Studies in Electrodeposition of Molybdenum for Solar Absorber Coatings

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MOLYBDENUM was electrodeposited from an ammonium molybdate bath on to different substrates like aluminium and galvanised iron, using a nickel anode. The specimens were normally heated to 250°C for 10 minutes after electrodeposition, prior to their use for spectral reflectance measurements. The stability of the coating after thermal treatment was generally good. Four different compositions of electrolyte containing Nickel sulphate or Nickel ammonium sulphate in addition to ammonium molybdate were used. The effect of variables like (a) current density (b) zincating time (c) deposition time and (d) etching of the aluminium substrate in different media prior to zincating, on the spectral characteristics has been studied. Scanning electron microscope observations on a few specimens show that zincated aluminium is a better substrate than galvanised iron.

SOLAR radiation as potential source of thermal energy is being widely debated at present. Several approaches to utilize solar energy efficiently and economically are being studied all the world over. Among these, chemical conversion coatings and electrodeposited coatings have received considerable attention, Electrodeposited coatings such as black Nickel and black Chromium have been studied in great detail and valuable data on their characteristics, limitations, and viability have been published. Black Nickel deposit as is generally known is a mixture of zinc and nickel sulphides codeposited, with very good spectral charecteristics desirable for use as solar absorber coatings. However the consideratton has been its stability both thermal and environmental. In this respect black chrome electrodeposits which are a mixture of chromium and chromium oxide have been found to be superior. However, maintenance and operational control for obtaining these deposits are more stringent compared to black nickel deposits,

The present investigation has been with a view to study if molybdemn coatings after thermal trearment could be comparable in their characteristics to black nickel and black chrome.

EXPERIMENTAL

Specimens $2\frac{1}{2}'' \times 2\frac{1}{2}''$ (6.35×6.35 cms) cut out of commercial aluminium and galvanised iron sheet were used in these experiments. The aluminium specimens were cleaned with several grades of emery paper upto 600 grade, washed in water, pickled in 10% Na OH, washed and dipped in 10% HNO_3 to obtain a bright surface, washed in distilled water and used immediately for zincating The zincating time was either 30 or 45 seconds. The specimens were then washed thoroughly and used for plating. The zincating time was varied to observe its influence on the spectral characteristics. The common bath was used for zincating. In the case of galvanised iron specimens, no mechanical treatment was given. The specimens were cleaned with a detergent to remove any likely grease or oil film washed with distilled water and used.

The bath compositions and the operating conditions are given in Tables 1 to 4. The spectral reflectance curves for the various specimens are given in Figures 1 to 4.

RESULTS AND DISCUSSIONS

The first bath (Table 1) was made up of ammonium molybdate and sodium hydroxide without any Nickel salt being added. The source of Nickel for codeposition of Nickel and molybdinum was the Nickel anode used.

(A) In serial numbers 3 and 5 two different etchants viz. 3 vol HNO_3 + 1vol HF and 10% V/V H_3PO_4 were used on the aluminium substrate before zincating. This was in addition to the usual treatment indicated earlier for aluminium. The plating time in S. No. 4 was increased to 3 minutes compared to S. No. 2.

From the reflectance curves (Fig. 1) it is observed that generally the rise in the spectral reflectance is in the region 2.5 to 3.5μ reaching a maximum in the range 48 to 65% at 22.5μ. The reflectance in the region 0.25 to 2.5μ is practically zero (almost 100% absorptance) which region is of interest for solar absorber coatings. The reflectance curve obtained in operation at a lower current density as on S. No. 1, for 2 minutes is

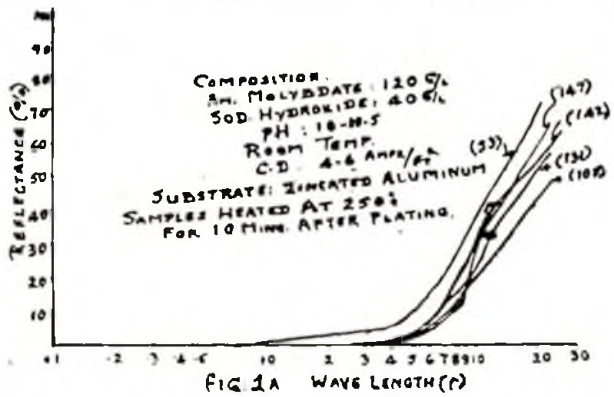


Fig 1A

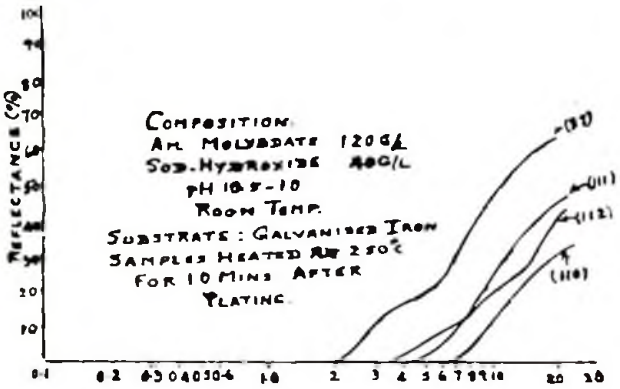


Fig 1B

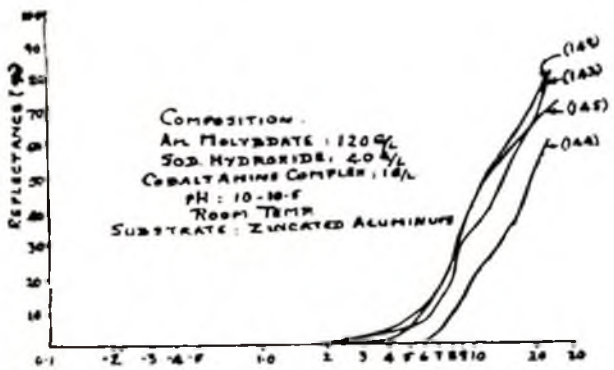


Fig 1C

better than that of operation at a higher current density as in S. No. 2 or for a longer time as in S. No. 4. Between the two etchants, 10% H_3PO_4 (S. No. 5) appears to be better in improving the characteristics over those on unetched specimens while operating at the higher current density of 4.6 amp/sq ft (0.46 amp/dm²).

(B) In the second set of experiments the substrate was galvanised iron. The plating time was kept constant and the current density was varied from 23 to 50 amps/ft² (2.3 to 5 amps/dm²). It was observed that the operating current densities are to be much higher in the case of galvanised iron, to obtain good deposits. This may be due to the iron substrate or the chemical surface conversion finished galvanised coating.

The reflectance curves are shown in Fig. 2. Curves obtained at higher current densities in the

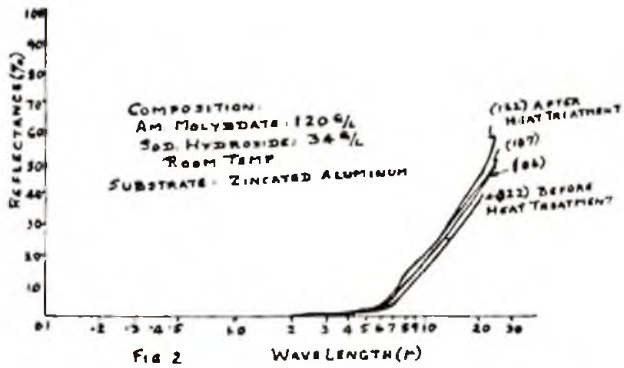


Fig 2

range 41.50 to 50 amp/ft², show poorer reflectance characteristics compared to the one operated at 23 amps/ft². In the case of S. No. 6 the curve rises at 2μ and the maximum reflectance is about 64% at 20μ. Scanning electron micrograph No. 1 shows the nature of the deposit obtained which appears flakey and cracked. (Similar is the nature of the micrograph No. 5 of another galvanised iron specimen in a different bath.)

(C) Addition of 1 g/L of cobalt as amine complex to the original bath improves the performance of the solution in that curves Fig. 3 show a reflectance of 80% at 22.5μ the rise in the curves

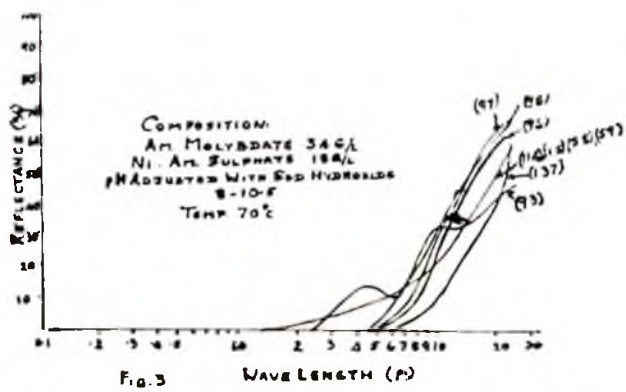


Fig. 3

starting around 2μ. Here again phosphoric acid compared to HNO_3 + HF, as etchant appears to improve the reflectance characteristics (compare S. No. 12 and S. No. 11). The increase in plating time does not also improve the characteristics. Comparing S. No. 10 and 13 it is observed heat treatment definitely improves the reflectance of the specimen all other conditions remaining the same. Scanning electron micrographs 2A and 2B show the globular type of deposit with cracks.

Similar micrographs 3A and 3B show almost identical deposits but slightly finer in grain size.

In the second composition studied the ratio of ammonium molybdate to sodium hydroxide was changed from 3 : 1 as in the first case to 3.5 : 1. The plating time was kept constant at 2 mins. and the current density and zincating time varied. The zincating time was increased to 45 seconds. in S. No. 15 as against 30 seconds used normally. In S. No. 108 the sample was not heated after plating unlike in S. No. 16A. Sample No. 16A deposited at a lower C.D. and heat treated shows a better reflectance curve than that obtained at higher C.D. Change in zincating time does not appear to influence the nature of the curve.

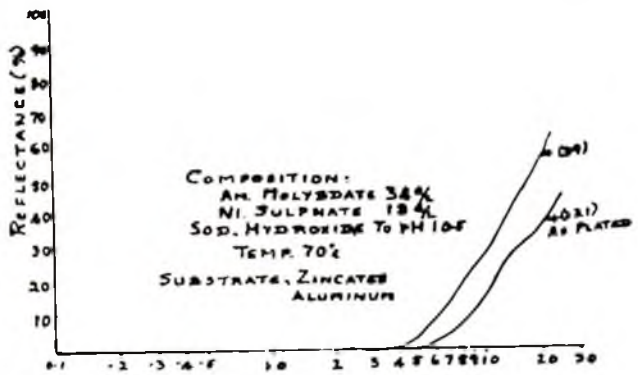


Fig. 4.

Scanning electron micrograph No. 4 of S. No. 16A shows an uniform spongy type of deposit without cracks, which is different from earlier ones.

The third composition studied contained Nickel ammonium sulphate with suitable adjustment of pH with sodium hydroxide, and the temperature was maintained at 70°C. The duration of plating, pH and the current density were varied. One sample was anodised prior to zincat- to observe the effect. Curves of specimens S. Nos. 17, 18, 22 and 23 are identical. This shows that none of these variables affects the reflectance. However plating in a lower pH range of 7-8 appears to improve the characteristics of the specimens. The three specimens S. No. 19, 20 and 21 show almost identical characteristics indicating that slight variation in plating time, or current density does not affect the reflectance. The maximum reflectance is of the order of 65 to 70% at 22.5μ. The identical curve for the first set of samples however rises from 1.5μ compared to 2.5μ in the latter case. Sample No. 24 etched in $HNO_3 + HF$ shows a poor reflectance curve compared to the rest indicating that it is not a desirable etchant, as also observed earlier. The reflectance curve obtained with the galvanised iron substrate is not quite regular in shape and the maximum reflectance at 20μ is around 45%. The scanning electron micrograph No. 5 also indicates the cracked nature of the deposit with a coarse structure and is unlikely to be an useful coated substrate.

In the fourth composition studied, Nickel sulphate was substituted for Nickel ammonium sulphate and the pH maintained at 10.5. The duration of deposition, the current density and temperature were kept constant. Two samples were plated : one heated at 250°C for 10 mins. and the other not heat treated. There is a marked difference in the refectancc curves obtained, in that heat treatment positively improves the characteristics. Incidentally the curve obtained from a heat treated specimen (S. No. 26) compares favourably with that obtained from S. No. 21 using bath containing Nickel ammonium sulphate.

Scanning electron micrographs No. 6A and B show discrete globular type of deposit with cracks similar to deposits in S.E.M. No. 2 and 3. The globules look prominent, projected over a smoother matrix. S.E.M. No. 7 A and B of the unheattreated samples show a smooth wavy al most directional cracked surface without discrete particles, Apparently heat treatment appears to modify the structure considerably.

Operating a bath containing ammonium molybdate with or without addition of Nickel as $NiSO_4$ or Nickel ammonium sulphate or cobalt, at low current densities with short plating times and at room or elevated temperature, it has been possible to obtain molybdenum deposits which show on heating for 10 minutes at 250°C spectral reflectance in the thermal region comparable to those of other electrodeposited black coatings. The ease of preparation, operation and maintenance of the bath is an advantage. It is perhaps possible to further improve the deposits to match those of black Nickel and Chromium in their reflectance characteristics.

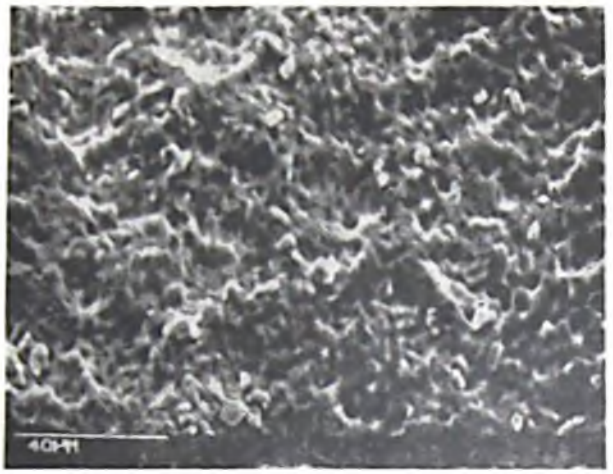


Fig. 4 Aluminium Substrate 500× (Zincated)
Bath : Table No. II, Sample No. 16 A

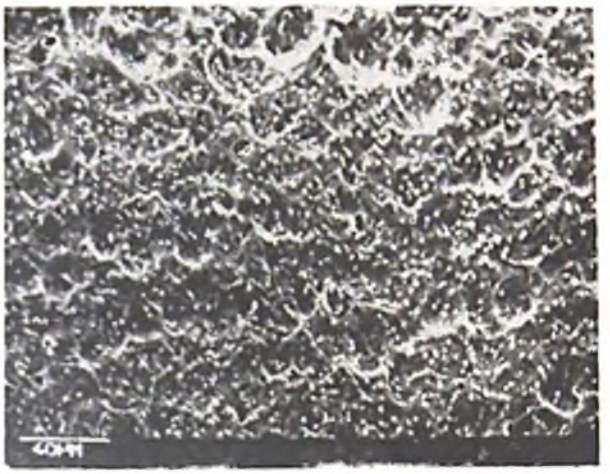


Fig. 6B. Aluminium Substrate 500× (Zincated)
Bath : Table No. IV, Sample No. 26

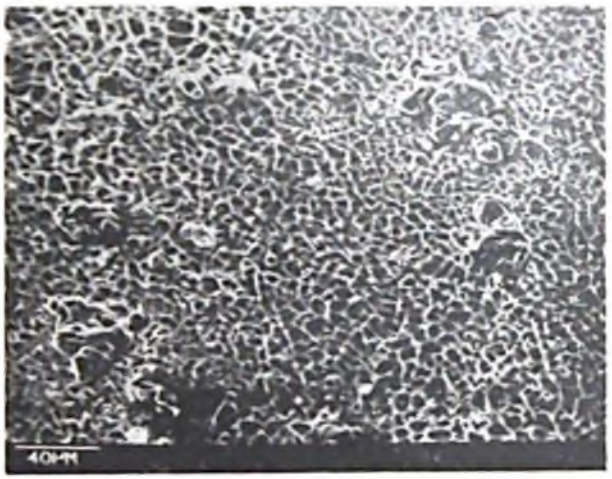


Fig. 5 Galv Iron Substrate 500×
Bath : Table No. III, Sample No. 25

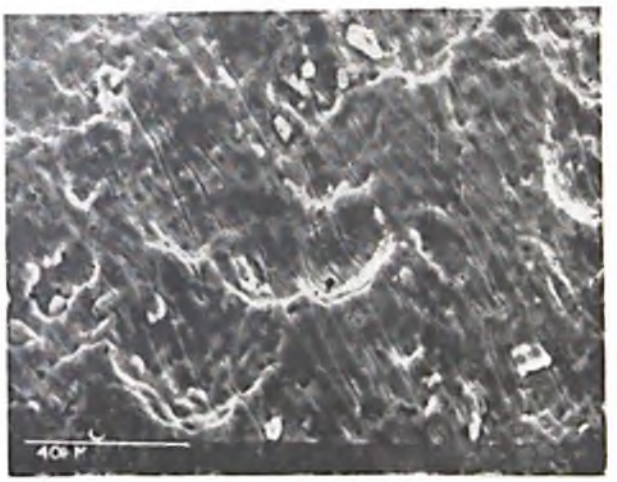


Fig. 7A Aluminum Substrate 500× (Zincated)
Bath : Table No. IV, Sample No. 27

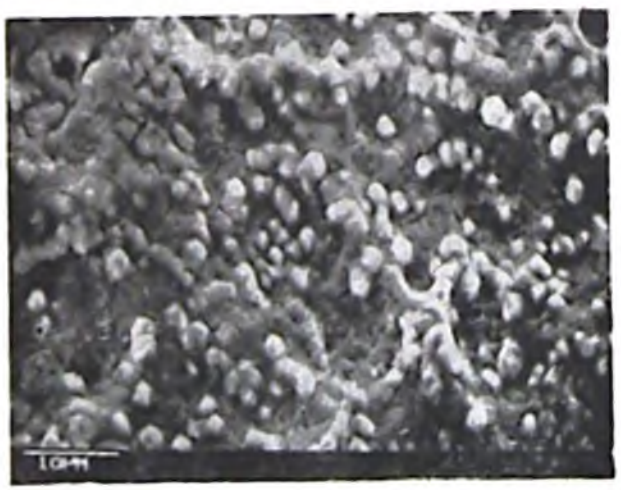


Fig. 6A Aluminium Substrate 2000× (Zincated)
Bath : Table No. IV, Sample No. 26



Fig. 7B. Aluminum Substrate 200× (Zincated)
Bath : Table No. IV, Sample No. 27

TABLE 1

Bath Composition

120 g/L Ammonium Molybdate

40 g/L Sodium Hydroxide

pH 10-10.5

Room temperature

A : Substrate : *Aluminium zincated Samples heated at 250°C for 10 minutes (Zincated for 30 seconds) after plating Anode : Nickel*

Sl. No.	Expt. No.	Plating time minutes	C.D. amps/ ft2	Remarks
1	53	2	2.3	
2	105	2	4.6	
3	131	2	4.6	Surface etched in 3 VolHNO_3 + 1 VolHF for 15 seconds before zincating
4	142	3	2.3	
5	147	2½	4.6	Surface etched in 10% v/v H_3PO_4 for 1 min. before zincating

B : Substrate : *Galvanised iron : Samples heated at 250°C for 10 mins. after plating ; time 2 mins. Anode : Nickel*

6	87	23.0	S.E.M. No. 1
7	110	41.5	
8	111	46.00	
9	112	50.00	

C : *Addition to the bath : 12 g/L Co as cobalt Amine complex. Substrate : Aluminium zincated Samples heated at 250°C for 10 mins. after plating except in S. No. 13. Zincating time : 30 seoonds*

Sl. No.	Expt. No.	Plating time minutes	C.D. amps/ ft2	Remarks
10	143	2½	2.3	
11	149	2½	2.3	etched in 10% H_3PO_4 for 3 mins before zincating
12	144	3	2.3	etched or 30 sec. in 3 Vol HNO_3 + 1 VolHF before zincating S.E.M. No. 2
13	145	2½	2.3	no heat treatmet S.E.M. No. 3

TABLE II

Bath Composition

120 g/L Ammonium Molybdate

34g/L Sodium Hydroxide

Room temperature

Substrate : *Aluminum zincated : Samples heated at 250°C for 10 minutes after plating except in S No. 168 Anode : Nickel. Plating time 2 minutes*

Sl. No.	Expt. No.	Zincating time	C.D. amp/ ft2	Remarks
14	106	30 secs	4.6	
15	107	45 ,,	4.6	
16A	122	30 ,,	2.3	Sample heated S.E.M No. 4
16B	122	30 ,,	2.3	Sample Not Heated

TABLE III

Bath composition :

34 g/L Ammonium Molybdate

18 g/L Nickel Ammonium Sulphate

pH adjusted between 8 and 10.5 with NaOH. temperature 70°C.

Substrate : *Alminum zincated except in S. No. 25 (galv. Iron base) samples heated at 250°C for 10 mins. zincating time 30 seconds Anode : Nickel*

Sl. No.	Expt. No.	Duration of deposition minutes	pH	C.D. amps/ ft2	Remarks
17	58	2	10-10.5	4.6	
18	59	3	10-10.5	2.3	
19	96	1½	7-8	4.6	
20	97	2	7-8	4.6	
21	98	2	7-8	2.3	
22	114	2	8.5-9	4.6	Anodised Al. base: anodising at 28 amp/ft2 for 40 minutes
23	115	2	8.5-9	4.6	
24	137	2	8.5-8	4.6	Sample etched for 30 secs. in 3 vol HNO_3 + 1 VolHF
25	93	3	9-10	41.5	Galv. Iron Substrate S.E.M. No. 5

TABLE IV

Bath composition :

34 g/L Ammonium Molybdate
18 g/L Nickel Sulphate
Sodium Hydroxide to pH 10.5
temperature 70°C

Substrate : *Almunium zincated for 30 seconds*
Anode : Nickel
Duration of deposition : 2 minutes
C.D. = 2.3 amps/ft²

Sl. No.	Expt. No.	Remarks
26	39	Sample heated at 250°C for 10 minutes. S.E.M. No.6
27	121	Sample as plated (not heated) S.E.M. No. 7

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