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Study the Effects of Some Organic Additives to the Galvanizing in Amonium Chloride Electrolyte Zinc Plating Baths

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ABSTRACT

The effects of some organic additives to the galvanizing in amonium chloride electrolyte zinc plating baths were studied. The results show that all additives added to the plating solution shifted the potential of the zinc precipitate towards a more negative side. Additive NAP 14-90 added to the plating solution increased cathode polarization and created a coating with a wide gloss and semi-gloss range. Additives Berol 840 and o-Chlorobenzaldehyde added with NAP 14-90 improved gloss and widen the semi-gloss range. When Berol 840 and o-Chlorobenzaldehyde were added to the plating solution without NAP 14-90, the deposit distribution decreased deeply and the coating could not form at low current densities. The additives added to the plating solution changed the coating morphology. The plating samples in the solution containing the additive NAP 14-90 gived a smooth and uniform coating morphology. The sample had all three additives providing the smoothest coating morphology. The additives added to the plating solution had little effect on the plating efficiency. Additives 2 ml/L NAP 14-90 + 1 ml/L Berol 840 + 0.2 ml/L o-Chlorobenzaldehyde were selected to improve the properties of the coating and the plating process in the ammonium chloride system.

1. Introduction

Metal coating is one of the methods of corrosion protection that has been researched and used quite popularly in the world and in Vietnam. Among them, the zinc coating is one of the most used metal coatings to protect carbon steel components, parts and structures thanks to its low cost, ease of fabrication and ability of cathode protection for steel [1]. However, zinc plating systems with no additives give the coarse, dark, gray, poor adhesion, no-gloss coating which cannot be used in industry. Therefore, a variety of additives have been added to improve some of the coating properties [2]. Y. A. Naik and T.V. Venkatesha used condensation product formed between DL-alanine (DLA) and glutaraldehyde to improve some of the coating's properties and plating process on the non-cyanide alkaline bath [3]. U. Haque, A. Khan and M. U. Ahmad studied and introduced some additives for bright zinc deposition [4]. Shanmugasigamani et al. studied some additives in bright zinc deposition from cyanide free alkaline bath [7,8].

Since the 1990s, thanks to technical advances, chloride plating bath has been put into use and occupy a high market share. The advantage of this solution is that samples with complex shape can be plated, samples can be suspended and rotated, and the coating has a high gloss, and has a large cathode efficiency [2]. Several studies using additives to improve some properties of coatings and plating processes on amonium chloride electrolyte zinc plating have been published. A wide range of organic additives such as: Thiosemicarbazide (TSC), Acetophenone (AcP), Cinnamaldehyde (CnA), Crotonaldehyde (CrA), Furfuraldehyde (FrA), Salcylaldehyde (SaA), Acetophenone-thiosemicarbazone (ApTSCN), Cinnamaldehyde-thiosemicarbazone (CnTSCN), Crotonaldehyde-thiosemicarbazone (CrTSCN), Furfuraldehyde-thiosemicarbazone (FrTSCN), Salcylaldehyde-thiosemicarbazone (SaTSCN) [11], and polyethylene glycol 20,000 [12] were used as the additives. Some additives added to the plating solution that smooths the crystal, creates a semi-gloss coating, and improves the deposit distribution. However, the studies only stop at the single additive, which has not yet studied the combination of additives, and the coatings are not of quality for industrial use.

2. Materials and Methods

2.1. Materials

The amonium chloride electrolyte zinc plating baths solution contains major constitutes: 250 g/L NH_4Cl, 60 g/L $ZnCl_2$ and additives with various content. The additives are NAP 14-90, Berol 840, and o-Chlorobenzaldehyde. HCl solutions were used for pre-treatment of steel surfaces at 5-15%V. All of chemicals were used at pure grade and dissolved by deionized water.

2.2. Sample preparation

Low carbon steel plates (100 × 50 × 1.2 mm) were degreased by immersion in the solution of 60 g/L UDYPREP-110EC (Enthone) at 50-60^oC for 5-10 min. After that the samples were immersed in solution containing HCl (10%V) and urotropine (3.5 g/L) at ambient temperature for 2-5 min. In the zinc plating process, all of samples were electrodeposited by using a rectifier.

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2.3. Methods of analysis

Effects of some organic additives on the bright and semi-bright range of the zinc deposits were determined by Hull cell test method. The bright of the zinc deposits was determined by Progloss 3, model 503 (Germany) according the ISO 2813 standard. The cathodic polarization curves were examined by using Autolab PGSTAT 30 connected with 3 electrodes including: auxiliary electrode Ag/AgCl, counter electrode platinum, and working electrode as steel with area of 0.785 cm^2, with scan rate of 2 mV/s. SEM images were taken by scanning electron microscope JEOL-JSM-6510LV. Effect of organic additives on deposit distribution by Haring-Blum and on plating efficiency by weight method.

3. Results and Discussion

3.1. Effects of some organic additives on cathodic polarization

Tafel slope shows the effect of additives on the reduction of metal ion. If the system has Tafel slope at high level, the polarization will have significant effect on the plating speed and the zinc deposits created will become smoother, and high bright.

The cathode polarization lines in Figure 1 show that all organic additives added to the plating solution changed the zinc precipitate potential toward the negative side. However, the lines S2 (base + B) and S3 (base + O) was parallel to line S0 (base). This shows that adding the additives Berol and o-Chlorobenzaldehyde to the plating solution did not increase cathode polarization compaired to solution not containing additives. The line S1 (base + N) was more inclined than the line S0 (base), so that only the additive NAP 14-90 added to the plating solution increased the cathode polarization compared to the solution without additives.

Figure 1 to 4 show that the polarization lines measured in the NAP 14-90 free plating solutions including S2 (base + B), S3 (base + O), and S6 (base + BO) do not increase cathode polarization compared to line S0 (base) in the plating solution without additive. All polarization lines from S1 to S7 show that the single additive and combination of additives added to the plating solution shifted the potential of the zinc precipitate towards the negative side. The results of Figure 2 show that the potential for zinc precipitation in an additive-free plating solution is about -0.77 in the line S0 (base) to -1.2 in the polarization lines S5 (base + NO) and S7 (base + NBO).

3.2. Effect of some organic additives on gloss range

The Hull cell design helps to form a continuous range of small to large current densities on the same cathode. Therefore, only with one experiment, it could also identify the optimal current density region that the surfactants and the polyamines affect to and the intensity of these effects can determine through surface observation and bright measurement.

From the experimental process by the Hull method (with t = 10 minutes, I = 1 A) to consider the effect of organic additives on the gloss and gloss range of coating, the results in Figure 5 and Table 2 were obtained.

The plating sample in solution S0 (base) gives a gray coating at a current density > 4 A/dm^2, a matte coating at current density of 0.05 $A/dm^2 \div 4$ A/dm^2, and no coating at a current density < 0.05 A/dm^2. The gloss of coating cannot be measured.

The plating sample in solution S1 (base + N) gives the semi-gloss coating at a current density > 0.4 A/dm^2, the black coating at a current density < 0.4 A/dm^2.

The plating sample in solution S2 (base + B) gives black coating at a current density > 4 A/dm^2, a matte coating at a current density of 0.05 $A/dm^2 \div 4$ A/dm^2, and a glossy coating at a current density < 0.05 A/dm^2.

The plating sample in solution S3 (base + O) gives gray coating at current density > 4 A/dm^2, matte coating at current density 0.1 $A/dm^2 \div 4$ A/dm^2, and semi-glossy coating at current density current < 0.1 A/dm^2.

The plating sample in solution S4 (base + NB) gives the semi-gloss coating at a current density > 4 A/dm^2, the black coating at a current density < 0.1 A/dm^2.

The plating sample in solution S5 (base + NO) gives a glossy, porous coating at a current density > 0.67 A/dm^2, and a glossy coating at a current density of < 0.67 A/dm^2.

The plating sample in solution S6 (base + BO) gives black coating at a current density > 4 A/dm^2, a semi-gloss coating at a current density of 1 $A/dm^2 \div 4$ A/dm^2, and no coating at a current density < 1 A/dm^2.

The plating sample in solution S7 (base + NBO) gives a glossy, porous coating at a current density > 1.6 A/dm^2, and a glossy coating at a current density < 1.6 A/dm^2.

The research results show that additive NAP 14-90 for the coating has a wide semi-gloss. Additives Berol 840 and o-Chlorobenzaldehyde combined with additive NAP 14-90 help to expand semi-gloss range and increase gloss. The combination of additives gives a wider gloss range than that using only single additive in the document [11]. Although using many different additives, the author only obtained the widest gloss range from 1 ÷ 3.5 A/dm^2 with Salcylaldehyde-thiosemicarbazone (SaTSCN). Additive o-Chlorobenzaldehyde increases the gloss of the coating but causes porousness due to the process of creating hydrogen gas on the surface.

3.3. Effect of organic additives on surface morphology

The samples were polished surface with abrasive paper and plated in solutions (with t = 15 minutes, I = 2 A/dm^2) to consider the effect of organic additives on the surface morphology of the coating. All additives added to the plating solution change the coating morphology. The plating samples in the solution containing the additive NAP 14-90 give a smooth and uniform coating morphology. The sample has all 3 additives in solution S7 (base + NBO) for the smoothest coating morphology. The plating sample in S5 (base + NO) solution gave less fine coating morphology compared to S7 plating. The plating samples in the NAP 14-90 additive-free solution include S0 (base), S2 (base + B), S3 (base + O) and S6 (base + BO) for fine coating morphology with large particles.

The plating morphology of the coatings is clearly improved, and particles are finer than that in the solution containing additive PEG 20,000 [12].

3.4. Effect of organic additives on deposit distribution and plating efficiency.

From experimental processes according to Haring - Blum method (with t = 10 minutes, k = 5, I = 2 A/dm^2) to consider the effect of organic additives on deposit distribution, and according to the mass method (with t = 10 minutes, I = 2 A/dm^2) to consider the effect of organic additives on plating efficiency, the following results are obtained:

The results in Table 3 show that all organic additives added to the plating solutions had little changes in plating efficiency compared to the additive-free plating solution. Plating efficiency in ammonium chloride zinc plating solutions is quite high, ranging from 83.3 to 99.2%. However, all organic additives added to the plating solutions significantly alter the deposit distribution of the plating process compared to an additive-free plating solution. In

general, the deposit distribution of the plating process increases, except in the case of plating in solution S6 (base + BO) whose the deposit distribution of the plating process decreases deeply to -11.5%. The deposit distribution in an additive-free plating solution is 26.2%, the coating does not form at a current density < 1 A/dm^2.

4. Conclusions

The results of cathodic polarization measurements show that all additives added to the plating solution shifted the potential of the zinc precipitate towards a more negative side. Additive NAP 14-90 added to the plating solution increased cathode polarization. The polarization lines measured in the plating solutions only added Berol and o-Chlorobenzaldehyde do not increase polarization compared with that in the solution without additives.

Additive NAP 14-90 added to the plating solution created a coating with a wide gloss and semi-gloss range. Additives Berol 840 and o-Chlorobenzaldehyde added with NAP 14-90 improved gloss and widen the semi-gloss range. When Berol 840 and o-Chlorobenzaldehyde were added to the plating solution without NAP 14-90, the deposit distribution decreased deeply and the coating could not form at low current densities.

The additives added to the plating solution changed the coating morphology. The plating samples in the solutions containing the additive NAP 14-90 gived a smooth and uniform coating morphology. The sample had all three additives providing the smoothest coating morphology. The additives added to the plating solution had little effect on the plating efficiency.

Additives 2 ml/L NAP 14-90 + 1 ml/L Berol 840 + 0.2 ml/L o-Chlorobenzaldehyde were selected to improve the properties of the coating and the plating process in the ammonium chloride system.

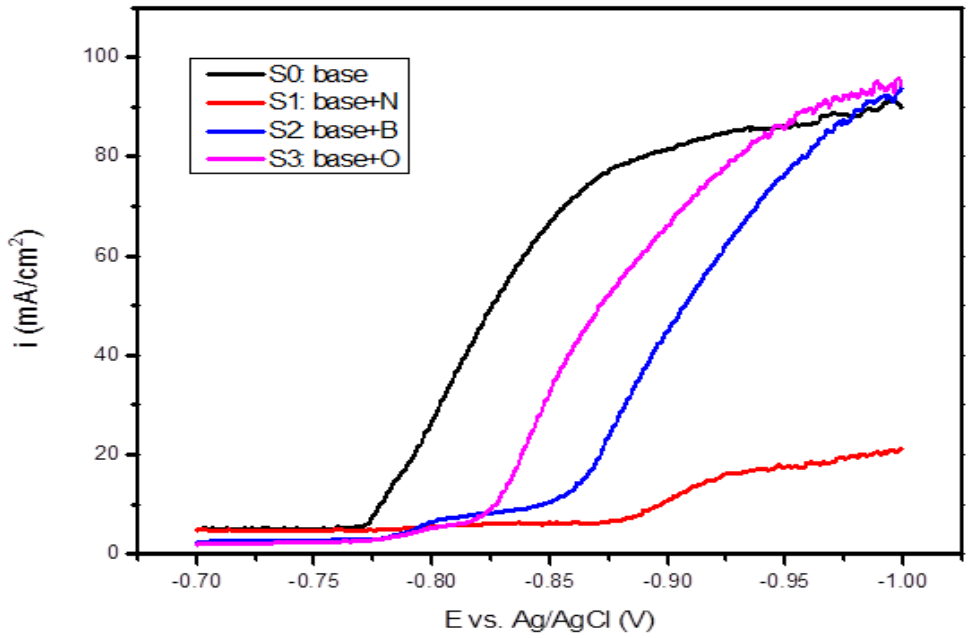

Figure 1. The effect of the single additive on cathode polarization

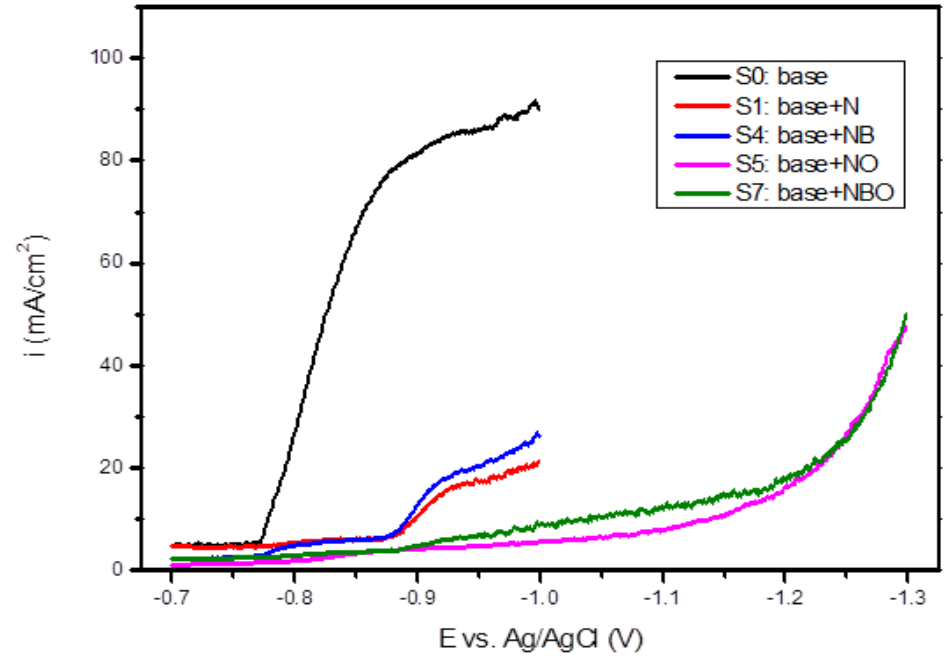

Figure 2. The effect of the NAP 14-90 additive combination with other additives on cathode polarization

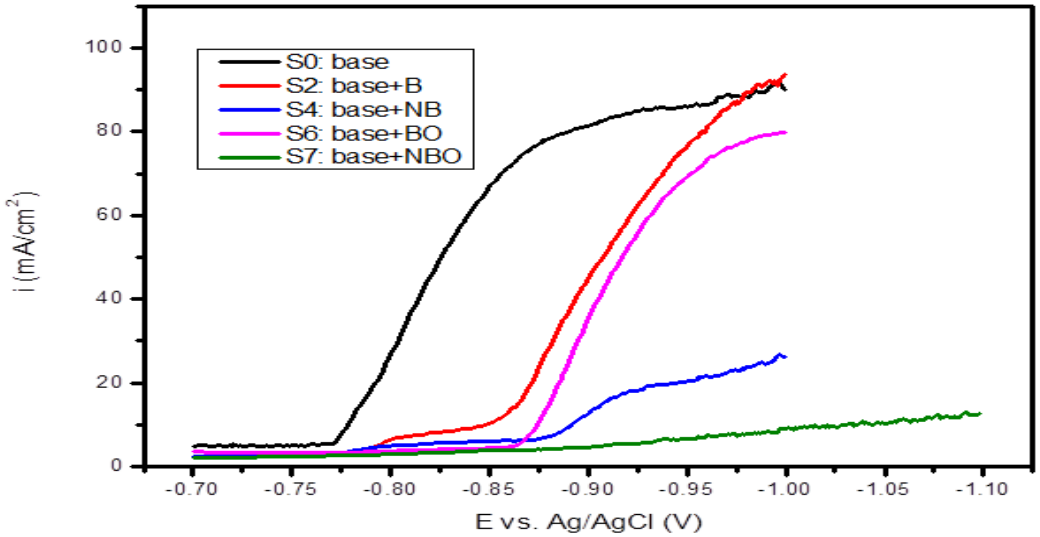

Figure 3. The effect of the Berol 840 additive combination with other additives on cathode polarization

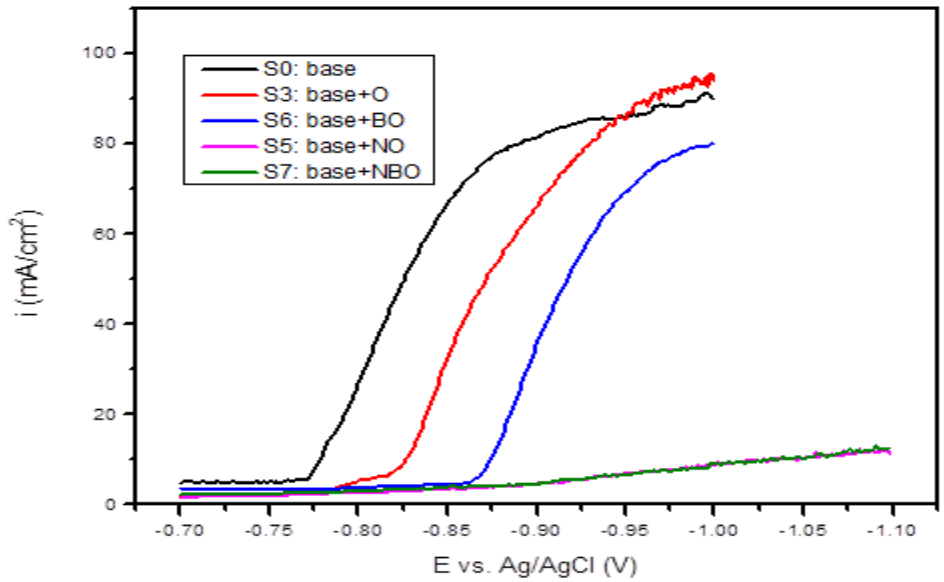

Figure 4. The effect of the o-Chlorobenzaldehyde additive combination with other additives on cathode polarization

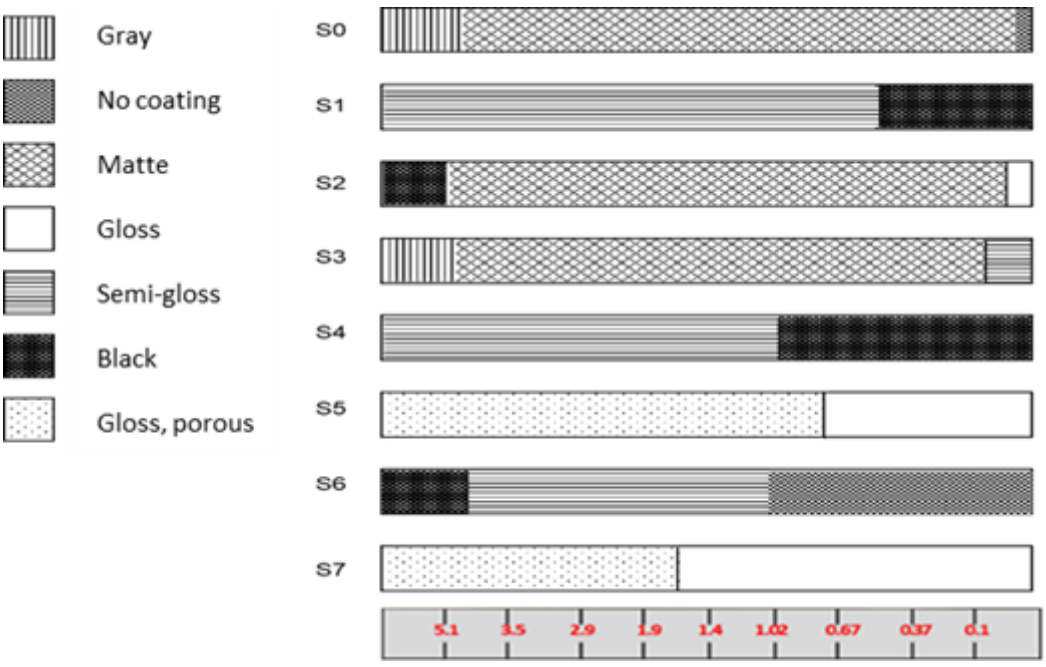

Figure 5. Gloss range of coatings in solutions with and without additives

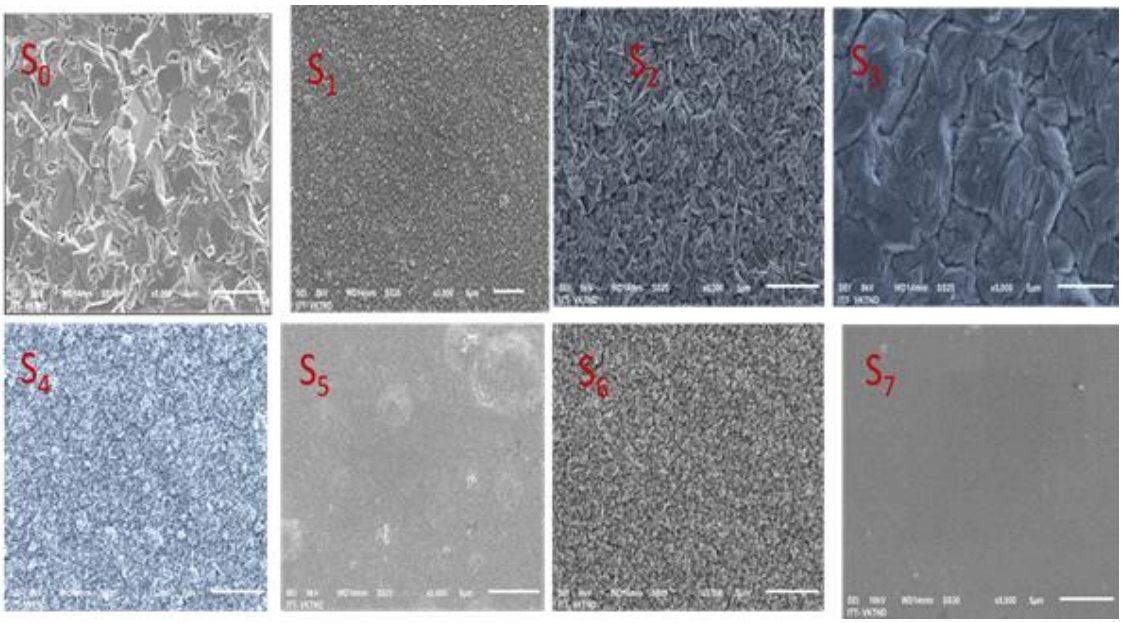

Figure 6. Morphology of coatings in solutions with and without additives

Table 1. Designation and composition of plating solutions (unit: g/L)

Solutions	Base	NAP 14-90	Berol 840	o-Chloro benzaldehyde
S0	$ZnCl_2$ + NH_4Cl	-	-	-
S1	$ZnCl_2$ + NH_4Cl	2	-	-
S2	$ZnCl_2$ + NH_4Cl	-	0.5	-
S3	$ZnCl_2$ + NH_4Cl	-	-	0.2
S4	$ZnCl_2$ + NH_4Cl	2	1	-
S5	$ZnCl_2$ + NH_4Cl	2	-	0.2
S6	$ZnCl_2$ + NH_4Cl	-	0.5	0.2
S7	$ZnCl_2$ + NH_4Cl	2	1	0.2

Table 2. Gloss of coatings in solutions with and without additives

Solutions	Composition	Angle 20°	Angle 60°	Angle 85°
S0	Base	0	0	0
S1	Base + N	101	2.6	114
S2	Base + B	0	0	0
S3	Base + O	0	0	0
S4	Base + NB	5.6	69.2	93.93
S5	Base + NO	83.8	49.4	82.4
S6	Base + BO	1.8	52.7	84.9
S7	Base + NBO	1539	749	130

Table 3. Deposit distribution and plating efficiency in plating solutions with and without additives

No.	Solutions	Plating efficiency, %	Deposit distribution, %
1	S0	99.2	26.2
2	S1	85.4	38.9
3	S2	98.8	35.1
4	S3	98.8	28.8
5	S4	95.2	42.2
6	S5	83.3	45.2
7	S6	99.1	-11.5
8	S7	86.5	49.8

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