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IMMERSION BLACKENING OF GALVALUME COATINGS FOR PHOTOTHERMAL CONVERSION OF SOLAR ENERGY

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ABSTRACT

A method for producing black coatings on 'Galvalume' by immersion technique has been studied for solar thermal energy utilization. An electrolyte containing 100 g/l nickel sulphate, 25 g/l ammonium molybdate, 30 g/l ammonium sulphate operating at 70°C at a pH of 3.5–4.5 for an immersion time of 20 seconds produces black coatings with optical properties of $\alpha = 0.90$ and $\epsilon = 0.30$. The coating is post treated in 5 g/l sodium dichromate at 60°C for 30 seconds to enhance the corrosion resistance, as otherwise the black coating gets discoloured to brownish shade upon exposure to atmosphere. The influence of bath composition, pH, temperature and immersion time on the optical properties (α, ϵ) is studied. Influence of post treatment is also considered. Thermal cycling test showed that the coating is fairly stable.

Key Words: Galvalume coating, Immersion blackening, photothermal conversion, solar energy.

INTRODUCTION

One of the nonfossil energy resources to be taken up for exploitation is solar energy because solar energy is available in abundance, inexhaustible, nonpolluting and free of cost. Efficient conversion of solar radiation to heat requires selective absorber surface which has high absorptance (α) across the incoming solar radiation (0.2–2.5 μ) with low thermal emittance (ϵ) in the infrared region (>2.5 μ). Such selective coatings play a major role to improve the efficiency of flat plate collectors. Among the various selective coatings that have been studied, high performance coatings based on black chrome [1–7] and black nickel [8–10] increase the efficiency of the collectors. As the cost of production of these coatings is high, attempts are being made to develop cheap and durable coatings. Among the various conversion coatings [11–16] chemical blackening of aluminium [14] has moderate corrosion resistance. Hot dipped aluminium-zinc coatings on steel can replace aluminium [17]. Hot dipped aluminium-zinc coating on steel, called as Galvalume (Trade mark of Bethlehem Steel Corporation, USA) is somewhat similar to galvanized iron in that it consists of mild steel carrying a hot dipped protective coating. The coating, however, consists of aluminium-zinc rather than zinc [18–19]. Since Galvalume coatings on steel is a newcomer to the market, with five to ten times salt fog resistance and three to four times atmospheric corrosion resistance than galvanized iron and better corrosion resistance than aluminium, the authors reported a method for immersion blackening of Galvalume coatings for use as a selective surface for solar collectors. Such coating has a solar absorptance (α) 0.90–0.92 and thermal emittance (ϵ) 0.22–0.32.

A method for producing immersion blackening of Galvalume coatings in a solution containing nickel, zinc and thiocyanate ions has been reported [15]. The black coating contains nickel, zinc and sulphur and has got moderate corrosion resistance. An attempt has been made to blacken the Galvalume coatings by immersion in a solution containing nickel and molybdenum salt alone without thiocyanate ion. The present work deals with nickel-molybdenum system which is far more corrosion resistant than nickel, zinc and sulphur system. The characteristics of the black coating has also been studied with regard to suitability for solar thermal energy utilization.

EXPERIMENTAL

Galvalume panels (supplied by Bethlehem Steel Corporation, USA) of size 100 × 100 mm were degreased with a solvent such as trichloroethylene to remove organic compounds, cleaned in an alkaline solution containing 50 g/l sodium hydroxide, washed, desmudged in 10% V/V nitric acid, washed and then immersed in a solution containing nickel sulphate 100 g/l, ammonium molybdate 25 g/l and ammonium sulphate 30 g/l. Solar absorptance (α) and thermal emittance (ϵ) of the black coatings were measured using alphatometer and emissometer.

The adhesion of the coating was examined by tape test. In this test an adhesive tape was pressed evenly on the black coating and then pulled off suddenly with a swift rapid motion. If deposit particles did not come off on the tape then the coating was considered good and adherent. This test shows that the coating is strongly adherent.

Thermal cycling test

The samples were placed in an electric oven and the temperature was raised from ambient to 250°C within half-an-hour and maintained for the next eight hours. The oven was switched off and the samples were allowed to cool overnight. This was repeated for seven consecutive days. The object here was to test the coating under conditions of overheating due to failure in the circulation of heat extracting fluid through flat plate collector. After this test the samples were scanned under an optical microscope at a magnification of 100 × to detect any possible corrosion or visible damage occurred to the coated surface. α and ϵ values were measured before and after conducting this test to note the changes in optical properties.

Post treatment

Since the black deposit is thin and porous in nature, upon exposure to atmosphere the colour of the coating changes to brown within three days. So, it was decided to give a suitable post treatment which will minimise the degradation of the coating. The coating immediately after blackening exhibits gas evolution upon dipping in water and the black coating decolorised to whitish shade. Hence to test the effectiveness of the post treatment the panels were immersed in boiling distilled water for 30 minutes [15]. If there was any gas evolution and the coating decolorised then the post treatment was not good. If there was no gas evolution and the black coating was retained then the post treating solution was considered as good.

RESULTS AND DISCUSSION

Influence of nickel sulphate concentration

Nickel sulphate concentration was varied between 25 and 200 g/l by keeping the concentration of ammonium molydate 25 g/l, ammonium sulphate 30 g/l. The operating conditions are: solution temperature 70°C and immersion time 20 secs. At lower concentrations (< 25 g/l) the coating is brown in colour and having optical properties of $\alpha = 0.80$ and $\varepsilon = 0.22$. At higher concentration (> 150 g/l) the coating obtained is grey in colour and has optical properties of $\alpha = 0.85$ and $\varepsilon = 0.28$. The coatings with better optical properties are obtained at nickel sulphate concentrations between 50–150 g/l. Hence an optimum concentration of 100 g/l was used for our studies. At this level the coatings produced have optical properties of $\alpha = 0.90$ and $\varepsilon = 0.30$.

Influence of ammonium molybdate concentration

Ammonium molybdate in solution produces better coatings than sodium and potassium molybdate. The concentration of ammomium molybdate was varied between 0 and 50 g/l by keeping the concentration of nickel sulphate at 100 g/l, ammonium sulphate 30 g/l, temperature 70°C, and immersion time 20 secs. Without ammomium molybdate, only nickel is deposited on the surface of the panel. Addition of molybdate ions as ammonium molybdate produces black coatings. At lower concentrations (< 10 g/l) the coating is grey in appearance. At higher concentrations (> 50 g/l) powdery nonadherent deposit was produced. Better black coatings are obtained within the concentrations between 10 and 35 g/l. The optimum concentration was chosen as 25 g/l. At this concentration the black coatings have optical properties of $\alpha = 0.90$ and $\varepsilon = 0.30$.

Influence of ammonium sulphate concentration

The addition of ammonium sulphate to the solution has been found necessary in the production of good coatings. Without ammonium sulphate the deposit is whitish, nonadherent and smutty. The function of ammonium sulphate is to prevent too great a rise in pH by their buffering action and to prevent the formation of basic salts of metal ions. The amount of ammonium sulphate was varied between 10 and 50 g/l. After conducting a few experiments an optimum concentration of 30 g/l was fixed to produce quality black coatings.

Influence of solution pH

The solution pH is an important parameter for the production of better coatings by immersion or by electrodeposition. The pH of the solution was varied between 3 and 5 and was adjusted electrometrically using dilute sulphuric acid and ammonia for an electrolyte containing nickel sulphate 100 g/l, ammonium molybdate 25 g/l and ammonium sulphate 30 g/l. Uniform and adherent black coating was produced at pH values between 3.5 and 4.5 and was considered as the optimum value.

Influence of solution temperature

At temperatures < 40°C the reaction is very slow and the coating is brownish black in colour and also requires longer duration (> 120 secs). When the solution temperature is increased the immersion time is reduced for producing black coatings with better optical properties. At elevated temperatures (> 90°C) copious gas evolution is seen from the substrate and also the required time is reduced very much (i.e. < 5 secs). At this level, control is made very difficult and the coating produced is rough and dark black having optical properties of $\alpha = 0.95$ and $\varepsilon = 0.52$. Better results can be obtained at temperatures between 60 and 70°C. The optimum temperature chosen for our studies is 70°C. At this temperature the coating obtained by immersing the substrate for 20 secs. had optical properties of $\alpha = 0.90$ and $\varepsilon = 0.30$.

Influence of immersion time

Pretreated galvalume panels were immersed in the solution containing nickel sulphate 100 g/l, ammonium molybdate 25 g/l and ammonium sulphate 30 g/l at 70°C. The immersion time was varied between 10 and 40 seconds. Shorter durations (< 10 secs) produce grey coloured coatings and at longer durations (> 30 secs) rough and dark black coatings having optical properties of $\alpha = 0.92$ and $\varepsilon = 0.45$. Table I shows the change of optical properties with different durations of immersion time. Hence an immersion time of 20 secs was considered as the optimum value. Immersion in the above solution for 20 secs produces a coating of $\alpha = 0.90$ and $\varepsilon = 0.30$.

Table I: Influence of immersion time on optical properties (α, ε)

Nickel sulphate 100 g/l
Ammonium molybdate 25 g/l
Ammonium sulphate 30 g/l
70°C, pH 4.0

Immersion time (secs)	Optical properties	
	Absorptance (α)	Emittance (ε)
15	0.87	0.28
20	0.90	0.30
25	0.91	0.36

Influence of post treatment

For post treatment a number of solutions have been tried among which the following condition exhibits good corrosion protection: sodium dichromate 5 g/l, temperature 50–60°C, immersion time 30 secs. The post treated samples were immersed in boiling distilled water for 30 minutes and there was no decoloration of the coating.

Immersion time in the above solution is very important as it affects the optical properties because of the formation of an yellowish film. Table II shows the variation of optical properties for different durations of dipping time at 60°C. It is evident that an immersion time of 30 secs is optimum from the point of view of corrosion resistance without affecting the optical properties.

Table II: Influence of dipping time in the post treating solution on optical properties (α, ε)

Sodium dichromate 5 g/l, 60°C

Dipping time (secs)	Optical properties	
	Absorptance (α)	Emittance (ε)
0	0.90	0.30
15	0.90	0.31
30	0.90	0.32
45	0.91	0.34

Thermal cycling test

After conducting thermal cycling test at 250°C for seven consecutive days the coating was scanned under an optical microscope at a magnification of 100× and found that there was no corrosion or visible damage occured to the coated surface. Absorptance (α) and emittance (ε) values were measured before (α = 0.90, ε = 0.30) and after (α = 0.91, ε = 0.31) and this test shows that there was not much change in optical properties.

CONCLUSION

A method for producing black coating on Galvalume by immersion technique has been studied for solar thermal energy utilization. Based on the above investigation the following composition and operating conditions are recommended:

Nickel sulphate	100 g/l
Ammonium molybdate	25 g/l
Ammonium sulphate	30 g/l
pH	3.5–4.5
Temperature	70°C
Immersion time	20 secs

The coating is dipped in 5 g/l sodium dichromate at 60°C for 30 secs. to enhance the corrosion resistance of the coating. Otherwise the coating gets decoloured to a brownish shade upon exposure to the atmosphere. Optical properties of the coating produced under the optimum conditions are found to be α = 0.90 and ε = 0.30. Further work is necessary to improve the optical properties i.e. to increase absorptance to above 0.96 and to decrease emittance to 0.1. This is possible by modifying pretreatment conditions, adding suitable additives and by changing operating conditions.

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