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## SOLAR SELECTIVE BLACK Ni-Cd ALLOY COATINGS FOR ELECTRO DEPOSITION

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INTRODUCTION.- Electrodeposited black coatings have generally been used for decorative purposes, however, the application of these black electrodeposits as solar selective coatings has been of great interest in the past 6 to 8 years. A variety of black coating such as black Ni, black Cr<sup>1-3</sup>, alloy coatings have been studied by many authors.

In this paper the authors report the development of black nickel-cadmium coatings as a selective surface for solar energy utilization. The effect of composition of the electrolyte and operating conditions on the appearance and performance of the coating has been studied.

EXPERIMENTAL.- The samples plated were 35x100 mm. metal pieces. Steel substrate were nickel plated to a thickness of 10 micras prior to deposition of black Ni-Cd. Nickel plating was carried out from a low concentration Ni electrolyte used in our previous studies.

Nickel sulfate .....	100	g/l
Cadmium sulfate .....	15	"
Ammonium thiocyanate ....	10	"
Coumarin .....	0,1	"
Formaldehyde .....	0,1	ml/l

All the Chemicals used were of laboratory reagent grade.

Electrolytic nickel anodes were used for both Hull cell studies and plating. To judge the quality of the coating under a spectrum of current densities, Hull cell experiments were carried out with standard 267 ml cell.

Hull cell studies were carried out changing the concentration of nickel, cadmium, thiocyanate, addition agents and operating parameters such as temperature, pH, current density and acid etching time on the appearance of the coating. The code for recording Hull cell is shown in Fig. 1.

The plated samples were subjected to thermal cycling tests corrosion studies were made with 5% sodium chloride neutral salt spray test.

concontent, keeping all other variables constant, is shown in Fig. 5. The concentration of ammonium thiocyanate was varied from 5 to 20 g/l.

**INFLUENCE OF pH.**— The solution pH was adjusted electrolytically using dilute sulfuric acid and ammonia and varied from 3 to 6. Fig 6. shows the Hull cell pattern at different pH values.

**THERMAL CYCLING TEST.**— To determine the coating's ability to withstand short term overheating due to failure to extract heat from the collector, this test was carried out by heating the panels in an electric oven to 300°C within 30 minutes and maintained for next 8 hours. This was carried out for 12 consecutive days.

**CORROSION RESISTANCE.**—

The corrosion resistance of the coating was tested with a 5% neutral salt spray test using steel plated with 10 microns nickel and black nickel-cadmium.

#### CONCLUSION

A black nickel cadmium selective coating has been

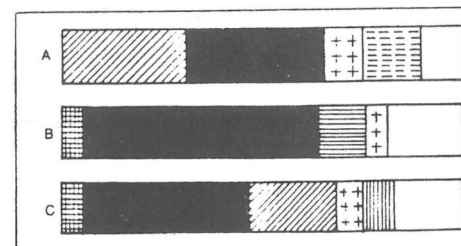


Fig. 4. Influence of nickel sulfate concentration. Nickel sulfate g/l: A) 50; B) 100; C) 150

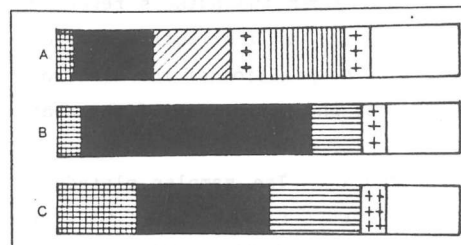


Fig. 5. Influence of ammonium thiocyanate concentration. Ammonium thiocyanate g/l: a) 5; b) 10; c) 20.

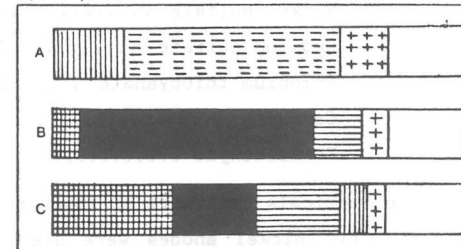


Fig. 6. Influence of pH. a) 3,5; b) 4,5; c) 6,0

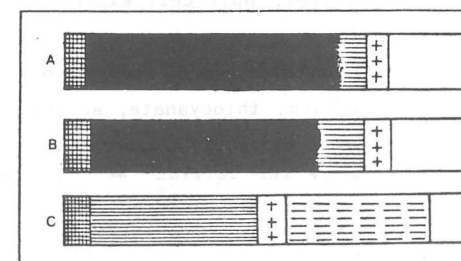


Fig. 7. Influence of temperature: a) 20°C; b) 30°C; c) 40°C

#### RESULTS AND DISCUSSION.

##### INFLUENCE OF ADDITION AGENTS.

Initial experiments were carried out in a number of electrolytes containing nickel sulfate, cadmium sulfate and ammonium thiocyanate. In all cases the coating was found to be streaky, non-uniform and coarse-grained.

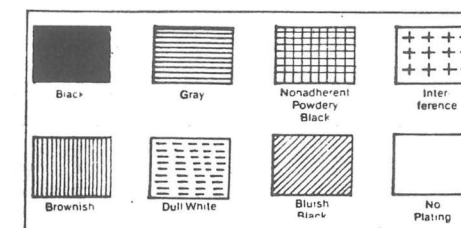


Fig 1. Code for recording Hull cell pattern.

To improve the quality of deposit various addition agents were incorporated in the solution, such as urea, thiourea, dihexil sulfosuccinate, coumarin with formaldehyde etc. Indicated that coumarin with formaldehyde is the best additive for promoting and adherent, uniform black coating.

##### INFLUENCE OF CADMIUM SULFATE CONCENTRATION.

The cadmium sulfate concentration was varied from 0 to 30 g/l by keeping the concentration of nickel sulfate 100 g/l, ammonium thiocyanate 10 g/l, coumarin 0,1 g/l, formaldehyde 0,1 ml/l, pH 4,5 and temperature 30°C.

##### INFLUENCE OF NICKEL SULFATE CONCENTRATION.

Nickel sulfate concentration was varied from 50 to 150 g/l.

Figure 4 shows the Hull cell pattern using 2 A Hull cell current for 60 seconds.

**INFLUENCE OF THIOCYANATE CONCENTRATION.**— The effect of variation of thiocyanate

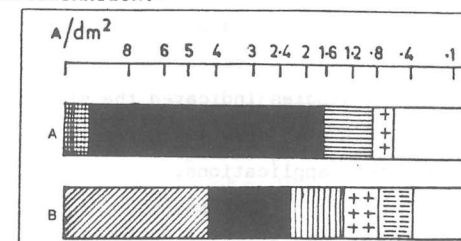


Fig. 2. Influence of addition agent a) Coumarin 0,1 g/l and formaldehyde 0,1 ml/l b) Sodium dihexil sulfosuccinate 0,5 g/l

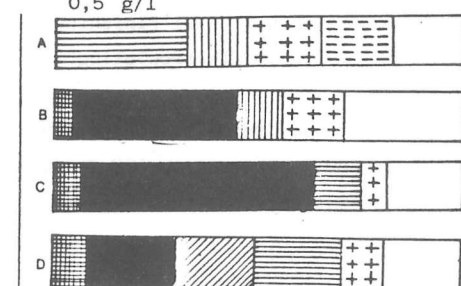


Fig. 3. Influence of cadmium sulfate concentration. a) 0 gr/l. B) 10 gr/l. C) 15 gr/l. D) 30 gr/l.

studied for solar energy conversion.

Based on the investigation, the following composition and operating conditions are recommended:

Nickel sulfate ..	100	g/l
Cadmium sulfate .	15	"
Ammonium thiocyanate	10	"
Coumarin .....	0,1	"
Formaldehyde ...	0,1	ml/l
pH .....	4,5-5,0	
Temperature ....	20-30°C	
Current density	3-4	A/dm <sup>2</sup>
Plating time ..	45-60	sec

The deposit immersed in 5% v/v hydrochloric acid for 20 to 30 seconds to develop its full black color. Based on this investigation, a 5 liter solution has been operated satisfactorily.

Further work is necessary to measure absorbance and emittance.

Corrosion studies indicated the stability of the coating. Thermal cycling tests also show the durability of the coating for use in higher temperature applications.

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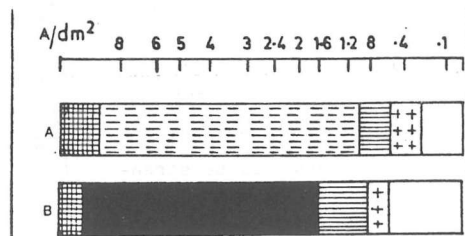


Fig. 8. Influence of acid etching a) before etching; b) after etching in 5% v/v hydrochloric acid 25 sec.

#### POLARIZATION CURVES OF THE ATMOSPHERIC CORROSION PHENOMENA

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#### INTRODUCTION

Since atmospheric corrosion is a slow process, natural tests for the direct measurements of corrosion require very long periods of time.

Many researchers have striven to find an alternative electrochemical approach to replace the classical gravimetric procedures. The pioneer works of Tomashov (1) and Sereda (2) regarding the design and use of multilamellar electrochemical cells known as EACM (Electrochemical Atmospheric Corrosion Monitors) are worth mentioning.

A great deal of progress in this line is, nevertheless, due to Mansfeld (3-5) and to Swedish and Norwegian research workers (6-8) who have forwarded an empirical relationship between the current flowing through the cell and the atmospheric corrosion rate.

#### MATERIALS AND METHODS

With the usual EACM (figure 1a) use is made of the dual electrode technique for determination of the polarization resistance,  $R_p$  (9). It is assumed that the imposed polarization,  $\pm 10$  mV, is equally distributed between anodes and cathodes, since they are of the same material. For higher polarizations, however, the sharing between anodes and cathodes of the  $\Delta E$  imposed by the potentiostat is unknown and plotting of polarization curves is impossible. Some additional information is thus lost which could be valuable for a better understanding of the atmospheric corrosion phenomenon.

In an attempt to overcome the limitation mentioned, the design of the usual EACM was modified, a central metal foil is left unconnected to the others, so that it can serve as a reference electrode not polarised by the potentiostat during the measurement (figure 1b). With the new EACM the 3-electrode technique can be used, in order to apply the high polarizations required to obtain polarisation curves.