

## ANODISING OF ALUMINIUM

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A mixture of alcohol and water containing suitable amount of sodium hydroxide has been investigated as a new electrolyte for anodising of aluminium articles. The anodised film developed with this electrolyte is more transparent compared to those of other processes and can be dyed subsequently by the usual techniques.

Aluminium metal on being exposed to air is readily covered by a thin film of aluminium oxide (or aluminium hydroxide) formed by atmospheric oxidation of the surface molecules.<sup>1</sup> This atmospheric oxidation soon stops due to the great hindrance offered by the film. Although the natural film thus formed possesses the anti-corrosive and antiabrasive properties, yet it is too thin and can be easily damaged. The thickness of the film and hence its anti-corrosive and anti-abrasive properties can, however, be improved to be of commercial importance by an electrolytic process which is technically known as anodising. In anodising, the aluminium article is made the anode in a suitable bath and when an electric current is passed, the thickness of aluminium oxide is increased due to the active oxygen liberated at the anode during the process. Another important property of the film produced through anodising (or anodic oxidation) is its capability of absorbing different dyes and pigments. This property provides a new basis in the decorative industries.

Anodising of aluminium was first developed by Bengough and Stuart who got two patents in 1923,<sup>2</sup> one for anodising of aluminium articles in a solution of chromic acid and the other to treat the anodised surface immediately with a solution of a suitable dye (e.g. alizarine red) to colour it. Later on, many other electrolytes were developed for anodising aluminium although chromic acid, sulphuric acid and oxalic acid are the only three which are enjoying commercial importance. In the present investigation, sodium hydroxide dissolved in a mixture of alcohol and water has been used as the electrolyte to achieve this purpose.

### Experimental

**Materials.**—(1) Aluminium strips of 99.9% impurity. Their surface area varied from 4 sq. inches to 8 sq. inches. They served as anode. (2) Two lead plates, each being 4" × 3". They served as cathode. (3) Commercial grade sodium

hydroxide and methanol. These chemicals were used in the anodising bath. (4) Apparatus including voltmeter etc. This is shown in Fig. 1.

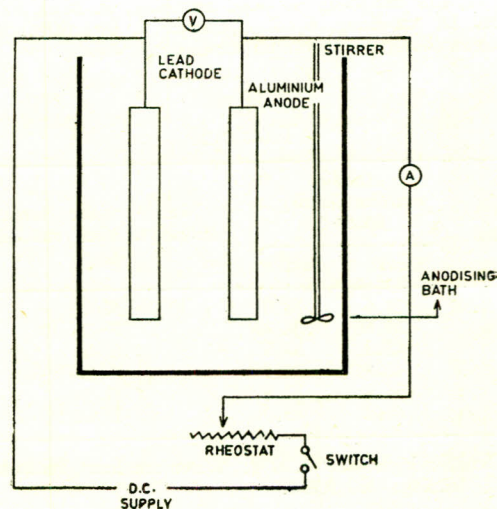


Fig. 1.

### Procedure

Anodising effect was first studied in aqueous solution containing sodium hydroxide. The concentration of sodium hydroxide was gradually increased after each observation, keeping the voltage, temperature etc. constant. Anodising effect and the operating conditions are shown in Table 1.

In the second experiment, the optimum concentration of sodium hydroxide, as found in the first experiment, was fixed and anodising effect was observed by varying the voltage. The results and the operating conditions are recorded in Table 2.

TABLE 1.

Na OH (g.)	Anodic Current Density (asf)		Nature of the surface developed after anodising*
	Initial	Final	
0.4	10.80	6.48	I
0.8	16.20	10.80	I
1.2	22.32	15.12	I
1.6	29.52	23.04	D
2.0	36.00	28.08	F+B
2.4	45.00	37.80	F+B
2.8	50.40	39.60	G+B
3.2	55.80	43.20	O+B
3.6	57.60	46.80	F+B
4.0	59.40	52.50	D+B

Water, one litre. Voltage, 15 volts. Temperature 25°C. Stirring, 360 RPM.

\*F, Fair anodising, G, Good anodising; B, Black film formation; D, Anodising of full appearance; I, Irregular anodising; N, No anodising; O, Optimum anodising; P, Pitting.

TABLE 2.

Voltage (Volts)	Anodic Current Density (Asf)		Nature of the surface developed after anodising
	Initial	Final	
4	21.6	18.0	N
10	39.60	28.80	F+B
13	43.2	30.6	G+B
15	46.8	32.4	F+B
20	55.8	37.8	D
25	61.2	45.0	D

Sodium hydroxide, 3.20 g; Water one litre; Temperature, 25°C.; Stirring; 360 RPM.

The effect of anodic current density on anodising was studied in the third experiment by applying external resistance and keeping other variables like voltage, concentration of sodium hydroxide etc. constant. The observations are given in Table 3.

TABLE 3.

Initial Anodic Current Density ( asf )	Nature of the surface developed after anodising
10.8	I + B
21.6	I + B + N
32.4	I + B
43.2	G + B

NaOH, 3.20 g; Water, one litre; Voltage, 15 volts; Temperature, 25°C.; Stirring, 360 RPM.

In the next experiment, different ratios of water and methanol were used and the concentrations of sodium hydroxide and other variables were kept constant. Table 4 represents the observations and operating conditions of this experiment.

Finally the optimum conditions were established by taking the composition of water and methanol which gave the best results and varying the voltage for each observation. The results are noted in Table 5.

### Discussion

In all well known processes, low current densities (usually below 30 amp. per sq. ft.) favour the proper anodising of aluminium. Keeping this fact in view, very small concentrations of sodium hydroxide were tried for anodising. The results were found encouraging in that they absorbed organic dyes well after anodising. Various concentrations of sodium hydroxide were then tested by gradually increasing its amount and it was found that when the concentration was in the range of 3 to 4 g./litre, the results were good. The optimum amount of sodium hydroxide was found to be 3.2 g. and this amount was kept constant in all other experiments. It was also found, as it is clear from Table 3 that even a small external resistance caused a bad effect and that it was better to carry out the process at minimum voltage to get the required current density. From Tables 1,2 and 3, the following operating conditions were found to be the best.

Sodium hydroxide	= 3.20 g.
Water	= 1 litre.
Voltage	= 13-15 volts.
Anodic Current Density	= 43.2 asf.
Stirring	= 360 RPM.

It was noticed, however, that, in the above composition, a thin black film began to appear on the surface, the thickness of which went on increasing upto a certain limit, of course, with the passage of time. This black layer not only hindered the successful anodising but also deteriorated the original shine of the metal. This black film formation could not be avoided by changing the variables as voltage, current density, temperature or the concentration of NaOH. But in the presence of methanol (which is miscible with water in all ratios) this black film was totally checked without any other defect being observed. On the other hand, the anodised surface became more transparent.

TABLE 4.

Water ml.	Methanol ml.	Anodic Current Density asf.				Nature of the surface developed after anodising
		a	b	c	d	
20	980	18.0	—	—	0.07	N
40	960	18.0	—	—	0.07	N
60	940	18.0	0.28	0.72	0.50	N
80	920	18.0	0.50	1.35	1.15	N
100	900	18.9	1.98	3.06	2.70	F
120	880	18.9	2.70	3.96	2.70	F
140	860	18.9	2.70	4.14	2.70	G
160	840	18.9	3.06	4.14	2.70	O
180	820	18.9	3.06	4.14	2.88	G
200	800	18.9	3.06	4.14	2.88	I
250	750	18.9	4.68	6.48	3.24	I
300	700	19.8	5.04	6.48	4.23	I
350	650	22.32	12.24	13.68	4.32	I
400	600	22.50	10.80	14.40	0.72	I
450	550	28.80	15.30	18.90	0.36	N+B
500	500	46.80	19.80	21.60	9.00	I
550	450	46.80	21.60	23.40	9.00	I+B
600	400	46.80	25.20	28.80	14.40	F+B
650	350	50.40	23.4	25.2	16.2	G+B
700	300	43.20	21.60	25.20	18.00	I
750	250	54.00	21.60	26.10	18.00	G+B
800	200	54.00	28.80	34.20	24.30	G+B
850	150	64.00	34.20	39.60	28.80	G+B
900	100	54.00	28.80	32.40	25.20	G+B
950	50	54.00	39.60	45.00	37.80	G+B

Sodium hydroxide, 3.2 g.; Voltage, 15 Volts; Temperature, 25°C.; Stirring, 360 RPM.

TABLE 5.

Voltage (Volts)	Anodic Current Density asf.				Nature of the surface developed after anodising
	a	b	c	d	
5	9.90	1.26	2.34	1.44	G
10	11.70	1.44	2.70	1.62	G
15	18.00	2.16	3.60	2.52	O
20	25.20	2.16	3.60	2.52	F+P
25	34.20	2.16	3.60	2.52	D+P
30	43.20	2.16	3.60	2.52	D+P

Sodium hydroxide, 3.20 g.; Water, 860 ml.; Methanol, 140 ml.; Temperature, 25°C.; Stirring, 360 RPM.

Various compositions of methanol and water were investigated to find out the optimum composition. During this investigation, one peculiar thing was noticed that the moment the current

was switched on, the current density shot to a considerably high value, then suddenly dropped to a sufficiently low point, again increased and finally dropped to the minimum slowly and gradually. All this becomes clear if we just have a look on Table 4. This peculiarity was also observed when methanol was replaced with ethanol. It was also observed that potassium hydroxide gave as good results as sodium hydroxide. Finally, the following operating conditions were established to be the optimum:

Sodium hydroxide = 3.2 g.  
 Water = 140 ml.  
 Methanol = 860 ml.  
 Voltage = 13-15 volt.  
 Anodic Current Density = 5-3 asf.  
 Stirring = 360 RPM.

In addition to ethanol, methanol was also replaced by the following solvents and these were tried for anodising under the same optimum conditions: n-propanol, n-pentanol, Glycol, Glycerol and Acetone.

Among these, ethanol was the only solvent which could be used successfully although it was not as good as methanol. With n-propanol the anodic oxidation was lowered to a very small extent. The remaining compounds gave negative results.

In the said composition, it was found that tap water gave bad results. That this was due to

calcium and magnesium salts was proved when distilled water was used alongwith calcium chloride or magnesium sulphate and anodising ceased to be successful. Contrarily, sodium aluminate or alumina when present in the bath facilitated the proper anodising.

#### References

1. W. A. Kochler, *Principle and Applications of Electrochemistry* (John Wiley & Sons, Inc., Chapman & Hall, Ltd., London), vol. II, p. 541.
2. G. D. Bengough and J.M. Stuart, British Patent 223,994 and 223, 995, Aug. 2, 1923 (C.A., 19, 1101 (1925)).