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Effect of Additives on Zn-Ni Alloy Electrodeposition

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Zn-Ni alloys were electrodeposited from chloride bath to investigate the effect of various additives on the alloy composition and surface morphology of coating layer. The additives tried were the surfactant of naphtalene-derivative, saccharin and aliphatic alcohol. Ni content of alloy deposit was increased by the addition of saccharine and alcohol, while decreased by the surfactant. The surface roughness and morphology were also influenced by the type of additive, and the addition of surfactant contributed to the fine grains and surface smoothness. The effect of process parameters such as electrolyte temperature, current density and flow rate were also discussed in case of the mixed additives applied.

1. Introduction

Zinc coated steel sheet has been used for the autobody panels since the 1970's, but the relatively heavy coating is required to guarantee the appropriate corrosion resistance by its strongly cathodic protection to the substrate. Recently, automakers are inclined to adopt the light coating with corrosion resistance similiar to zinc heavy coating because they can facilitate the manufacturing process such as welding. Zn-Ni coated steel sheet was developed to meet such a demand, and are now widely applied to the autobody panels.

Zn-Ni coating accomodates forming, welding, painting as well as good corrosion resistance^{-1,2)}, especially nickel content of 11-13% are well performed, which would provide four or five times more corrosion resistant than zinc coating at the same coating weight. However, nickel content and surface morphology of coating layer should be carefully controlled to satisfy the quality requirements.

Although the electrodeposition of Zn-Ni alloy is generally characterized by the anomalous type that the less noble zinc deposits preferentially, the codeposition behavior is reported to approach to the normal type in the chloride bath with high concentration^(3,4). Normal CI type of codeposition is important in the real process using the soluble anodes for the control of plating bath. In addition, the additives are applied and sometimes effective in the modification of coating qualities among various plating parameters. Such an effect has not been discussed in Zn-Ni chloride bath, especially at high current density until now. Under such conditions, three types of additives were selected to investigate the effects on deposit composition and qualities as well as current-overpotential behaviors in this study, and the effect of other plating parameters on the alloy composition was also discussed in the condition of mixed additives.

2. Experimental

Zn-Ni electroplating was conducted in the experimental apparatus, which is mainly composed of the rectangular plating cell with the size of 100(w)x200(1)x20(gap) mm and the elecrolyte circulation tank of 45 liter connected to the pump. The cold-rolled steel sheets were used as the cathode, and zinc plate as the anode. The electrolyte was prepared with the industrial grade chemicals and the distilled water. The additives tried in this study were the surfactant of naphtalene-derivative type, saccharin and the aliphatic alcohol, which was added to the electrolyte in the concentration of 1 or 2 m mol/L. The electrolyte and plating conditions are summarized in Table 1. Each additive was tested in the condition A, while the mixed additives were tried in the condition B to confirm the effect of plating conditions. The coating weight was controlled to 30 g/m². The coating layer was stripped in a 1:3 HCl solution, and the composition was pr. the analysed atomic absorption spectrophotometer. The surface morphology was observed by a scanning electron microscope, and the roughness measured by a three-dimensional surface roughness tester. The whiteness and the brightness were evaluated with a color difference meter and a glossmeter, respectively.

The current-overpotential relations were investigated using the rotating rod cell with three electrode in the electrolyte of condition A, whose capacity was 800 ml. The working electrode of rod type was made of extra-low carbon steel, and the counter electrode of ring type was nickel, and a saturated calomel electrode was used as a reference electrode. The diameter of working electrode was 15 mm, and the exposed area to the electrolyte was 8 cm². The distance between the working and the counter was 20 mm, and the unnecessary area was masked with a teflon. The potentiostat/galvanostat of high capacity(30V,50A) was used to simulate

Idontity	E	lect	rolyte Cond	itic	ons	Platir	ng Condi	tions
Identity	Ni ²⁻	ł	Cl	;	Temp.	Current Density	pН	Flow Rate
А	13.8 (%)	ŝ.	260 (g/L)		60 (°C)	80 (A/dm ²)	2.5	1.5 (m/sec)
В	13.8 (%)	1	260 (g/L)	-	55~65 (°C)	60~100 (A/dm ²)	2.5	1.2~1.8 (m/sec)

Table 1 Experimental Conditions of Zn-Ni Deposited Specimen

the conditions of high current densities, and the rotating speed was controlled to 100 mpm. The current- overpotential plots were obtained from the steady state current under the potentiostatic conditions with or without the additive.

3. Results and Discussion

3.1 Composition of Alloy Deposit

Fig.1 represents the variation of nickel contents of alloy deposits from the bath containing the additives of 1 or 2 m mol/L. The composition reference line(CRL) noted in the figure corresponds to the hath concentration, and a little anomalous depositions are observed regardless of the additives. Ni content is increased with the addition of saccharin or alcohol compared to the additive-free bath, while decreased with the surfactant. The concentration of additive also affects the alloy composition adversely according to the type of additive. The increase of concentration lowers Ni content in case of the surfactant or alcohol, while adverse in saccharin. The effect on alloy composition comes out to be different with the type of additive, which seems to be related to the different chemical state in the solution and the adsorption behavior on the cathode.

3.2 Coating Qualities

The surface structures of alloy deposits are varied with the additive as shown in Fig.2. The loose and irregular shape of grains is observed in the absence of additive, and the cloudy and nodular type in the saccharin-added bath.



Fig. 1 Variation of Ni Content of Zn-Ni Deposits with Additives (A:no Add. B: Surfactant, C:Saccharin, D:Alcohol)

The fine and compact grains can be obtained from the surfactant or alcohol-added bath. Especially the uniformity and compactness are prominant in case of the surfactant. Such results would be connected with the surface roughness measurements as compared in Fig.3. $\triangle Ra(\triangle Rmax)$ represents the difference of average(max) surface roughness on the alloy deposit between the additive-added and the additive-free bath. $\triangle Ra$ and $\triangle Rmax$ are decreased in the alloydeposit from the surfactant or alcohol-added bath, especially much from the surfactant. while slightly increased from the saccharin-added bath, that can be matched to the surface structure of Fig.2. The surfactant was ascertained to be the most



Fig. 2 Morphology of Zn-Ni Alloy Electrodeposits with Additives (a:no Add., b:Surfactant c:Saccharin, d:Alcohol at 2.0 m mol/L Concentration). Magnification:2000X

effective in obtaining the fine-grained and smooth surface structure.

The surface appearances of alloy deposits were compared in terms of the whiteness and the brightness as shown in Fig.4. The whiteness or the brightness index also represents the difference between the additive-added and the additive-free bath. Both the whiteness and the brightness are improved by the addition of surfactant, and only the brightness is improved by the addition of saccharin, while the addition of alcohol degrades the whiteness and the brightness. Compared with the results of Fig.2 and 3. it is difficult for the surface appearance to relate with the surface

structure in case of alcohol and saccharin. Although the addition of saccharin or alcohol gives a positive effect on nickel content of alloy deposit, a negative effect is noted in view of the surface structure or appearance.

3.3 Current-Overpotential Relations

The current-overpotential relations are plotted up to 100A/dm² with the rotating rod cell in Fig.5. The reductions of metal ions are in general inhibited in the additive-added bath compared with the additive-free bath. At the low overpotential up to about -3.2V vs. SCE corresponding to 40A/dm², the more overpotentials are needed to obtain the same current density in the order of alcohol,



Fig.3 Influence of Additives on Surface Roughness of Deposits (B:Surfactant, C:Saccharin, D:Alcohol)

saccharin and surfactant, whereas the order becomes to be reversed at the high over-potential above -3.2V. That means the behavior of alloy deposition would be changed with the current density according to the type of additive, which seems to influence the reduction procedures of metallic ions and the adsorptive states on the cathode⁽⁵⁾. Moreover, the variation of current density or overpotential would affect the nickel content and surface morphology of alloy deposit, and further studies are required to elucidate the behavior of additive. especially at the high current density.

3.4 Effect of Plating Parameters

The effects of plating parameters were confirmed in the electrolyte B with the mixed additives(surfactant+saccharin+alcohol, each 1 m mol/L), and the results are summarized in Fig.6. The nickel content of alloy deposit is increased with the increase of electrolyte temperature, while tends downwards with the increase of current



Fig. 4 Influence of Additives on Surface Appearance of Deposits (B:Surfactant C:Saccharin, D:Alcohol)





density. The flow rate of electrolyte has almost no influence on the alloy composition. The effect of temperature can be explained on the basis that the polarization and the diffusion phenomenon are the dominant



Fig.6 Variation of Ni Content of Zn-Ni Deposits with Process Patameter

influences as proposed by Brenner⁽⁶⁾. The increase of temperature seems to mainly affect the polarization in this plating conditions, since the content of more noble metal is increased with increasing the temperature of electrolyte in anomalous codeposition. However, the preferrential depositon of less noble metal at high current density means that the depositon behavior of this alloy should be under diffusion control. That is, the increase of electrolvte temperature is assumed to lower the polarization, but on the other hand the increase of current density accelerate the diffusion of less noble metal.

Fig.7 illustrates the surface morphology of alloy deposit from the bath of mixed additives, which is characterized by the compact and fine nodular grains with some cracks. This morphology seems to come from the composite effect of each additive when compared with Fig.2, but the more survey will be required to find out the adequate combination of additives or



Fig.7 Morphology of Zn-Ni alloy Electrodeposit obtained in bath of mixed additive

concentration in view of the surface quality as well as the nickel content.

4. Summary

Zn-Ni alloys were electrodeposited at high current densities from chloride bath to investigate the effects of some additives on the alloy composition and surface morphology, and then the current-potential relations were compared using the rotating rod cell. The effect of plating parameters on the alloy composition was also discussed in the condition of mixed additives. The results can be summarized as follows :

1) The addition of saccharin or alcohol increases the nickel content, while the surfactant gives an adverse effect. The concentration of additive also affects the alloy composition.

2) The fine and compact grains can be obtained from the surfactant or alcohol-added bath, while the cloudy and nodular type from the saccharin-added bath. Such results are also related with the surface roughness of alloy deposit.

3) The surfactant or saccharin improves the surface appearance, but the alcohol degrades the quality, which is difficult to explain on

the basis of surface morphology or roughness.

4) The reductions of metal ions are inhibited in the presence of additive, and the effect of additive on the overpotential would be changed at the current density of 40 A/dm² between the surfactant and the alcohol.5) The nickel content tends to increase with increasing the electrolyte temperature, while tends downwards with increasing the current density. Such trends are assumed to be related with the polarization or the diffusion phenomenon.

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Performance Characteristics of Zinc Alloys

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Abstract

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Electroplated alloys of zinc with iron, cobalt or nickel are being used to improve the corrosion resistance of the coating compared with normal zinc coatings. Acidic and basic plating solutions are being used to deposit these alloy coatings resulting in a wide array of choices for the electroplater and the parts designer. This paper explores the characteristics of the plating baths used to deposit the zinc alloys and describes the properties of the resulting deposits.

Introduction

Zinc alloy electroplated deposits are being used more frequently because they have the ability to provide improved corrosion protection to a wide range of items. While normal zinc electroplated deposits perform an important task that will certainly not be completely eliminated, the alloys perform that job better.

The fundamental function of the iron, cobalt or nickel in the zinc alloy is to modify the corrosion potential of the deposit. The alloy becomes slightly more noble than zinc and for this reason the corrosion rate of the deposit is slowed. At the same time the deposit is still sacrificial with respect to the steel substrate. Thus, the same thickness of an alloy has the ability to protect the underlying steel for a longer time than conventional zinc.

In addition to this, some of the chromates used over alloys provide better corrosion protection than a similar chromate over conventional zinc. For example, with some of the alloys it is possible to form a black chromate that does not contain silver, thus providing black chromate that provides much improved resistance to white corrosion.

The market demand for alloy deposits comes mostly from the automobile industry that accounts for about 75% of the market. A smaller 20% portion comes from aerospace. The remaining 5% of the market includes a wide range of applications.

In the automotive market, alloys are used extensively in Europe and Asia and the use in North America is increasing. Most companies publish their own specifications for the alloys as is the case for the major US companies; General Motors [1], Ford [2], and Chrysler [3]. The Society of Automotive Engineers has published specifications as well [4].

Hydrogen embrittlement relief is important for some fastener applications and specifications have been written [6,7] to address the plating, baking and testing of parts. While the alloys do not have the lubricity of cadmium this is important for fasteners and there are lubricants [8] that can be applied to provide a predictable torque and clamping force. The aerospace industry has special concerns that lead Boeing to publish a specification for zinc/nickel alloy [5]. The major concern for the aerospace industry is to replace cadmium.

The ASTM has also published specifications for zinc/cobalt, zinc/nickel, and zinc/iron alloy electrodeposits [9].

In response to the demand for better corrosion protection, alloy processes have been developed that are acid and alkaline. Zinc/cobalt and zinc/nickel processes are available both acid and alkaline, and zinc/iron is available only as an alkaline process. As with conventional zinc, bc:h the acid and alkaline processes have advantages and disadvantages. In general, the acid processes exhibit higher cathode efficiency, but because of this the distribution of plate is poor. Alkaline processes tend to have lower cathode efficiency but in return exhibit very good plate distribution over the normal current density range. The acid processes have the added advantage of being able to plate over hardened steels and cast iron.

Measurement Methods

It is difficult to overemphasize the importance of the correct use of analysis methods when determining the properties of any deposit. It is especially important in the case of alloys. The simple analysis of alloy content or the measurement of thickness can be misleading if not performed with care. It is not within the scope of this paper to describe in detail the methods that are useful in alloy plating. However, we would like to list the methods that we find most useful and point out a few obvious pitfalls. With every instrumental method the best source of information should be the operating manual for the instrument itself and the best training will be from the service technicians who service the equipment. The instrument must be calibrated frequently and standards must be used along with the work to constantly assure reliability. With every analytical method the analyst must adhere to generally accepted methods. The failure to use an instrument precisely or to follow proper analytical procedures will result in an erroneous measurement.

Cadmium Replacement Through Zinc Alloy Technology; A Customer-Supplier Joint Research Effort Victor Waldman and Mark Barnes

Automotive corrosion specifications drove the early development of zinc alloy plating with mil. spec. requirements for cadmium, fueling the second phase of zinc alloy research. Cadmium replacement through zinc alloy research encompasses many factors, such as a comparison of corrosion results for various finishes, costs associated with complying with current cadmium regulations vs. complying with zinc regulations, and plating costs associated with both zinc alloys and cadmium. Also important is the adaptation for commercial use of zinc alloy applications that were originally employed as cadmium alternative in mil. spec. requirements.

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Figure 5 Alkaline Zinc Nickel Profile



Figure 4 Acid Zinc Nickel Profile



Figure 3 Alkaline Zinc/Iron Profile



Figure 2 Alkaline Zinc Cobalt Profile



Figure 1 Acid Zinc Cobalt Profile



Table VII Neutral Salt Spray Corrosion Resistance (0.3 mil Thickness)

Chromate	Zinc	Zinc Plate		Alkaline Zn/Co		Alkaline Zn/Fe		Zinc Nickel	
	FWC	FRR	FWC	FRR	FWC	FRR	FWC	FRR	
Blue Bright	24	48-72	24-30	72-150					
Yellow	60-120	160-250	160-240	400-700	160-250	400-700	300-400	700-900	
Olive Drab	96-150	350-450	240-300	600-700	250-300	500-800	800-1000	1200-1500	
Black (silver)	48-72	400-700	120-180	400-700	250-300	700-900			
Black (non silver)			240-280	520-800	240-280	52 800			

Note: Blue Bright Chromates are available for Zinc/Cobalt alloys below 0.3% Cobalt

	Zinc Cobalt Acid	Zinc Cobalt Alkaline	Zinc Iron	Zinc Nickel Acid	Zinc Nickel Alkaline
Typcal Alloy Content	0.4-1.0%	0.4-1.0%	0.3-1.0%	7-13%	4-7%
Electrolyte	Potassium Chloride Ammonium Chloride Boric Acid	Caustic	Caustic	Ammonium Chloride	Caustic
Torque-Tension (No Post Treatment)	Less than zinc	Less than zinc	Equal to zinc	Less than Zinc	Less than zinc
Plating Efficiency	95-100%	50-80%	50-80%	90-95%	30-50%
Throwing Power	Poor	Good	Good	Poor	Good
Equipment	Acid Resistant	Mild Steel	Mild Steel	Acid Resistant	Mild Steel
Chromate Finishes Available	Yellow, Drab Black	Yellow, Drab Black	Yellow, Black	Yellow, Drab	Yellow Drab

Table VI Zinc Alloy Overview

Specifications

- Zinc Alloys GM 6280M, Zinc/Nickel with organic coating GM 6138M, Zinc/Nickel with conversion coating GM 7153 General Motors Corp.
- Zinc/Nickel WSA-M1P87-A1, Zinc/Cobalt WSH-M1P86-A. Ford Motor Co.
- 3. Zinc Alloys PC 8955, Chrysler Motor Co.
- 4. Plating Zinc-Nickel Alloy ASM 2417E, Society of Automotive Engineers.
- 5. Zinc Nickel Alloy, BAC 5637, Boeing.
- 6. Hydrogen Embrittlement F519, ASTM.
- 7. Hydrogen Embrittlement PS 9500, Chrysler Motor Co.
- 8. Lubricant for Torque/Clamping Force Control, WSD-M13P7-A, Ford Motor Co.
- 9. Zinc/Cobalt B840, Zinc/Nickel B841, Zinc/Iron B842, ASTM.
- 10. Microscopic Cross Section B487, ASTM.
- 11. Magnetic Thickness Measurement B499, ASTM.
- 12. Beta Backscatter Thickness Measurement B567, B659, ASTM.
- 13. XRF Thickness Measurement B568, ASTM.
- 14. Neutral Salt Spray B117, ASTM.
- 15. Kesternich B605. ASTM.

Table V
Typical Operating Parameters for Alkaline
Zinc/Nickel

Operating Parameters	Rack	Barrel
Zinc Metal	1.6 oz/gal	1.6 oz/gal
Nickel Metal	1.2 oz/gal	0.8 oz/gal
Caustic Soda	16 oz/gal	16 oz/gal
Soda Ash	4 oz/gal	4 oz/gal
Temperature	70-80°F	70-80°F
Anodes	Steel	Steel

in the plating bath but other bath conditions like temperature and other additives have strong roles as well.

Typical neutral salt spray performance for the alloys and acid chloride zinc are provided in Table VII. The deposits listed here were all plated to about 0.3 mil thickness as it is important to compare equal thickness for the red corrosion numbers. Neutral salt spray results for zinc/cobalt and zinc/iron are for alloys with about 0.5-0.8% of the alloy metal. Lower alloy percentages do not allow for a non-silver black chromate to form and produce lower salt spray numbers.

Kesternich corrosion testing results are provided in Table VIII.

Table VIII Zinc Alloy Kesternich Results

Alloys	Performance
Zinc Cobalt	2-3X Better than Zinc
Zinc Iron	Equal to Zinc
Zinc Nickel	Equal to Zinc

The typical hardness for some of the deposits is listed in Table IX.

Hydrogen embrittlement relief is important for parts that have been hardened. In general all the alloys mentioned may be baked but special

Table IX Zinc Alloys Vickers Hardness

Process Type	Hardness VK50
Chloride Zinc	100-125
Alkaline Noncyanide Zinc	80-130
Zinc Cobalt	180-210
Zinc Iron	100-150
Zinc Nickel (acid)	140-160

techniques may be required to obtain a good chromate afterward.

The zinc alloy deposits and the conventional zinc deposits do not exhibit the lubricity of cadmium. There are post treatments that improve the torque and tension properties of a part that are suitable for a wide range of applications.

Summary

The zinc alloy deposits discussed were developed to provide improved corrosion protection over and above what can be expected from conventional zinc deposits. The use of these alloy deposits has seen increases in Europe, Asia and the US, largely in automotive and aerospace applications.

The properties that designers look for include appearance, corrosion protection, good thickness distribution over the part, good alloy distribution over the part, and in some cases hydrogen embrittlement relief and lubricity.

Processes designed to plate these alloy deposits are both acid and alkaline because each process type has certain advantages. The acid processes are more efficient but then distribution suffers somewhat. The alkaline processes are less efficient and as a result exhibits better distribution. Acid processes are easier to use when the parts are made of cast iron or when parts have been hardened by heat treatment. Table III Typical Alkaline zinc/iron process parameters

	Rack	Barrel
Operating Parameters		
Zinc Metal	1.6 oz/gal	1.6 oz/gal
Iron Metal	80 ppm	30 ppm
Zn/Fe Ratio	150:1	400:1
Caustic Soda	16 oz/gal	16 oz/gal
Soda Ash	4 oz/gal	4 oz/gal
Temperature	70-85°F	70-85°F
Anodes	Steel	Steel
Cooling	Recommended	Required

Zinc/Nickel Deposition Processes and Chromates

Zinc/Nickel alloy deposits are somewhat different from the cobalt and iron deposits discussed so far. First the alloy content is significantly higher. The acid zinc/nickel deposits typically range from 7-13% nickel and the alkaline deposits typically range from 3-7%. In part because of this, the corrosion protection is also considerably higher. Generally the only types of chromates available for zinc/nickel alloys are yellow or olive drab. However, the very low zinc/nickel alloy deposits will take a silver or a nonsilver black chromate but there is very little of this seen commercially at this time.

The zinc/nickel alloys provide the best salt spray corrosion resistance performance of all the zinc/alloy processes as well as the best performance for the cyclic heat/corrosion tests.

The acid process is ammonia chloride based. In earlier work the dual anode system was often used with zinc and nickel anode baskets being attached to different rectifiers. Today the practice has changed to using zinc anode baskets with carbon auxiliary anodes. Table IV provides the typical operating parameters for the acid zinc/nickel process. Figure 4 shows the thickness and alloy content profile for this process showing the high efficiency of the acid process as well as good alloy distribution over the current density range. Table IV Operating Parameters for Acid Zinc/Nickel

Operating Parameters	Rack	Barrel
Zinc Metal	5.3 oz/gal	5.3 oz/gal
Nickel Metal	3.3 oz/gal	2.7 oz/gal
Zinc Nickel	1.6-2.0	1.8-2.3
Ammonium Chloride	37 oz/gal	37 oz/gal
рН	5.5-5.9	5.5-5.9
Temperature	90-110°F	90-110°F
Anodes	Zinc/Titanium Baskets	Zinc/Titanium Baskets
Auxiliary Anodes	Carbon	Carbon
Filtration	Continuous	Continuous

There is a matte acid zinc/nickel process that was designed specifically for the aerospace industry [5]. The process is designed to provide only the minimum of grain refinement. The purpose is to provide a porous matte deposit that will allow hydrogen to be baked out of the hardened substrate more readily.

The alkaline zinc/nickel process is somewhat similar to the conventional alkaline zinc processes with the addition of additives containing the nickel ions and a complexor mixture designed to promote nickel alloy content. Some types of processes require that the temperature remain below 80°F while others operate at 90-110°F. The anodes are typically steel with the zinc content being maintained using the side tank. Table V gives the typical operating parameters for the alkaline zinc/nickel process and Figure 5 shows the typical thickness and alloy content profile showing the lower efficiency of the alkaline process resulting in better thickness distribution.

Performance Comparisons of Zinc Alloys

Any discussion of alloy zinc deposits results in an attempt to compare the properties and operating conditions. To this end, Table VI provides a list of salient features of the range of processes. The alloy content obtained depends largely on the concentration of the alloying metal advantages of other acid zinc processes. The process is better at plating iron castings and hardened or heat treated steels than alkaline processes. The plate distribution is not as good as alkaline processes but alloy content is fairly constant over the current density range as shown in Figure 1. The alloy content of the deposit depends on several factors including the amount of cobalt metal in the plating bath. the temperature, and the concentrations of some of the additives.

The acid zinc/cobalt alloy process can be ammonia free, low ammonia, or high ammonia. In general the barrel and rack formulations are slightly different in composition, as are the conventional acid zinc plating baths and for many of the same reasons. Table I shows the typical composition of the ammonia free acid zinc/cobalt bath. The anodes used are conventional zinc balls in a titanium basket.

Table I
Typical acid zinc cobalt bath concentrations

Operating Parameters	Rack	Barrel
Zinc Metal	6 oz/gal	4 oz/gal
Cobalt Metal	1.3 oz/gal	0.9 oz/gal
Boric Acid	2.5-3.0 oz/gal	
Potassium Chloride	25 oz/gal	18 oz/gal
pН	4.8-5.3	4.8-5.3
Temperature	90-110°F	90-110°F
Anode	Zinc Titanium Basket	Zinc Titanium Basket
Filtration	1-2 turnover/hour	1-2 turnover/hour

Alkaline zinc/cobalt is similar to conventional alkaline zinc in composition and practice. Typical rack and barrel bath compositions are slightly different as shown in Table II. The anodes are generally steel and the zinc concentration is maintained using a side zinc dissolving tank. The advantage of using the alkaline process is that distribution is better over the current density ranges and cobalt content is not greatly changed by current density as well. Figure 2.
 Table II

 Typical alkaline zinc cobalt bath concentrations

Operating Parameters	Rack	Barrel
Zinc Metal	1.6 oz/gal	1.2 oz/gal
Cobalt Metal	60 ppm	30 ppm
Zn/Co Ratio	200:1	260:1
Caustic Soda	16 oz/gal	16 z/gal
Soda Ash	4 oz/gal	4 oz/gal
Anodes	Steel	Steel
Cooling	Required	Required
Temperature	70-90°F	70-80°F

Zinc/Iron Deposition Process and Chromates

The zinc/iron alloy process is typically alkaline and has many of the properties of conventional alkaline zinc and alkaline zinc/cobalt The thickness distribution is more uniform than acid processes and the alloy distribution is very good over the current density range normally used. Like zinc/cobalt the zinc/iron deposit accepts a non-silver black chromate for the same reasons mentioned above for zinc/cobalt and the corrosion resistance of the non-silver black chromate is very good compared with typical silver black chromates. The zinc/iron deposits also readily accept yellow and olive drab chromates. Also, as with zinc/cobalt, the zinc/iron deposit does not provide a good blue bright chromate unless the alloy content of the deposit is very low. The best corrosion protection is obtained if the alloy is above 0.4% iron.

The alkaline zinc/iron plating bath composition is somewhat similar to that of conventional alkaline zinc, with the addition of the iron ions with a complexor blend that is designed to promote the deposition of iron. The anodes are typically steel anodes and the zinc metal concentration is maintained by the use of a side tank. Typical concentrations of the barrel and rack baths are given in Table III. The profile for thickness and alloy distribution for the alkaline zinc/iron process is shown in Figure 3.

The thickness methods that have been used successfully for zinc alloy deposits in our laboratories are microscopic cross section [10], magnetic measurement [11], beta backscatter [12] and x-ray fluorescence (XRF) [13]. Other methods may apply as well. The cross section method is generally considered the most reliable method and is generally used to provide standards for other methods. This is, of course, a destructive method and is very time consuming. The magnetic method is generally the next best method but requires the deposit be on steel that has not become magnetic itself during machining operations. X-ray fluorescence has found wide application because standards can be prepared for a wide variety of deposits over a wide variety of substrates.

The determination of the alloy content of a zinc alloy is best determined by atomic absorption. Electron Dispersive X-ray (EDX) is useful for zinc/iron. zinc/cobalt and zinc/nickel alloys and X-ray fluorescence (XRF) is useful for zinc/nickel but these methods are not as reliable as atomic absorption.

Some difficulties should be noted here. If the thickness of a zinc/nickel deposit is below about 0.25 mil the XRF readings will often show that the nickel content is high, but AA analysis shows the opposite. It appears that the XRF method has some difficulty in determining the zinc/nickel alloy content when the deposit is thin. Zinc/iron deposits present a special problem since once the deposit is plated onto a steel substrate it is impossible to strip the deposit without also stripping some of the part as well. In addition the EDX method "sees" the iron from the substrate if the deposit is below about 1 mil. Thus, for zinc/iron the deposit must be prepared on a nonferrous surface.

For atomic absorption work the deposit must be dissolved completely from the substrate. If a smut remains on the substrate it is likely some of the cobalt or nickel alloy. This will result in erroneous results. The use of 3-5% hydrogen peroxide with hydrochioric acid assists in dissolving the deposit completely. Also, when atomic absorption is used it is very important to operate within the linear concentration range of the instrument. Best results are obtained if internal standards are used. Corrosion protection is commonly measured by salt spray [14] or the Kesternich method [15] for quality control purposes. Obviously, the deposits must be tested in the expected use environment before they can be certified for service in a particular application.

A comparison of the alloy processes requires a measure of thickness and alloy distribution of the various deposits. For this discussion standard Hull cell panels were plated from a 500 mL cell at 2 amps for 20 minutes to build up enough deposit to measure thickness and alloy content. The thickness was measured by the magnetic method and XRF and alloy content was measured by EDX. XRF (for zinc/nickel) and by atomic absorption. The results are plotted to facilitate the comparisons

Zinc/Cobalt Deposition Processes and Chromates

Zinc alloys with cobalt can be deposited from acid or alkaline plating baths. The processing baths are very similar to those used for normal zinc plating but with the addition of cobalt and a complexor package that is designed to promote the deposition of cobalt with the zinc. The composition of the alloy that has been proven to provide the best corrosion protection is in the range of 0.4-1.0 weight percent of cobalt in the alloy. Lower cobalt content does not provide a significant improvement in corrosion protection.

Cobalt alloys will receive yellow, olive drab and black chromate conversion coatings. The cobalt alloys also permit the development of a black chromate that is not based on silver. In conventional zinc plating the black chromate obtains its color from metallic silver that forms during the chromating process. With zinc/cobalt alloys the black color can be developed from the cobalt that dissolves from the zinc/cobalt deposit and silver is not needed. The resulting black chromate film is more protective than traditional silver based chromates. For a non-silver black chromate to work well the zinc/cobalt alloy must generally contain at least 0.4% cobalt. Zinc/cobalt alloy deposits that contain cobalt in the range of 0.4-1.0 weight percent cobalt will generally not provide a good looking blue bright chromate conversion coating.

The acid zinc/cobalt deposition has the

ALLOY ALTERNATIVES TO HEXAVALENT CHROMIUM

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Recent environmental regulations mandating extensive testing and equipment investments for hexavalent chromium electroplaters have generated much interest in alternative processes for decorative and functional purposes. Among the growing list of available technologies designed to replace electrolytic chromium are a variety of alloy electrodeposits. These alloy processes possess diverse physical and operational characteristics affecting their suitability to specific applications. Operation of several commercially available alloy alternatives to hexavalent chromium and the resulting deposit properties are described.

Introduction

The U.S. EPA has promulgated national standards for chromium emissions. These impact regulations hexavalent chromium anodizing and electroplating operations. Hexavalent chromium processors must control chromium emissions by a combination of two fundamental methods. These include the use of add-on air pollution control device(s) and/or chemical fume suppressants.1

Using control devices, the ventilation and scrubbing system for decorative hexavalent chromium plating must achieve limits of 0.01 mg/dscm. Hard chromium plating must meet levels of 0.015 to 0.03 mg/dscm depending on the size of the electroplating tank. A decorative process employing chemical fume suppressants can comply by continuously controlling the surface tension below 45 dynes/cm. Either technique involves additional responsibilities. Developing stricter maintenance plans, monitoring, record keeping and reporting is required.

These stringent requirements for chromium plating have intensified the search for alternatives. However, even decades before the recent regulations, interest in replacing hexavalent chromium systems existed.

Hexavalent chromium plating is a troublesome component of the electroplating cycle. The difficulties associated with plating from this process are numerous. Certainly, negative environmental factors are apparent. The concentrated chemistry is extremely corrosive. Also, risk to personnel caused by exposure to hexavalent chromium mist is well documented.

However, operational problems are its most serious limitations. The hexavalent chromium process is often the largest cause of plating rejects.

The most common problems are whitewash, chrome skips and inefficiency. Whitewash results from the need for extremely well rinsed and activated nickel deposits prior to the chromium step. This is difficult to obtain and may require additional tanks to install a special "chrome sour" activation step. Sensitivity to substrate activation prohibits use of hexavalent chromium in bulk plating applications.

The extremely poor throwing power of hexavalent chromium causes "misplates" or "chrome skips" in low current density areas. This property often results in the need for costly auxiliary anode fixtures.

Most importantly, rack design for the entire plating operation is based on the poor covering power of the chromium process. Fewer parts are placed on a rack to prevent misplates. Consequently, the chromium plating tank is the limit to productivity.

The low cathodic efficiency of the process affects operating cost. Expensive equipment is required to achieve the necessary voltages and amperages. This significantly increases utility usage and costs.

This combination of health and operational problems spurred the interest in alternative chemistries. In the late 1970's, commercial trivalent chromium plating was introduced. Besides the environmental advantages of being safer and non-corrosive, trivalent chromium overcomes several of the difficulties observed in hexavalent chromium plating processes. The operating window is wider. With greater throwing power and less sensitivity to substrate activation, many rejects were eliminated.

Trivalent chromium has made a large impact in the plating market. However, it also has limitations. There are several problems with the deposit properties. First, there is a significant color difference between the trivalent and hexavalent deposits. The trivalent deposit is darker compared to hexavalent chromium. Extensive research has improved the appearance but trivalent and hexavalent chromium plated parts are seldom mixed on single assemblies. Trivalent chromium is also a softer deposit. Finally, over thin nickel substrates, the corrosion resistance is a fraction of the protection afforded by the coating from a hexavalent solution.

There is a large disparity between the physical properties of hexavalent versus trivalent chromium. Due to these shortcomings, trivalent

chromium is primarily utilized as a decorative coating in non-corrosive applications.

Along with the physical shortcomings of the trivalent chromium deposit, the chemistry also has limitations. These processes are sensitive to metallic contamination including hexavalent chromium, zinc and copper. In applications where significant contamination is possible, use of ion exchange resins is recommended. Furthermore, some processes can become destabilized by a polymerization mechanism of the chromium complex² causing thin deposits.

Electroless nickel is also being used as a replacement for hexavalent chromium in It exhibits several functional applications. excellent properties including hardness. corrosion resistance and uniform coating thickness These characteristics make electroless nickel ideally suited for functional chromium applications. However, electroless nickel is not designed for decorative uses and may be too expensive for some functional applications.

The desire to switch from hexavalent chromium processes to safer and more controllable technologies is intensifying. A variety of alloyed coatings are being investigated for these applications. Some technologies have been available for years and others are newly being introduced to the marketplace. The available chemistries and resulting deposits significantly differ from each other and the standard, hexavalent chromium. Each process has its unique set of advantages and disadvantages. Several commercially viable electrodeposited alloys are examined and compared.

These alloys include tin-nickel, cobalt-tin, cobalt alloys, and nickel-tungsten. The alloys are designed primarily for decorative applications. However, nickel-tungsten is also a functional coating.

Tin-Nickel

One of the most interesting alloys available for use as an alternative to hexavalent chromium is the tin-nickel coating. It possesses a combination of some of the best advantages and the greatest disadvantages of the alloys discussed. This coating is among the oldest technologies available as alternatives to chromium. The deposit is an intermetallic compound forming a distinct alloy of 65% tin and 35% nickel over a wide variety of operating conditions. This corresponds to a 1:1 molar ratio of the elements.

The appearance of a thin deposit over a reflective surface such as decorative nickel is bright and generally appealing. The most striking aspect of the deposit appearance is its color. The tin-nickel electrodeposit has a definite pink cast. The warm, rosy appearance may be advantageous since it is a distinctive coating causing the work to stand out from competitive products. However, if the appearance of chromium is sought, the pink tinge negatively impacts the uses of this coating.

Like hexavalent chromium and most available alternatives, the tin-nickel process does not incorporate brightening and leveling agents. Consequently, the deposit will only reflect the luster of the underlying surface. If the base metal is dull, the resulting finish with the tinnickel alloy will be dull. Like chrome, as the deposit thickness increases, the brightness from the undercoat gradually dulls. The luster is restored by a light buffing, but thicker tin-nickel deposits become very brittle. Care must be exercised when attempting to buff the surface.

Tin-nickel retains its brightness over time without the use of a top coat. This strength does not quite match hexavalent chromium's ability to maintain its appearance but tin-nickel is better than most alternatives to hexavalent chromium. Additionally, tin-nickel resists staining caused by fingerprints.

Not only does tin-nickel demonstrate tarnish resistance, the deposit is also very resistant to chemical attack. The alloy can only be dissolved by use of strong, hot mineral acids. Unfortunately, the resistance of the alloy does not extrapolate directly as a coating over plated work. The corrosion resistance of a two minute tin-nickel deposit over nickel plated steel is roughly equivalent to trivalent chromium. Use of a hexavalent chromium passivate will improve the base metal protection. The resistance to chemical attack does have one negative side effect. The deposit is extremely difficult to strip. One available technique is to remove the coating anodically in near boiling sodium cyanide solution. Obviously, the requirement to use such drastic techniques limits this process.

Deposit hardness is another strength of the tin-nickel coating. The 65-35 tin-nickel alloy has a reported hardness of 650 VHN³. This value surpasses bright nickel which has a value of around 500 to 550 VHN. However, it is much softer than decorative hexavalent chromium with reported hardnesses of over 900 VHN. Tinnickel is one of the harder coatings compared to the other alloys. Contributing durability and scratch resistance to a bright nickel coating is not the only advantage gained from harder The ability to bulk plate larger or coatings. heavier parts is often determined by the hardness of the final deposit.

The chemistry of the tin-nickel process is one of the most severe limitations on the viability of this process. A typical formulation for this process includes⁴:

NiCl ₂ •6H ₂ 0	250 - 300g/L
SnCl ₂ •2H ₂ O	45 - 50 g/L
NaF	30 g/L
NH ₄ F	35 - 38 g/L
pH	4.5 - 5

The electrolyte of the tin-nickel alloy requires high concentrations of fluoride ion. Fluoride functions as a complexor and stabilizer for the tin molecule. Without fluoride, tin would not dissolve at the weakly acidic pH. Also, fluoride performs the vital task of stabilizing the proper (+2) valence state of the tin. Stannous tin in weakly acidic solutions is prone to oxidize to the stannic (+4) form.

The need for fluoride causes the chemistry to be extremely aggressive. While the pH is weakly acidic, the equipment required to operate the process must be designed as if operating an acid tin or a hexavalent chromium bath. Excellent ventilation is required since hydrogen fluoride gas can be generated during the electrolysis of the tin-nickel solution. Proprietary additives improve the overall appearance of the deposit. These additives are used at very high concentrations, often higher than 10 g/L. The type of advantages observed relate to the overall tone and luster of the deposit. These additives do not contribute any leveling to the coating.

Operation of the tin-nickel plating bath is straight forward. The following table highlights typical operating parameters and aspects of the process for decorative applications.

Time	2 to 6 minutes
Current Density	15 to 30 ASF
Temperature	130 to 140 °F
рН	4.5 - 5
Cathode Efficiency	95%+
Anodes	Nickel
Agitation	Mild - no air

Control of the tin-nickel solution involves routine maintenance of several components. The tin content is controlled by addition of tin salts. Tin is not only lost by electrolysis, but also by oxidation to stannic tin. Stannic tin does not plate out during electrolysis. Consequently, tin gradually builds in the solution requiring corresponding increases in fluoride concentration to keep tin stable in solution. Because of the potential for oxidation of tin, air agitation can not be used on this process. The nickel is maintained by use of the nickel anodes.

Tin Cobalt

Tin is a main component in another commercially available alloy designed for use as a decorative topcoat for nickel. This alloy, tincobalt, is designed for use primarily in bulk plating applications. There are two distinctly different chemistries utilized, an acidic process and a weakly alkaline chemistry. The two processes deposit equivalent alloys and exhibit similar (although not identical) properties.

Acidic Tin-Cobalt

The acidic tin-cobalt alloy has a chemical matrix similar to the tin-nickel process. The solution requires high levels of fluoride concentration to stabilize the tin in its proper valence (Sn^{+2}) and retard oxidation to the stannic

state. The tin-cobalt composition differs from tinnickel by its strongly acidic pH.

One reported composition for this process follows 5 .

CoCl2•6H20	375 g/L
SnCl ₂	45 g/L
NH ₄ HF ₂	82.5 g/L
NH ₄ Cl	37.5 g/L
pH	2.5

The, high fluoride, high chloride and low pH make this process extremely corrosive.

The composition of the allov is approximately 80-20 tin-cobalt. The resulting deposit properties yield a variety of advantages. The most distinctive advantage is the deposit Compared to all other alloys appearance. covered in this text, the acidic tin-cobalt alloy appears most similar to hexavalent chromium. Not only is the color of a decorative deposit of about 0.50 to 0.75 µm (20 to 30 µ-in.) light and highly reflective, but it also has a tint of blue to its Additionally, like most of the appearance. chromium alternatives, the throwing power of tincobalt is superior to hexavalent chromium.

Along with the excellent color and throw, a passivate is not required to maintain a tarnish resistant surface. However, a hexavalent chromium passivate is needed in order to achieve corrosion a resistance similar to hexavalent chrome. Corrosion resistance is improved by plating thicker deposits.

The most negative aspect of the deposit properties is its hardness. Due to the high levels of tin in the alloy, the deposit is soft. Hardnesses range around 350 to 400 Vickers. This softness compared to hexavalent chromium limits the available uses for the coating.

Operation of acidic tin-cobalt in barrel applications is similar to operation of a bright nickel process. However, insoluble anodes are required and the solution composition is maintained by addition of the metal salts. The conditions for barrel plating include:

4-0 minutes
3-5 ASF
150 to 160 °F
2.5
90%+
graphite

Given the excellent color and corrosion resistance, this process appears to have the best physical properties as an alternative to hexavalent chromium in bulk plating processes. However, the extremely corrosive nature of the acidic tin-cobalt electrolyte is a serious deficiency. The combination of low pH, high halides. insoluble anodes and elevated temperatures (160 °F) make this process very difficult to operate. Along with the required concern for the process tanks, the high fluoride and high temperatures will result in significant levels of hydrogen fluoride gas formation. Excessive attack of the buss work and other equipment can result. Additionally, the corrosive gasses that evolve make the process dangerous to operate.

Alkaline Tin-Cobalt

Research efforts were performed to develop a tin-cobalt alloy with a less corrosive electrolyte. A weakly basic tin-cobalt process was developed. The basic chemical make-up is:

CoSO ₄ •7H ₂ 0	3 - 5 g/L
SnSO₄	3 - 5 g/L
Organic Complexor	10 - 20 g/L
Wetter	0 - 2%
рН	8.5

The alloy from this electrolyte is also 80-20 tin-cobalt. The major advantages of this formulation over the acidic process include noncorrosive pH, non-corrosive metal salts and a significantly dilute solution.

Like the acidic electrolyte, the alkaline bath is best for bulk plating processes. The principal difference in the physical properties is the color difference of the deposits. While the acidic solution is the most chromium-like deposit of all the alloys, the deposit from the alkaline bath has a slightly darkened tinge with no blue to its cast. This deposit looks more like a trivalent chromium coating. Another difference in properties is the corrosion resistance of the deposit. The alkaline bath is similar to trivalent chromium in its corrosion resistance. The variance in corrosion protection afforded by the two tin-cobalt alloys is primarily from the inability of the alkaline process to plate thicker deposits. The alkaline process is limited to a thickness of approximately 0.25 μ m (10 μ -in.).

Conditions for operation of the alkaline process are as follows:

Time	4 - 8 minutes
Current Density	2 - 10 ASF
Temperature	100 - 120 °F
pH	8.0 - 9.0
Cathode Efficiency	90%+
Anodes	Stainless Steel

The chemistry tends to be unstable for all of the tin based alloys. This results from negative side effects caused by oxidation of tin. It is not uncommon to need to dump and remake the tank due to this instability issue. Additionally, the tin-cobalt alloys do not perform well in rack applications and the tin-nickel alloy has an objectionable pink tone. These problems have significantly reduced the commercial acceptance of tin based alloy processes.

Cobalt Alloys

Recent efforts centered on developing a stable chemistry capable of depositing a hexavalent chromium type deposit for decorative applications. Progress has been made using cobalt based alloy chemistries.

Cobalt alloys are among the most stable alloys available as alternatives to hexavalent chromium. This results from the basic electrolyte employed. The chemistry is very similar to a dilute sulfate based electrolytic nickel composition.

Cobalt is readily alloyed with other members of the iron series metals. The nature of the alloys is as codeposits of the metallic species in solution. Consequently, as the concentration of the metals in solution is varied, the composition of the alloy will change. This differs from an intermetallic compound such as tin-nickel that consistently plates similar alloys over wide metallic concentration ranges.

Typical elements used in forming cobalt alloys are iron and nickel. The resulting alloys generally contain up to 50% nickel and up to 10% iron. Generally, much lower amounts of alloying elements are used and the cobalt ranges from 70 to 95% of the deposit. Cobalt alloys can be produced without nickel in the matrix. Processes such as cobalt-iron are being used for applications requiring nickel-free deposits.

The electrolyte is acidic and sulfate based. A typical alloy process electrolyte is given below.

CoSO4 • 7H20	10 - 40 g/L
NiSO4 · 6H20	0 - 20 g/L
FeSO ₄ •7H ₂ 0	0 - 5 g/L
Addition Agent	0-4 %
Wetter	0 - 2%
рН	3.2

When plated as thin deposits of 0.50 to 0.75 μ m (20 to 30 μ -in.) over bright nickel in rack and barrel applications, the appearance is bright and nearly full white. There is no blue in the tone. When compared to hexavalent chromium, the deposit does appear to look yellowish. However, when compared to bright nickel, the appearance is obviously white.

As with most decorative hexavalent chromium alternatives, cobalt alloys do not have brightening or leveling capabilities. The coating simply mirrors the brightness of the undercoat. Additionally, as the deposit increases to a thickness of greater than 5.0 μ m (200 μ -in.), the appearance dulls to a matte gray.

Cobalt alloys yield excellent coverage. Typically, the cobalt covers any area that is nickel plated. This characteristic is similar to the other chromium alternatives. The deposit hardness ranks between the soft tin-cobalt processes and medium hard tin-nickel. Hardnesses of about 450 to 500 VHN are observed.

Operation of cobalt alloy processes requires use of a hexavalent chromium based passivate. Similar passivates are recommended for the other alloys to maximize corrosion resistance. However, for the cobalt alloys, the passivate is required to obtain acceptable deposits. This results from the active nature of cobalt metal. If a passivate is not employed, the cobalt deposit will tarnish before the part is dried. Once passivated, the coating remains free of tarnish and yields corrosion resistance superior to trivalent chromium processes and approaching hexavalent chromium.

Operating conditions for rack applications include:

1 - 4 minutes
15 - 25 ASF
120 - 130 °F
2.9 - 3.4
90%+
Graphite
Mild - no air

The cobalt alloys operate using insoluble anodes. To maintain the proper solution composition, metal salts are added back into the tank. During operation, the pH continually falls and must be maintained closely. As with the tin alloys, air agitation should not be used to prevent oxidation of the bivalent ions. Besides these issues, control of the cobalt alloy processes is straightforward and consistent.

Acceptance of the cobalt alloy deposits is limited for three basic reasons. First, the color of the deposit is white and does not contain any of the blue hues observed in chromium coatings. This is a problem when trying to color match parts. Secondly, barrel plating has proven difficult due to sporadic staining that can not be fully eliminated. Finally, the need for a hexavalent chromium based passivate appears to diminish its use as a chromium alternative.

This need for a hexavalent chromium passivate is justified for two reasons. First, the passivate is very dilute. Consequently, use of chromium alternatives significantly reduces chromium usage in the plant. Also, the passivate is an immersion process. Misting of the chromium caused by electrolysis does not occur in this application.

Nickel-Tungsten

Nickel-tungsten is the most recent chemistry introduced to the market. This coating

promises to be the most versatile alternative to chromium. Nickel-tungsten is being used commercially in rack and barrel processes. Additionally, it is the only alloy presented here that is designed for both decorative and functional applications.

The alloy deposited from a nickel-tungsten electrolyte is approximately 30 to 40% tungsten, 60 to 70% nickel. Other elements such as boron can also be incorporated into the deposit. Tungsten can not be plated out as a pure metal. By introduction of a Group VIII Transition Metal into the chemistry, tungsten will deposit as an alloy. Cobalt-tungsten and iron-tungsten alloys have also been obtained. The alloy deposited is consistent over a wide range of metallic concentrations in the solution.

Incorporating tungsten into a nickel matrix contributes a number of exceptional deposit properties. Of key importance in decorative applications are the appearance and corrosion resistance. The color of the coating is white with a slightly dark tinge. It is a close match to a light trivalent chromium deposit. Only the acidic tincobalt process has a more chromium-like appearance.

Corrosion resistance needs to be considered two separate properties, as resistance to surface tarnishing and resistance to base metal corrosion. The nickel-tunasten deposit has moderate resistance to surface By incorporation of a hexavalent staining. chromium passivate, this property is greatly However, when considering base enhanced. metal protection, nickel-tungsten over bright nickel is superior to hexavalent chromium and its alternatives. A passivate is not required to obtain excellent base metal protection.

The ability to quickly plate thick coatings coupled with the deposit hardness makes the nickel-tungsten alloy an excellent alternative to hexavalent chromium for functional applications. The as-plated hardness of nickel-tungsten is about 650 to 750 VHN. This value compares very well with most of the chromium alternatives although it does not match the 1000+ VHN hardness values of functional hexavalent chromium. However, nickel-tungsten can be further hardened by heat treatment. Four hours of heat tempering at 400° F will raise the alloy coating hardness up to 850 VHN. In addition, the resulting deposit hardness increases wear resistance.

The basic chemical make-up of the solution includes:

Na ₂ WO ₄ •2H ₂ 0	10 - 80 g/L
NISO4+6H20	3 - 20 g/L
Organic Complexors	50 - 90 g/L
NH₄OH	5 - 20 g/L
Brightener	0-4 %
Wetter	0 - 2%
pН	6.0 to 8.5

The cited ranges for the chemical constituents are purposefully wide because of the many potential uses for the process and ongoing research efforts.

Overall, the chemistry is dilute and can be operated at a wide range of metals to achieve similar alloys. Consequently, the process is easily maintained and a consistent alloy is obtained despite fluctuations in the chemistry.

Also, brightener systems can be used with the nickel-tungsten process. This allows for bright plating of thick deposits. This characteristic differs from all of the other alloy processes that can not plate thick, bright deposits.

Process control parameters for decorative rack applications are as follows:

Time	1 - 4 minutes
Current Density	15 - 25 ASF
Temperature	135 - 145 °F
pH	6.0 - 8.5
Cathode Efficiency	25 - 30%
Anodes	Stainless Steel
Agitation	Mild
Plating Rate (20 ASF)	0.1 µm /minute

When operating the process for functional applications, the process must be run at higher current densities to achieve acceptable plating rates. Typical parameters include:

Time	0.5 - 10 hours
Current Density	60 - 85 ASF
Temperature	135 - 145 °F
pH	6.0 - 8.5
Cathode Efficiency	30 - 35%
Anodes	Stainless Steel
Agitation	Mild
Plating Rate (60 ASF)	25 µm/hour

Nickel-tungsten can also be barrel plated. Bulk plating is effective for thin decorative applications and also for thick functional applications.

All of the alloys discussed here have performed successfully in commercial installations. However, nickel-tungsten has only been used commercially on a limited basis. More experience is needed to prove the viability of this process.

Summary

A variety of alloy electroplating processes are available as alternatives to hexavalent chromium. These processes differ in their chemistry, operation and deposit properties. Each of these coatings possess their own specific advantages and disadvantages. Depending upon the application, one or several of these chemistries may be suitable replacements for chromium.

The interest in hexavalent chromium alternatives is environmentally motivated. Relief from regulatory compliance requirements and concern for worker health and safety are the driving forces. To achieve these goals, organizations expect that they must tolerate reduced quality and increased cost for the chromium replacements.

However, in many cases the alternatives outperform chromium and may actually be more economical. All of these alloys are efficient processes requiring significantly less current and voltage compared to chromium. Also, the high rate of rejects typically experienced in chromium plating due to "whitewash" and "misplates" is avoided. The excellent throwing power of these alloys can greatly increase production by allowing for redesigned racks which accommodate more parts. Finally, the ability to bulk plate parts with a chromium-like finish can dramatically increase productivity.

There are numerous advantages of these alloys compared to hexavalent chromium. In many cases, process performance and economic gains may be the compelling reason to switch to these processes.

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