Influence of condensation product on electrodeposition of Zn-Mn alloy on steel

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Electrodeposition of zinc-manganese alloy was attempted from sulphate bath containing condensation product (CP) of furfuraldehyde (FRL) and L-lysine monohydrochloride (LL). The effect of bath constituents, *p*H, current density and temperature on nature of deposit was studied through Hull cell experiments. The throwing power was measured using Haring and Blum cell. The bath constituents and operating parameters were optimized. Deposit properties and corrosion resistance were discussed. Current efficiency and polarization studies were carried out. SEM photomicrographs of the deposit obtained from optimum bath revealed that the condensation product modifies the morphology of zinc-manganese alloy deposit. IR spectrum of the scrapped deposit showed inclusion of addition agent.

Keywords: Brightener, Condensation product, Electrodeposition, Sulphate solution

Electrodeposited zinc coatings are widely used for the protection of steel structures. Many studies have been performed in order to improve the durability of zinc coatings[1-3]. Various Zn based alloys such as, Zn-Ni, Zn-Co and Zn-Fe are currently used in industries. Such zinc alloy coatings possess higher corrosion resistance than pure zinc coatings[4,5]. There is a growing interest on the electrodeposited Zn-Mn alloys because of their superior protective properties[6-13]. Zn-Mn alloys are mainly obtained from sulphate-citrate baths[5-15]. The electrodeposition conditions permit to obtain high manganese content in the coatings at high applied current densities. Gabe and co-workers[5,12] have reported that a Zn-Mn alloy with a manganese content of approximately 30% shows the highest corrosion resistance. This highest corrosion resistance is associated with the monophasic structure of the coating. Boshkov *et al.*[17-19] studied the influence of bath composition on the corrosion behaviour of Zn-Mn coatings and reported that alloys with manganese contents around 11% had a high corrosion resistance due to their monophasic structure. The other electroplating solutions that have been considered were an alkaline sulphate pyrophosphate bath[20,21] and an acidic chloride bath without complexing agents[22]. These alloys present a double protective mechanism combining a sacrificial protection and the formation of a practically insoluble protective surface layer.

In the present study acid sulphate bath was employed. The bath solution was prepared using zinc sulphate, manganous sulphate, sodium sulphate, ammonium sulphate and boric acid. The condensation product (CP) was used as a brightener for the investigation. For the preparation of CP various primary amines and aldehydes are subjected to condensation reaction[23]. Among these, the CP formed between furfuraldehyde and L-lysine monohydrochloride gave bright deposit and was used for the deposition process. Hull cell experiment was employed to optimize the current density, *p*H and temperature, over which good quality deposit was obtained. The throwing power and current efficiency of the solution were also determined at various current densities.

Experimental Procedure

The chemicals used were of AR grade and easily soluble in water. For the preparation of solutions distilled water was used. The standard Hull cell of 267 mL capacity was used to optimize the bath constituents. The Hull cell experiments with the basic bath solution (Table 1) were carried out without agitation. The *p*H of the bath solution was adjusted with 10% sulphuric acid or sodium carbonate

Table 1 — Basic bath composition and operating conditions

Bath composition	(Conc. gL^{-1})	Operating conditions
$ZnSO_4.7H_2O$	70	Anode: zinc metal (99.99%)
$MnSO_4.H_2O$	40	Cathode: mild steel
Na_2SO_4	70	Temperature: 298 K
$(NH_4)_2SO_4$	25	Cell current: 1A

solution. Zinc plate of 99.99% purity was used as anode. The anode was activated each time by immersing in 10% HCl followed by water wash. Mild steel plates (AISI-1079) of standard Hull cell size were mechanically polished to obtain a smooth surface and degreased by dipping in trichloroethylene. The scales and dust on the plates were removed by dipping them in 10% HCl and then subjecting them to electrocleaning process. These steel plates were washed with distilled water and used for the electrodeposition. After electroplating the plates were subjected to bright dip in 1% nitric acid for 2-3s followed by water wash. The nature and appearance of zinc-manganese alloy deposit was carefully studied and recorded through Hull cell codes.

All the experiments were conducted at 303 ± 1 K. The CP was prepared by dissolving 1.2 mL of furfural (FRL) in 10 mL glacial acetic acid and the resulting solution was heated to activate aldehyde. Then 2.1 g L-lysine monohydrochloride (LL) was dissolved in 10 mL distilled water and added to the above solution. The resulting mixture was refluxed for about 3 h at 343 K. The yellow coloured solution obtained was used for the Hull cell studies. A known volume of the condensation product was added to the bath solution. The bath solution was stirred for 30 min and then used for Hull cell experiments.

The deposits were obtained at constant current density from the optimized solution. Polished, degreased and electrocleaned cathodes of 3×4 cm^2 were used for plating. These plated steel cathodes were used to test different metallurgical properties. Experiments were done in triplicate. Standard experimental procedures[24] were adopted for ductility, adherence etc. In all the above studies the average thickness of the deposit was 20 μm.

For corrosion resistance test the coated steel plates were subjected for passivation in a solution containing 200 gL^{-1} sodium dichromate and 2 mLL^{-1} of sulphuric acid for 5 s. These passivated samples were dried for 24 h in a clean atmosphere and subjected to neutral salt spray test in accordance with ASTM standard method B-117 using 5% neutral sodium chloride solution at 303 K. All the tests were carried out at 303 K.

Polarization studies were carried out by using a three compartment cell. The exposed area of zinc anode was 2 cm^2. Mild steel was used as cathode with an exposed area of 2 cm^2. The cathode potential was recorded galvanostatically with respect to saturated calomel electrode at different current densities.

Haring and Blum cell was used to measure current efficiency and throwing power. The current distribution ratio between anode and cathodes was 1:5. For determining consumption of brightener, a rectangular cell of 2.5 L capacity was used.

IR spectra of the condensation product and the scraped deposit were taken to know the inclusion of addition agent. SEM photomicrographs were taken to know the morphology of the deposit in the presence of addition agents.

Results and Discussion

Effect of condensation product

Basic bath solution gave coarse dull deposit between the current density range of 1-7 Adm^{-2} at 2 A cell current. To improve the nature of deposit, CP was added to the bath solution. At lower concentration of CP the deposit was dull at low current density region and burnt at high current density region. With increase in the concentration, the nature of the deposit was improved and at a concentration of 8 mLL^{-1} of the CP, the Hull cell panels were bright between the current density range of 0.5-6 Adm^{-2}. Further increase in the concentration of CP, the nature of the deposit became bright at high current density region. Therefore, based on the above observations the concentration of CP was kept at 8 mLL^{-1} as optimum. The Hull cell patterns are shown in [Fig. 1(a)].

Effect of zinc sulphate

To find the effect of zinc ion concentration on nature of deposit, the zinc sulphate concentration was varied from 20-120 gL^{-1} keeping CP at 8 mLL^{-1}. At lower concentrations the bright deposit was observed in the current density range between 0.5-5.8 Adm^{-2}. At low current density region uncoated and at high current density region dull deposits were obtained. With increase in the concentration of zinc sulphate, the brightness range was extended to higher and lower current density regions. At a concentration of 80 gL^{-1}, a satisfactory bright deposit was obtained. Above this concentration no improvement in the deposit nature was observed. The concentration of zinc sulphate was fixed at 80 gL^{-1} as optimum [Fig.1(b)].

Effect of manganous sulphate

The concentration of manganous sulphate was varied from 15-90 gL^{-1}. At low concentration, the Hull cell panels suffered from burnt deposit at high current density region and uncoated at low current density region. The burnt and uncoated areas were

found to be reduced with increase in the concentration of $MnSO_4$ and at 30 gL^{-1}, the deposit was bright over the current density range of 0.5-6 Adm^{-2}. Further increase in the concentration (>30 gL^{-1}) did not produce any improvement in the nature of deposit. So, the concentration of manganous sulphate was fixed at 30 gL^{-1} in the bath solution. The Hull cell patterns are shown in Fig. 1(c).

Effect of sodium sulphate

Sodium sulphate was added to increase the conductance of the bath solution. The concentration of sodium sulphate was varied from 20-140 gL^{-1}. At low concentrations, the Hull cell panels suffered dull and uncoated areas at low current density region. The dull and uncoated regions were found to be reduced and at 60 gL^{-1} of sodium sulphate in the bath solution, the deposit was bright over the current density range of 0.5-6 Adm^{-2}. On further increase in the concentration (>60 gL^{-1}) the deposit became burnt at high current density region. The concentration of sodium sulphate was fixed at 60 gL^{-1} in the bath solution. The Hull cell patterns showing the effect of sodium sulphate are shown in Fig. 1(d).

Effect of ammonium sulphate

Ammonium sulphate was added to promote the deposition of zinc and to decrease the manganous content in the deposit. The concentration of ammonium sulphate was varied from 10-70 gL^{-1}. At low concentration, the Hull cell panels were burnt deposit at high current density region and uncoated at low current density region. The burnt and uncoated regions were found to be reduced and at a concentration of 30 gL^{-1} of ammonium sulphate, the deposit was bright over the current density range of 0.2-5.7 Adm^{-2}. Based on the above observations the concentration of ammonium sulphate was fixed at 30 gL^{-1} in the bath solution [Fig. 1(e)].

Effect of EDTA

EDTA was used as a complexing agent in the deposition process. The concentration of EDTA was varied from 5-40 gL^{-1}. At low concentration the deposit on Hull cell panels was burnt at high current density region and uncoated at low current density region. With increase in the concentration the burnt and uncoated deposits were found to be reduced and at 15 gL^{-1} of EDTA in the bath solution, the deposit

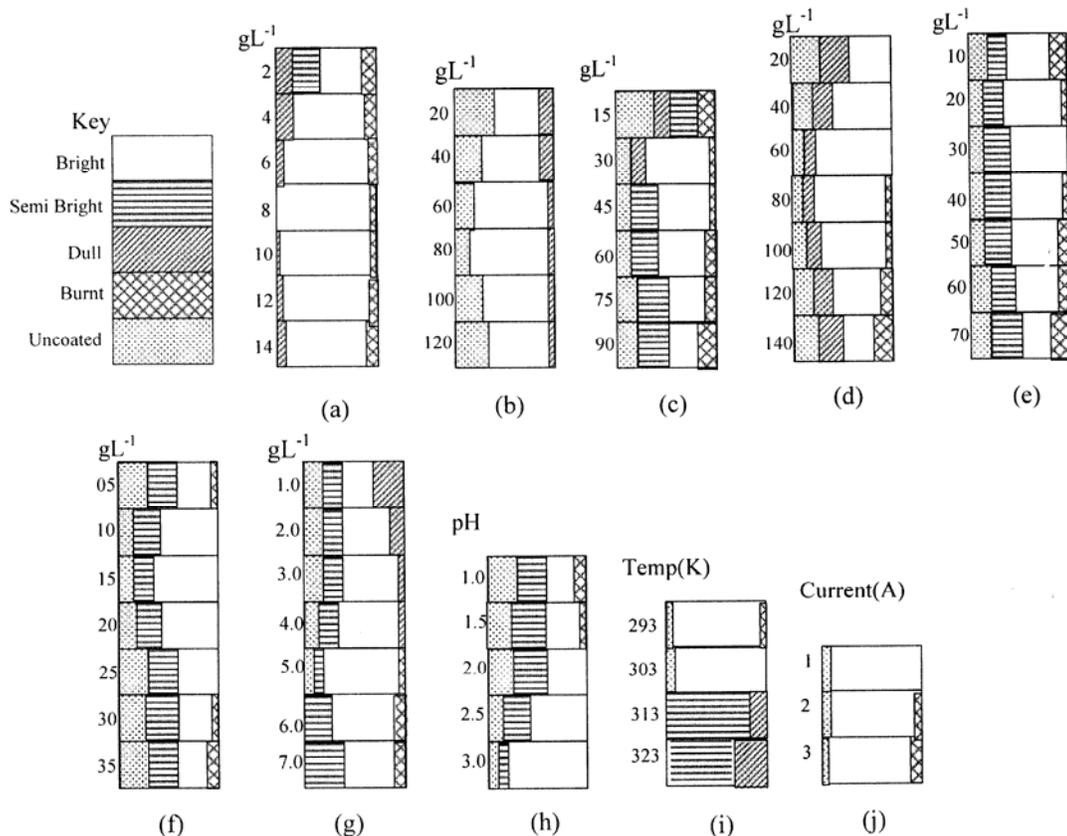Fig. 1 — Hull cell figures: (a) Effect of condensation product, (b) effect of $ZnSO_4.7H_2O$, (c) effect of $MnSO_4.H_2O$, (d) effect of Na_2SO_4, (e) effect of $(NH_4)_2SO_4$, (f) effect of EDTA, (g) effect of CTAB, (h) effect of *p*H, (i) effect of temperature, (j) effect of cell current

was bright over the current density range of 0.3-5.7 Adm^{-2}. So the concentration of EDTA was fixed at 15 gL^{-1} in the bath solution [Fig. 1(f)].

Effect of CTAB

In common practice surfactants are used in electrodeposition to control the metallic crystal shape and size in order to produce smooth and bright deposits. Common effect of additives are changes in the preferred deposit orientation, morphology and an increase in the deposition over potential. The specific activity of the surfactants are generally understood in terms of adsorption at the cathode surface during deposition and depends on the concentration of the surfactant molecules. When the concentration approached the critical micelle concentration (cmc) the formation of bilayers or multilayers at the electrode surface occurs[25].

The concentration of CTAB was varied from 1-10 gL^{-1}. At low concentration, the Hull cell panels suffer dull deposit at high current density region and uncoated at lower current density region. The bright deposit was obtained at the concentration of 6 gL^{-1}. The concentration of CTAB was fixed at 6 gL^{-1} in the bath solution. [Fig. 1(g)].

Effect of *p*H and temperature

The *p*H of the bath solution was varied from 1-3. At lower *p*H the specimens had uncoated areas at low current density region and burnt deposit at high current density region. At a *p*H 3 satisfactory bright deposit was obtained. At higher *p*H (>3) the Hull cell panels showed burnt deposit in the high current density region. From the above observations the *p*H of the bath solution was kept at 3 as optimum. The Hull cell patterns are shown in Fig. 1(h).

To study the effect of temperature on Hull cell panels, the plating experiments were carried out in a thermostat. The temperature was varied from 293-323 K. At low temperature (<303 K), the deposition was bright in the current density range 0.5-7 Adm^{-2} at 2 A cell current. Above 303 K the deposit was dull in the high current density region. Therefore, the optimum operating temperature fixed at 303 K. The Hull cell panels showing the effect of temperature are shown in [Fig. 1(i)].

Effect of cell current

The Hull cell experiments were carried out at different cell currents (1-3A) for 10 min using optimum bath solution. It was found that at a cell current of 1A the deposit was bright in the current

density range of 1-6 Adm^{-2}. At a cell current of 2A, the deposit was bright in the current density range of 0.5-8 Adm^{-2}. At a cell current of 3A the deposit was bright over the current density range between 0.5-8 Adm^{-2} [Fig. 1(j)].

Current efficiency and throwing power

Current efficiency and throwing power were measured at different current densities by using optimum bath solution (Table 2). The current efficiency was measured by taking a rectangular methacrylate cell. At lower current densities (1 Adm^{-2}) the current efficiency was found to be 53% (Table 3). At a current density of 2 Adm^{-2} the efficiency increased to 55%. The maximum current efficiency 61% was found at 4 Adm^{-2}. With increase in the current density above 4 Adm^{-2}, the current efficiency was found to be decreased.

Throwing power was measured by using Haring and Blum cell at different current densities. At low current densities the throwing power was 17% and with increase in the current density it increased to 20%.

Polarization studies

The potential of the steel cathode was measured galvanostatically with respect to saturated calomel electrode at different current densities. The variation of potential in the presence of different bath constituents is as shown in Fig. 2. The shift in

Table 2 — Optimum bath composition and conditions

Bath composition	(Conc. gL^{-1})	Operating conditions
$ZnSO_4.7H_2O$	80	Anode: zinc metal (99.99%)
$MnSO_4.H_2O$	30	Cathode: mild steel
Na_2SO_4	60	Temperature: 303 K
$(NH_4)_2SO_4$	30	*p*H: 3.0
EDTA	15	Plating time: 10 min
CTAB	06	Cell current: 1A
Condensation product, mLL^{-1}	08	Bright current density: 02-5.8 Adm^{-2}

Table 3 — Current efficiency and throwing power at different current densities

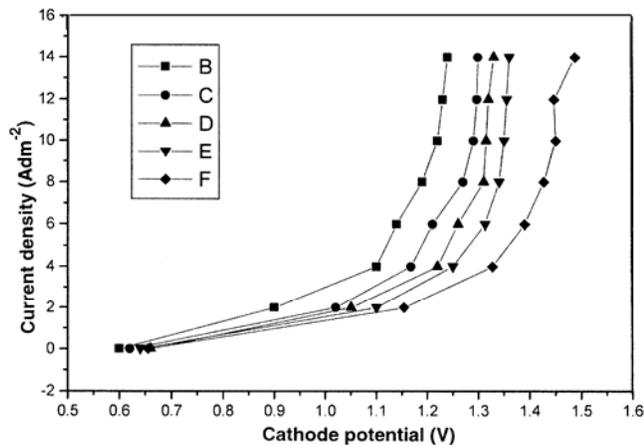| Current density (Adm^{-2})	Current efficiency (%)	Throwing power (%)
1.0	53	17
2.0	55	17
3.0	59	18
4.0	61	20
5.0	54	17

Fig. 2 — Effect of addition agents on cathodic potential: B= Basic bath, C= BB+EDTA, D= BB+CTAB, E= BB+EDTA+CTAB, F=BB+EDTA+ CTAB+ CP

Table 4 — Salt spray test conducted at different time intervals

Plating bath composition	Hours of treatment	Observation
Basic bath (BB)	24	No white rust
	48	White rust
Optimized bath	24	No white rust
	48	No white rust
	72	No white rust
	96	White rust
Passivated deposit	24	No white rust
	48	No white rust
	72	No white rust
	96	No white rust
	>96	No white rust

cathodic potential towards more negative direction was observed in presence of addition agents. This is attributed to the formation of more stable electrical double layer by the condensation product, which contains electroactive functional groups.

Corrosion resistance

For corrosion resistance study, the steel cathodes were given the deposit of varying thickness from 5-15 μm. The specimens after plating were subjected to bright dip in 1% nitric acid followed by passivation. The porosity of the deposit was tested with ferroxyl test. The soaked paper with potassium ferricyanide was placed on the deposit and no blue spots were observed. This test indicated pore free nature of the deposit. Further corrosion resistance test was carried out in a salt spray chamber. The deposited plates after passivation were subjected to a continuous spray of neutral 5% sodium chloride solution. The specimen did not show any rust even after 96 h of testing (Table 4). This showed good resistance of the deposit.
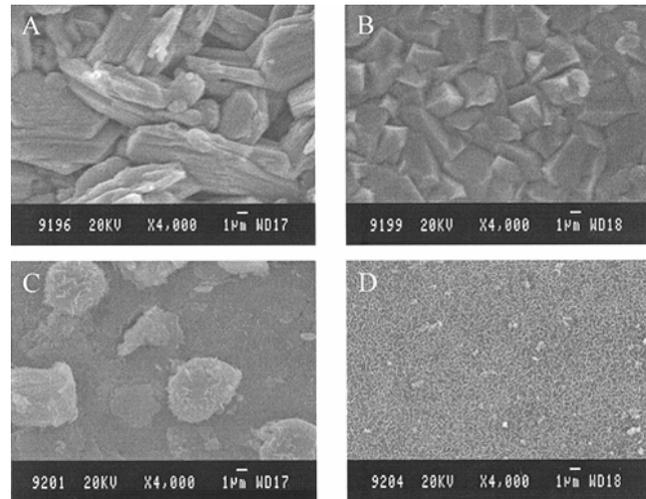

Fig. 3 — SEM photomicrographs of the deposits obtained at 4 Adm^{-2} in the presence and absence of addition agents at 298 K; A: Basic bath (BB), B: BB+EDTA, C: BB+CTAB+EDTA, D: Optimized bath.

Adhesion properties

Standard bend test was used to measure both adherence and ductility of zinc-manganese alloy deposits. Mild steel panels of 1 mm thick (1×10 cm^2 area) were electroplated with zinc-manganese alloy to a different thickness (5-20 μm). These samples were subjected to bending test through 180°. No crack or peel off in the deposit was noticed even after 180° bending of the specimen. This indicated the good adherence and ductility of the deposit.

Surface morphology and IR studies

The nature of the crystal growth in the presence and absence of addition agent is explained with the help of SEM photomicrographs and are shown in Fig. (3). SEM photomicrograph of the deposit obtained from the basic bath shows coarse-grained deposit having irregular crystal size [Fig. 3(a)]. The average grain size is ~2 μm. In presence of EDTA [Fig. 1(b)] the grain size in the deposit is comparatively smaller and regular with an average grain size of ~ 0.7 μm. In presence of CTAB [Fig. 1(c)], the grain size is smaller (~0.08 μm) indicating a modification in rate of crystal growth. It is also noteworthy to mention the porous free nature of the coating due to the smaller grain size. The change in morphology can be associated to a strong blocking effect of the cationic surfactant which causes an increased nuclei renewal rates leading to an increase in nucleation number and hence smaller grain size. The SEM photomicrograph [Fig. 1(d)] of the deposit obtained from the optimum bath shows perfect crystal growth, uniform arrangement of
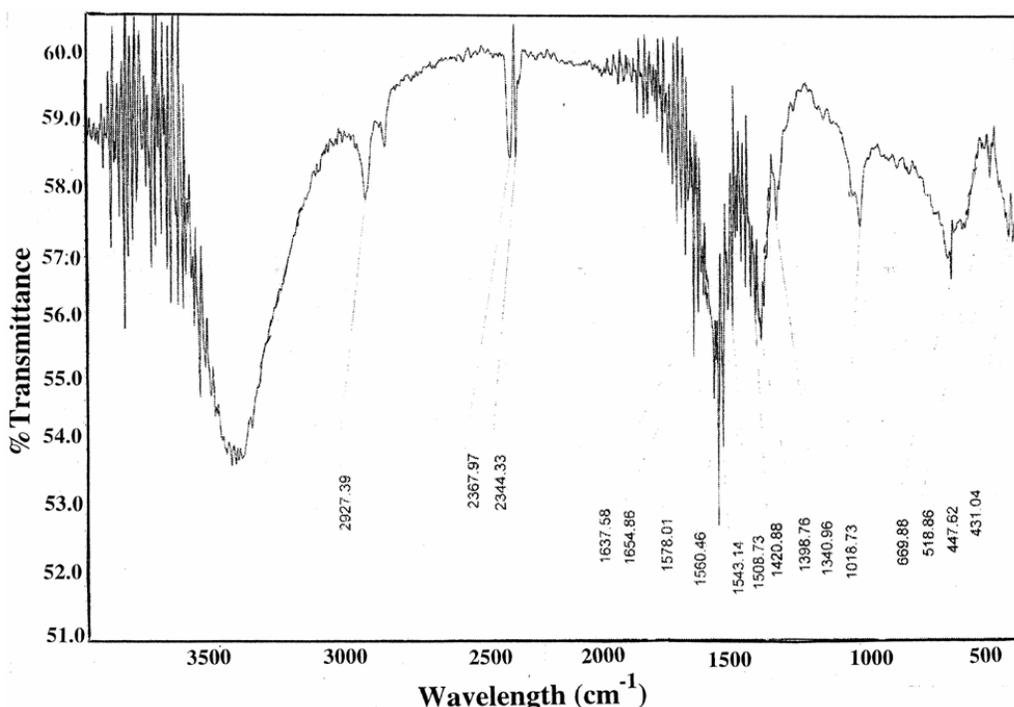
Fig. 4 — IR spectrum of the scraped zinc-manganese alloy deposit.

crystals, refinement in crystal size and hence bright deposit. The average grain size of the deposit is ~0.04 μm.

The IR spectrum of scraped deposit obtained from the optimum bath was used to test the inclusion of addition agent in the deposit (Fig. 4). IR spectrum shows an absorption peak at 1654.86 cm^{-1} which corresponds to –C=N group of CP. This indicated the inclusion of CP in the deposit during electrodeposition. Also the position of the peaks indicated the changes in the structure of the addition agent during electrodeposition.

Consumption of brightener

In electroplating the addition agents play an important role in producing lustrous deposits. The addition agents are consumed during plating and thus their concentration decreases. When this concentration goes below the optimum value the deposit becomes dull in appearance. To know the amount of addition agents consumed in the present bath 2.5 L of bath solution was taken and plating experiments were carried out at different current densities. The total number of coulombs passed to the bath solution was recorded at the time when the bath just started to give semibright deposit. The used bath solution was Hull cell tested by adding different amount of CP. The concentration of CP at which once

again bright deposit was obtained, was determined. The amount of condensation product consumed for 1000 amps-hour was 12 mLL^{-1}.

Conclusion

The optimized bath produces good deposit over wide current density range. The optimized bath composition is shown in Table 2. The deposit is pore free and corrosion resistant. The throwing power is reasonably good. The brightener can be easily synthesized. The addition agents are non-toxic, easily soluble in water and hence require no treatment of the effluent. The bath could be easily commercialized.

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