CCCCXIX.—*Surface Oxidation of Aluminium, Tungsten, and Molybdenum.*

By LEONARD CHARLES BANNISTER.

VARIOUS investigators have obtained colours on aluminium anodes and ascribed them to interference tints (Zimmermann, *Trans. Amer. Electrochem. Soc.*, 1904, **5**, 147; Mott, *Electrochem. Ind.*, 1904, **2**, 268), and Tammann (*Z. anorg. Chem.*, 1920, **111**, 78; *et seq.*) has used a similar assumption as a basis for much quantitative work on various colours on metals. Moreover, Evans has obtained evidence in support of this view in the cases of films on lead, iron (*Proc. Roy. Soc.*, 1925, *A*, **107**, 234), and copper (J., 1925, **127**, 2484). On the other hand, the sequence of colours obtained on tungsten by anodic treatment has been attributed by Koerner to the formation of different oxides (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 221). The present paper aims at reconciling the discrepancies in the cases of aluminium and tungsten and describes the extension of the investigation to the case of molybdenum.

EXPERIMENTAL.

In order to determine whether an optical colour sequence was produced, a film varying regularly in thickness was formed on a single piece of each metal in the following way. The metal, abraded with emery, was made the anode, and a platinum wire used as the cathode. The electrolyte was delivered into the cell in a fine jet of solution, filling it up at a slow but uniform rate. At the same time the voltage was steadily decreased, each successive portion of the metal being thus subjected to a different potential. Examination of the dried anodes showed that on aluminium and on tungsten there had been produced a film which displayed a series of colours, each merging into the next as usual in interference colours. In the case of molybdenum, a strip was placed horizontally in the electrolyte between a cathode and an anode of platinum without making metallic contact with them. After the current had passed for a short time, one half of the strip (the cathodic end) was still quite bright, but the other half was covered with a film which increased in thickness from the centre to the end, and produced a series of coloured bands merging into a black deposit. Therefore, under the influence of a potential gradient, the metals will exhibit an appearance similar to that produced on steel by tempering, which is dependent on a heat gradient.

Heat Tinting in Air.—It is difficult, if not impossible, to obtain on aluminium a colour sequence by heating in air. On tungsten, on the other hand, a sequence was produced by heating one end of a strip and so producing a temperature gradient along it. The thickest part of the film consisted of a black powder which turned yellow in parts after prolonged heating at a higher temperature. The films showing first- and second-order colours, irrespective of the method of production, were extremely hard, and resembled the anodic films of aluminium in this respect. They could be scratched with a diamond, but not with a steel blade; they could be removed with emery paper, but all attempts to obtain a quantity of the substance, by scraping it off the metal, failed owing to the minuteness of the deposit.

In order to preserve the heat tints on molybdenum, a strip of the metal was sealed up in a small glass tube and then heated at one end. The partial pressure of the oxide vapour set up within the tube prevented the resulting oxide film from volatilising, as it does when a piece of the metal is heated in the atmosphere.

When strips of freshly cleaned molybdenum were placed in a solution of potassium hydroxide containing dissolved oxygen, or in a solution of an oxidising agent such as potassium chlorate or nitric acid, the surfaces oxidised at rates depending on the temperature and the concentration of the oxidising solution. No visible films could be obtained by immersion in chromic acid, even at higher temperatures, and, incidentally, this treatment made subsequent oxidation by the other methods a slower process, doubtless owing to passivity caused by the presence of a very thin film, which is much more protective than films of interference thickness.

The colours were temporarily diminished in intensity by immersing the metal strips in liquids of high refractive index, showing that the mechanism is not the selective absorption of light.

It was found that if the thickness of a film were reduced to various extents by immersion for definite lengths of time in solvents, the colour also altered.

The foregoing observations lead to only one conclusion, *viz.*, that the film is an oxide film of variable thickness which can cause interference of light in the visible region of the spectrum and so produce colour.

Anodic Treatment.—A comparison is made of colour with voltage of formation (Tables I and II, for aluminium and tungsten, respectively) and with the number of coulombs (Tables III and IV). For aluminium it is possible to calculate the refractive index of the film.

TABLE I.

Anodic treatment of aluminium in $Na_2HPO_4,12H_2O$ (satd.) at 17°.

Voltage.	Colour.
40— 59	Pale yellow.
59— 69	Brown.
69— 77	Red.
77— 85	Purple.
85— 93	Blue.
93—107	Green.
107—120	Yellow.

TABLE II.

Anodic treatment of tungsten in *N*-KCl at 17°.

Voltage.	Colour.
10—21	Yellow.
21—25	Crimson.
25—28	Violet.
28—36	Dark blue.
36—56	Light blue.

TABLE III.

Aluminium (Area of anode, 38·05 sq. cms.).

Coulombs passed.	Thickness of Al_2O_3.	Colour observed.	Approx. wave-length of light missing.	Refractive index.
3·57	0·075 μ	Straw.	0·42 μ	1·73
4·14	0·087 μ	Brown.	0·46 μ	1·60
4·96	0·104 μ	Purple.	0·51 μ	1·59
6·50	0·136 μ	Violet.	0·56 μ	1·52

The values in the fourth column are the wave-lengths of the light complementary to the colour observed. The values obtained for the refractive index are in fairly good agreement with Cauchy's dispersion formula for transparent substances.

TABLE IV.

Tungsten (Area of anode, 4·0 sq. cms.).

Anodic treatment at 143 volts and 16°.

(*a*) In *N*-KCl.				(*b*) In *N*/100-KCl.	
Total coulombs.	Colour.	Total coulombs.	Colour.	Total coulombs.	Colour.
1·48	Yellow.	16·28	Blue.	0·275	Pale yellow.
2·96	Orange.	23·68	Pale green.	0·543	Crimson.
4·44	Purple.	26·64	Green.	0·803	Blue.
5·92	Crimson.	34·04	Deep yellow.	1·056	Light blue.
7·40	Violet.	41·44	Orange.		
11·84	Deep blue.				

Table IV shows that the process of film formation is more efficient when the conductivity of the electrolyte is considerably reduced.

Even if the specific gravity of the film were known, it would not be legitimate to determine the thickness from the amount of electricity passed, for the proportion of current used in film formation seems to vary with the concentration of the electrolyte, hence the refractive index of the film on tungsten is unknown.

The tables given by Koerner clearly indicate that his experiments were not conducted over a sufficiently wide range of conditions to lead to accurate conclusions. The evidence available suggests that the oxide is one lower than WO_3.

The Isolation of the Film.—By the method of Whitey and Millar (*J. Soc. Chem. Ind.*, 1926, **45**, 170T), the films on aluminium were isolated from their metallic base by volatilisation of the latter in a stream of hot hydrogen chloride, special precautions being taken to ensure the absence of traces of water vapour and air during the operation, for otherwise a white, chalky film of alumina was produced. Many of the specimens of film-covered aluminium showed a peculiar inertness towards the attacking gas, but it was observed that the reaction could be initiated by increasing the velocity of the current of gas. Unfortunately, the method was quite unsuccessful in isolating films from tungsten and molybdenum.

The phosphate content of the films was found to vary somewhat : in some, none was detected, and in others it was present up to 6%. It seems probable, therefore, that when phosphate or other acid radical is present, it is merely occluded or held in suspension within the pores of the film. When the films were heated to redness, a loss in weight of 4% took place, which indicates that they consist mainly of oxide with perhaps some water which became sealed within their pores during their growth.

The values for the ratio (Increase of anode weight during treatment)/(Weight of isolated film) were found to be 0·63, 0·58, 0·58, and 0·55 for four different anodes, whereas the theoretical value for O_3/Al_2O_3 is 0·47.

It may be noted that Sutton and Willstrop (*J. Inst. Metals*, 1927, **38**, ii, 259) have analysed the films formed on aluminium by standard anodic treatment in chromic acid, and have found them to consist of the oxide together with a trace of chromate.

The author wishes to thank Prof. W. C. McC. Lewis, F.R.S., by whose kind permission this work was done, Mr. W. J. Shutt, M.Sc., for practical advice, and also Mr. U. R. Evans, M.A., with whom subsequent discussion has been of great value.

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY,
UNIVERSITY OF LIVERPOOL. [*Received, October* 17*th,* 1928.]