table 1, and the colours developed on the anodized coatings.*

| *Formulation* ($g\,l^{-1}$) | | *Colours developed* |
|---|---|---|
| $SnSO_4$<br>$H_3BO_3$<br>$(HOCH_2CH_2)_2NH$ | 10–40<br>5–20<br>1–10 | pink, blue, brown, yellow, orange, red, green, reddish brown, dark reddish brown, yellowish green, black |
| $FeSO_4$<br>$H_3BO_3$<br>$(HOCH_2CH_2)_2NH$ | 10–40<br>5–20<br>1–10 | reddish brown, green, yellowish green, yellow, black |
| $CoSO_4$<br>$H_3BO_3$<br>$(HOCH_2CH_2)_2NH$ | 10–40<br>5–20<br>1–10 | brown, bluish purple, green, yellow, orange, reddish purple, yellowish green, dark reddish brown, black |
| $CuSO_4$<br>$H_3BO_3$<br>$(HOCH_2CH_2)_2NH$ | 10–40<br>5–20<br>1–10 | yellow, yellowish blue, reddish brown, pale yellow, pale yellowish green, blue, brown, dark brown, dark reddish brown |

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* Colour photographs are available from the author on request.

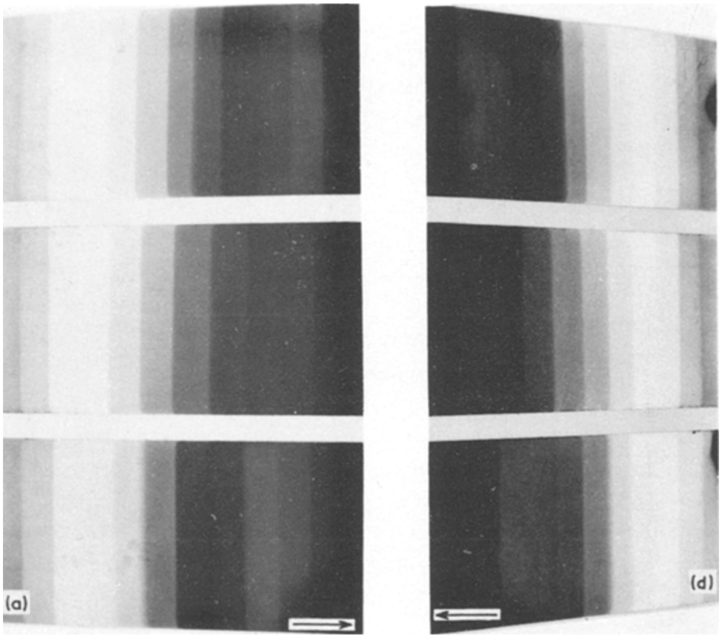

Fig. 1. Various colours developed on the anodized coating, with increasing a.c. electrolysis time. (a) Taken from the direction normal to the surface; (b) taken obliquely (arrow indicates increasing a.c. electrolysis time).

In Fig. 2a, the coatings can be classified into two groups: one containing those from the pretreatments at 5 V and 30 V, and the other for the coatings from 10 V, 15 V, 20 V and 25 V. The visually observed colour of the coating obtained by d.c. electrolysis at the voltages of the first group was not multicoloured. In the case of 5 V, the colour changed from dark brown, through bluish brown, to yellowish brown, while in the case of 30 V, the coating was slightly bluish green. On the other hand, the coating obtained from the d.c. electrolysis at the voltages of the latter group was multicoloured, similar to a rainbow. The $L$-value increases with increase of the d.c. electrolysis voltage and the higher the voltage, the faster the colour development. Sato *et al.* [17], who studied the relation between the a.c. electrolysis duration and the $L$-value of the colour of the coating prepared by the Asada method [5–7], indicated that the $L$-value decreased exponentially with increasing a.c. electrolysis duration. Comparing the present results and the results of Sato *et al.* [17], it seems that the mechanism for the formation of the deposits in the present work is different from that in the usual method [5–7].

In Fig. 2b, the coatings can again be classified into two groups: coatings from the d.c. electrolyses at 5 V and 30 V, and those at 10 V, 15 V, 20 V and 25 V. In order to avoid complication, the curves for 5 V and 30 V are not shown in Fig. 2b. The curves indicate that the colours of the coating developed after 150–180 s of a.c. electrolysis following d.c. electrolysis at 10 V, 15 V, 20 V and 25 V change from red to green; this was also observed visually.

In Fig. 2c, only the coating from the pretreatment at 15 V shows a different trend. Except for the sample pretreated at 15 V, the coatings developed by a.c. electrolysis for 60–120 s indicated colours of blue to yellow, as observed by the naked eye.

The variation of the visually observed colours of the coating obtained by d.c. electrolysis at 25 V with an increase of a.c. electrolysis duration can be represented as follows:

> dark brown → blue → yellow → orange → red → dark reddish green → green → dark reddish purple.

The colours of the deposits, prepared by dissolving the coatings produced as in Fig. 2, are shown in Fig. 3.

As can be seen in Fig. 3a, except for the curves for 5 V and 30 V, all the curves show a similar trend. In the present case, unlike the results shown in Fig. 2, the dependence of the $L$-value on electrolysis time is complex. However, the colours

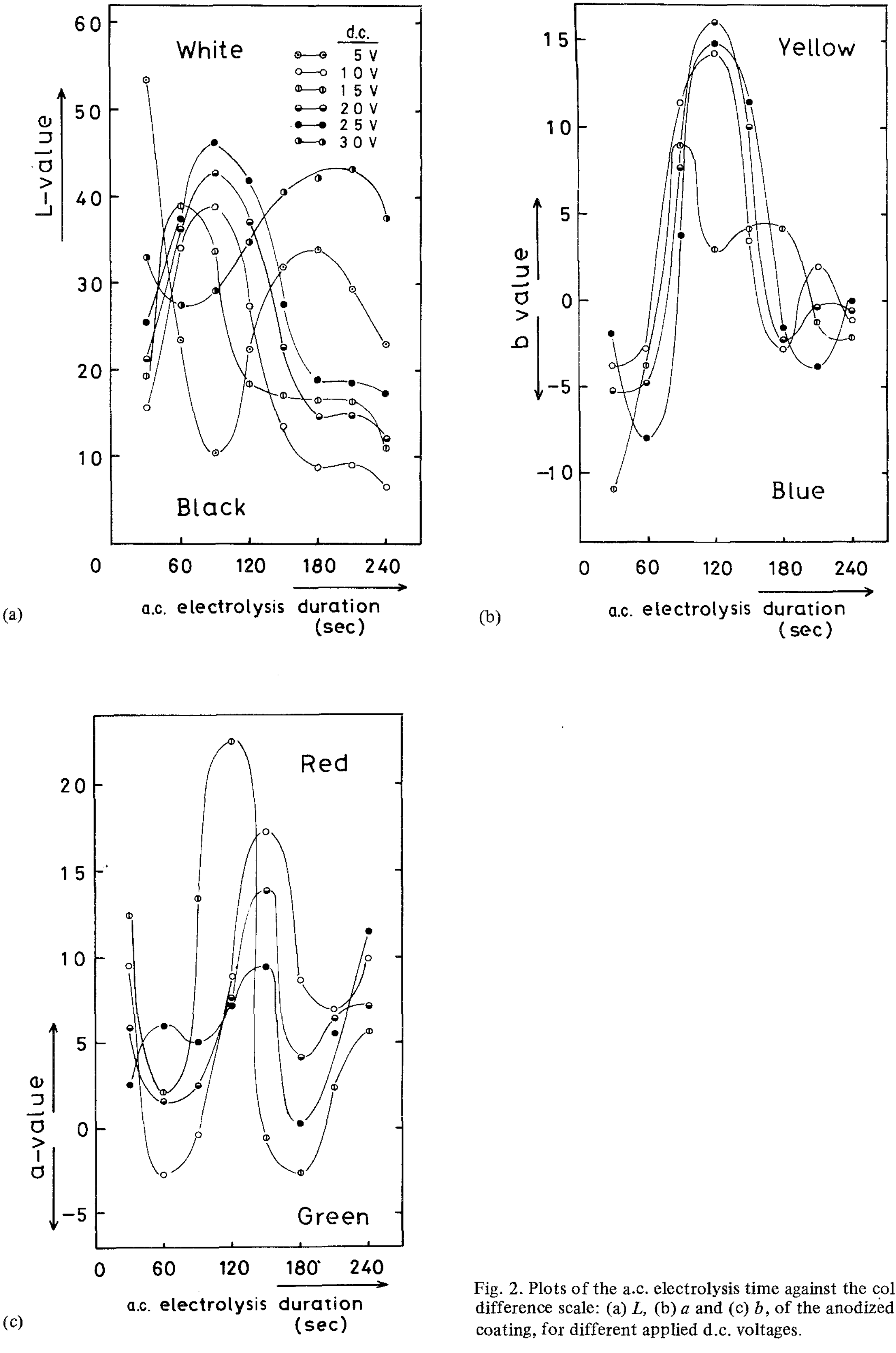

Fig. 2. Plots of the a.c. electrolysis time against the colour difference scale: (a) *L*, (b) *a* and (c) *b*, of the anodized coating, for different applied d.c. voltages.

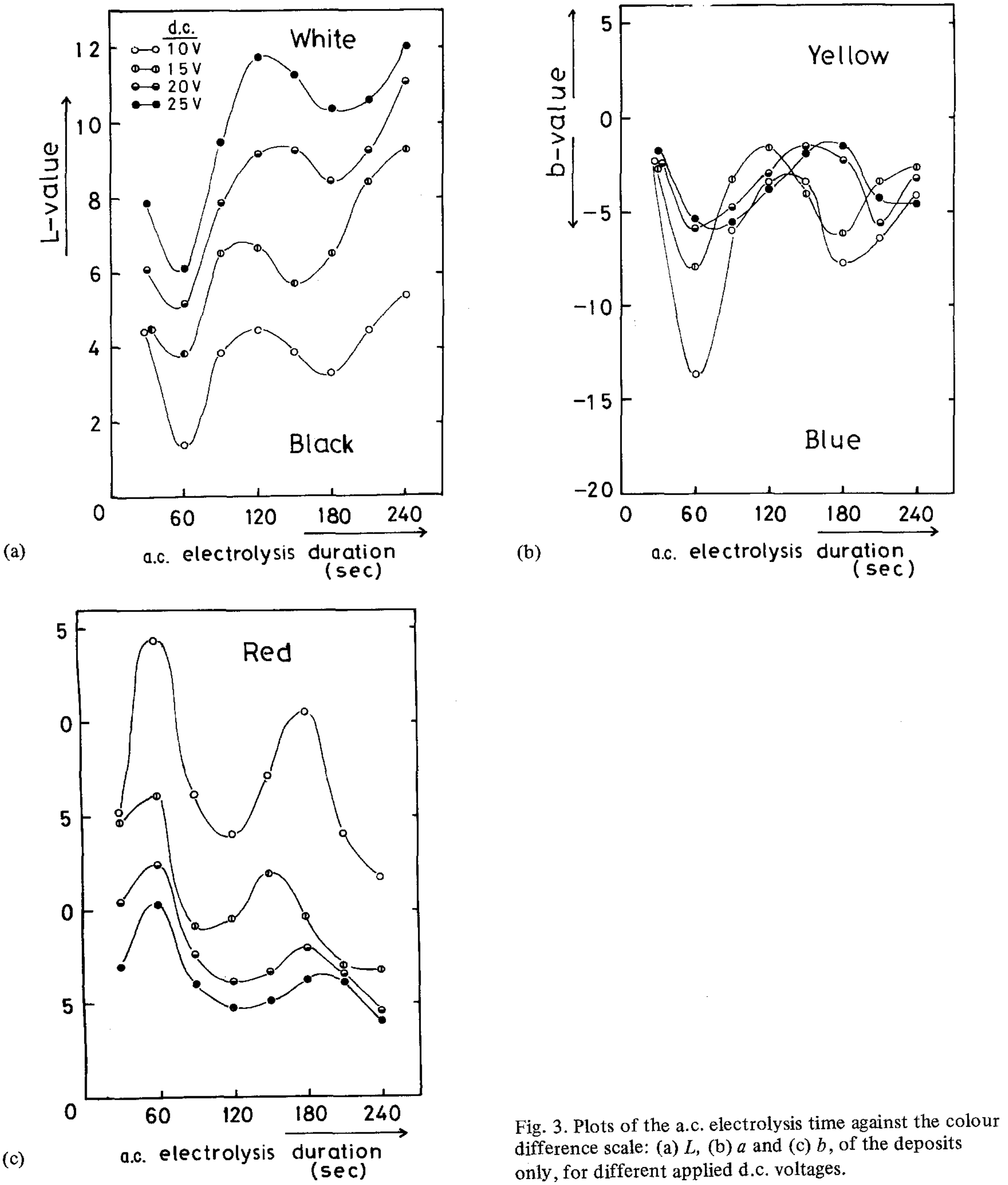

Fig. 3. Plots of the a.c. electrolysis time against the colour difference scale: (a) $L$, (b) $a$ and (c) $b$, of the deposits only, for different applied d.c. voltages.

suggested always disagree with those observed by visual examination, probably due to the fact that the colours identified along the direction normal to the surface of the sample are different from those identified obliquely.

In Fig. 3b, the curve for 10 V shows a higher $a$-value compared with the other three voltages. However, not much difference was observed by visual identification of the colour of the anodized coatings obtained by d.c. electrolysis at 10 V, 15 V, 20 V and 25 V and no greenish colour was observed in any of the samples, even by visual identification.

In Fig. 3c, all the curves have negative $b$-values and show almost the same trend. However, the colours of all the samples were observed visually to be bright yellow and blue. It is possibly due to

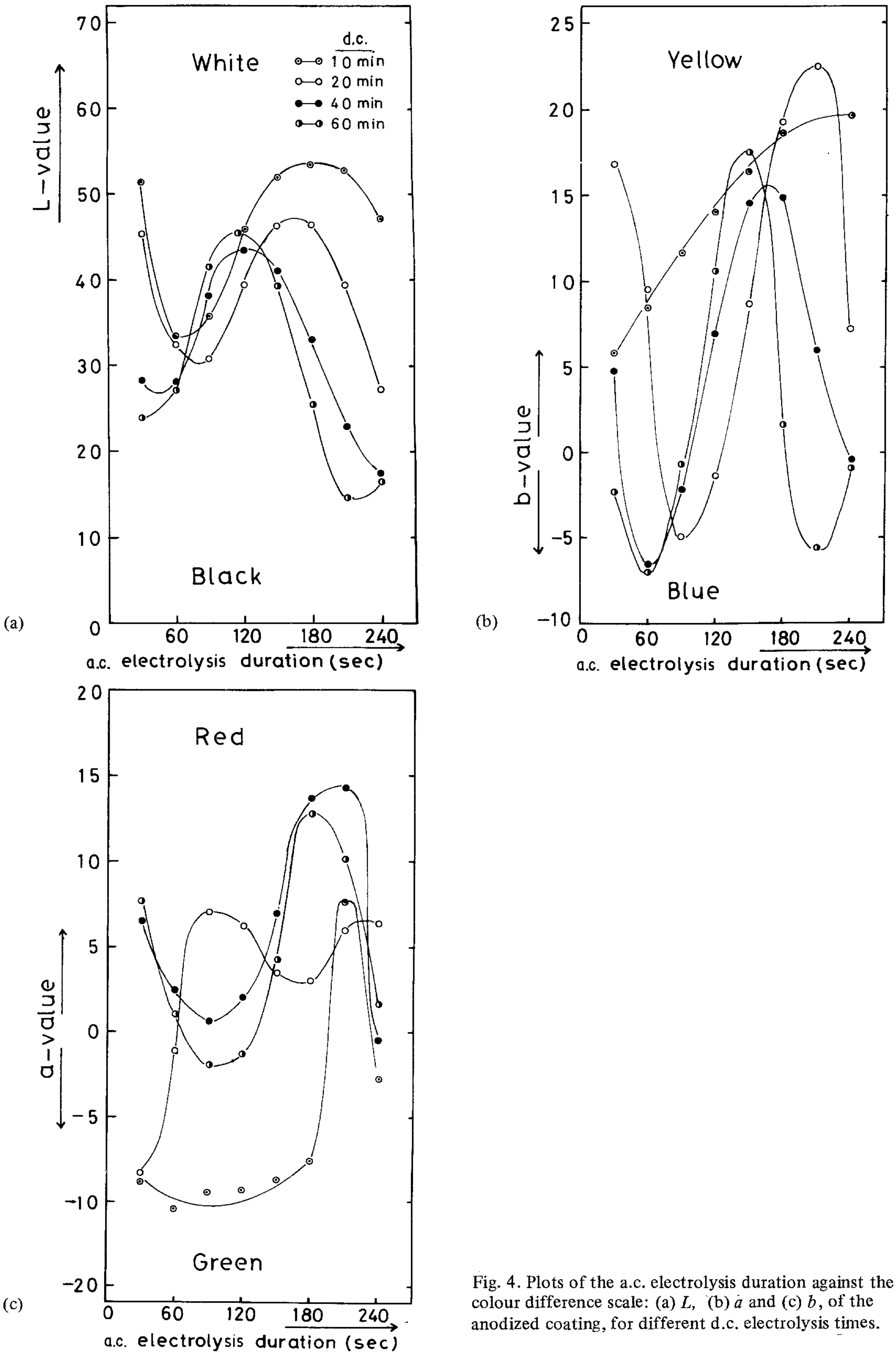

Fig. 4. Plots of the a.c. electrolysis duration against the colour difference scale: (a) $L$, (b) $a$ and (c) $b$, of the anodized coating, for different d.c. electrolysis times.

the effect of the direction of observation, as observed previously in Figs. 1a and b.

The variation of the colours of the deposits prepared by dissolving the coating obtained by d.c. electrolysis at 25 V, with increase of the a.c. electrolysis time can be represented as follows:

bright brown → brown → bright blue →
bright chocolate → chocolate → dark → black.

The colour of the deposits only is not identical to that of the coating except when pretreatment was at 5 V. Furthermore, the colours of the coating, which had been obtained by d.c. electrolysis at 5 V and those of the deposits only were found to vary similarly with increasing a.c. electrolytic duration. The effect of prolonged d.c. electrolysis (e.g. 10, 30, 80 and 120 min) at a constant voltage of 5 V, on the variation of the colour of the coating with increasing a.c. electrolysis duration was therefore studied. The results indicated that neither the multicolours, nor the change of the colour due to the direction of the observation was dependent on the pretreatment time.

From the results of the above experiments, the colours of the coating obtained by d.c. electrolysis at 25 V appear to be promising. Therefore, the dependence of the a.c. electrolytic duration on the colour of the anodized coating formed by pretreatment at 25 V was examined. The plots of $L$, $a$ and $b$ of the colours obtained against the a.c. electrolysis time for coatings formed at different durations of d.c. electrolysis are shown in Fig. 4.

All the curves in Fig. 4a show similar trends, although there are time lags in the change in $L$-value. In Fig. 4b the $a$-value changes irregularly for the sample pretreated for the shorter time (10 min), while the curves for the longer times (20, 40 and 60 min) show a different tendency.

The colours of the coating obtained through the d.c. pretreatment for 20 min were observed visually to vary from purple to orange and those for 40 min and 60 min vary throughout the colour range. In Fig. 4c the curve for 10 min d.c. pretreatment has a different trend and the colours obtained under this condition were identified visually to vary from yellow to dark yellow. The curve for 20 min and those for 40 min and 60 min show different trends. The visually observed colours of the coating from the latter case (40 and 60 min) were almost similar to the colours which can be expected from each corresponding curve. However, those from the former case (20 min) were not the same as anticipated from the curve.

As expected from both Figs. 4b and c, the colour of the anodized coating obtained by d.c. electrolysis for 10 min was observed visually to change continuously from light green to various shades of yellow with increasing a.c. electrolytic duration and that for 20 min d.c. electrolysis changed in the same way from purple to orange. On the other hand, the colours of the coating obtained from d.c. electrolysis for 40 min and 60 min were similar to those of the rainbow.

The dependence of a.c. electrolysis time on the change of current density of a.c. electrolysis was studied for the samples pretreated at various d.c. electrolysis voltages for 40 min duration. These are depicted in Fig. 5, from which it is seen that as the d.c. electrolytic voltage increases, the a.c. current density decreases. This is probably due to the well-known fact [1, 2] that increasing the d.c. voltage increases the thickness of the barrier layer formed beneath the pore bases in the coating. When the applied d.c. voltage is between 5 V and 10 V, the a.c. current density decreases continuously with duration of the a.c. electrolysis. This may be due initially to an increase of electrical resistance of the deposits, which eventually becomes almost constant although the deposits are still continuously growing. On the other hand, the curve for the run made under the conditions of the usual method [5–7], also shown in Fig. 5, indicates that the initial current density of the a.c. electrolysis is much higher than for the other curves and with increasing a.c. electrolysis duration, the a.c. current density decreases rapidly for a certain time, then decreases continuously and gradually. In the present method, however, the curves for the runs made at 20 V and 25 V of d.c. electrolysis indicate that the current density reaches an almost constant value within ~ 1/2 min of the a.c. electrolysis, i.e. the electrical resistance does not change although the deposits are continuously growing. Moreover, the curve for the run made at 30 V d.c. electrolysis indicates that as the a.c. electrolysis time increases, the current density increases to some steady value, and the surface obtained appeared to be spotty due to plating [18] rather than a coloured coating.

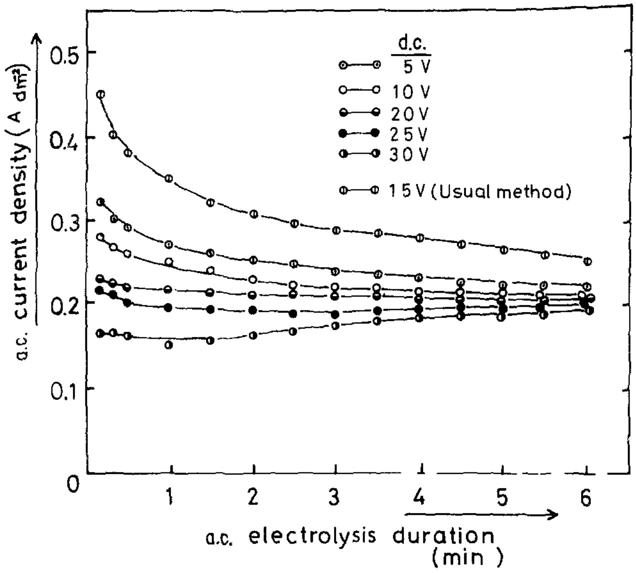

Fig. 5. Plots of the a.c. current density against the a.c. electrolysis time, for different applied d.c. voltages.

The microstructure of the deposits and the pores in the coating were observed electron-optically. The scanning electron micrograph in Fig. 6 illustrates the surface and the sectional view of the coating obtained by d.c. electrolysis at 22° C, 25 V, 0·08 A $\mathrm{dm}^{-2}$ for 60 min. The thickness of the original porous anodic film is ~ 0·7 $\mu$m. The formation of the rugged surface, which is not reported for the usual d.c. anodizing conditions [1], is shown in the micrograph. Fig. 7 shows the deposits prepared by dissolving the coating obtained by a.c. electrolysis at room temperature, 11 V, 0·2 A $\mathrm{dm}^{-2}$ for 180 s, through the d.c. pretreatment run under identical conditions as Fig. 6. It can be seen that many tiny columns grow uniformly. One of these columns was examined at higher magnification (shown in Fig. 8), from which the column is found to consist of fine particles, together with another different material. From electron diffraction patterns, the fine particles were identified as nickel metal and the material probably as amorphous nickel oxide and/or hydride. Also, the columns rich in the fine

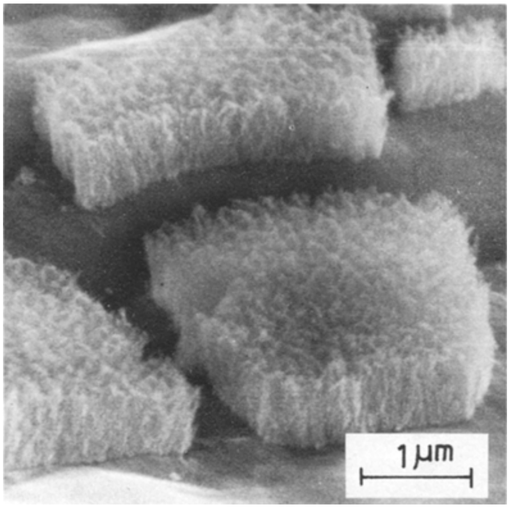

Fig. 6. Surface and sectional view of the anodized coating.

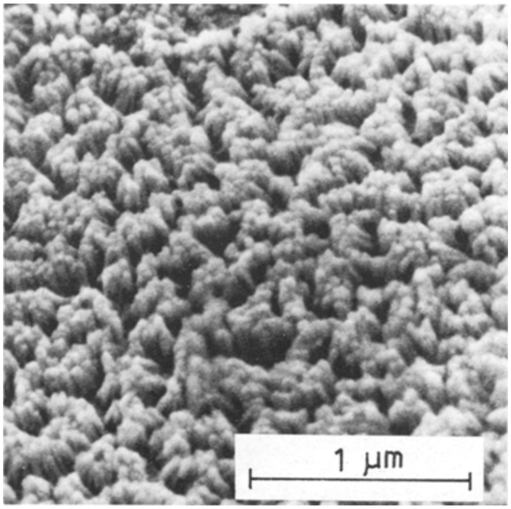

Fig. 7. Deposits, prepared by dissolving the coating, showing the growth of many columns.

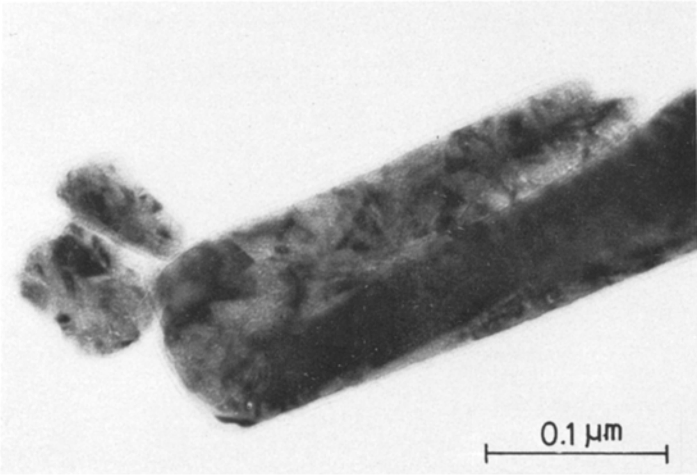

Fig. 8. The column composed of fine particles, together with amorphous material.

particles were detected to be magnetic and this fact supports the above identification. Unlike the deposits obtained from the usual method, in which most of the needle-like crystals grow in clusters along the parallel-sided pores, the particles formed in the present method have various shapes and they have no specific orientation.

Most of the metallic ions in the electrolyte are reduced [19, 20], and form the deposit at the bottom of the pores [21]. The deposits obtained from the usual method are reported to be grainy or plate shapes depending on the pore size, pore shape, electrolysis conditions, and the salt employed, and are composed of either the metal or metal oxide [22–26]. Baba [27] studied the mechanism of formation of the deposits by measuring the mobility of the ions in the pores using electrostenolysis and a completely oxidized coating was employed as a diaphragm. He concludes, however, that the mechanism could not be clarified unless the relationship between the current density of the a.c. electrolysis and the movement of the ions in the pores is known. No experimental work to elucidate the formation mechanism of the deposits was conducted in the present study.

Some explanation for the cause of the colouring of the anodized coating, such as the colloidal theory of the metals deposited at the bottom of the pores [3, 28] and the optical scattering theory on the dispersion of the metal particles [29, 30], has been made. However, the present experimental observation supports the idea that the colouring can be controlled by the electrolysis conditions, and it is possible that the colouring is due to the interference caused by the dimensional difference between the deposits and the pores.

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