Chrome Electrodeposition Additives

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The deposition of chromium is generally undertaken for one of two purposes: to provide a brilliant untarnishable finish, or to produce a hard abrasion resistant surface [1]. Chromium plating solutions are notorious in that only hydrogen gas evolves at usual plating current densities, and metallic chromium is deposited only at high current densities. In other words, the bath has exceedingly poor "covering power". The desired bright plate appears only within a relatively narrow current density range, which on the lower side is limited by a range with milky deposits and on the upper side by a range with frosty and burnt deposits. All of these difficulties are less pronounced when a fluorine-containing catalyst is employed, alone or with the sulfate in a low chromic acid content bath, and such bath finds an excellent application in barrel plating [2].

The actual concentration of the bath is not critical but the ratio of chromic acid/sulfuric acid is most important. This ratio usually falls within the range 80:1 to 120:1, with 100:1 being the popular value. The concentration of chromic acid is normally within the range 150-550 g/L. The throwing power of chromium baths is notoriously poor. The current efficiency of the chromium baths is very low compared with baths used for plating other metals. Baths used for depositing regular chromium have cathode efficiencies ranging between 6 and 16%, the more dilute baths having the high efficiencies[3]. Role of activators such as sodium silicofluoride and sulfuric acid in bright chrome electroplating was investigated using technical grade chromic acid, CrO_3, containing 0.15% sulfate, maximum. It was found that bath comprising CrO_3 300-350 g/L, Na_2SiF_6 2-3 g/L, H_2SO_4 1-2 ml/L at temperature 30-35°C and current density 8-10 A/dm^2 can be recommended as a self-regulating one for bright chrome plating [4].

The chemical composition, chemical state and possible compound for chromium deposits obtained from acidic, pH 1.5-1.7, chromium(III) oxalate-sulfate solutions were studied with the use of XPS. From the solutions containing ≥100 g/L $Cr_2(SO_4)_3.6H_2O$, an amorphous carbide close to $Cr_{23}C_6$ with inclusions of metallic chromium clusters was deposited on the cathode. From less acidic solutions poorer in chromium, metallic chromium was deposited [5]. The list of additives for chrome electrodeposits along with selected conditions is given in Table 1.

A chromium plating bath was recommended to produce bright electrodeposits at a high current efficiency, high microhardness and with -less porosity. The bath contained chromic acid 250 g/L and K sulfate 2.5 g/L at 325K and cathodic current density 15.5-31.0 A/dm^2 [6]. The reduction of Cr(III) to Cr(II) on copper electrode in trivalent chromium urea bath containing $Cr_2(SO_4)_3.6H_2O$ and $CrCl_3.6H_2O$ as the chromium source has been investigated using a potentiodynamic sweep method. The potential scope in which sustained chromium deposits can be prepared was from –1.3 V to –1.7 V (vs. SCE) in the urea bath. Bright chromium deposits with thickness of 30 μm can be prepared in the bath [7].

Thick deposit of chromium on copper was obtained by electrodeposition in a bath containing $CrCl_3.6H_2O$ 0.4, $Cr_2(SO_4)_3.6H_2O$ 0.2, H_3BO_3 0.4, NaCl 0.4M, stabilizing agent 10 g/L, HCOOH 20 ml/L, and urea. The effect of acidity, current density, urea concentration, and deposition method on current efficiency was discussed therein. Bright chromium deposits having a thickness 30-40 μm were obtained under optimum conditions: pH 1.9-2.3, current density 7-11 A/dm^2, and urea concentration 2M [8]. It was found that an

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Table 1: The list of additives for chrome electrodeposits along with selected conditions

Sr No	Major Constituents, Concentrations	Additives, Concentrations	Operating Conditions	Properties	Reference
1.	CrO_3, 300-350 g/L	H_2SO_4, 1-2 ml/L, Na_2SiF_6, 2-g/L	Temperature 25-35°C, current density 8-10 A/dm^2	Improved throwing power, adhesion and appearance of the electroplate was good.	[4]
2.	$Cr_2(SO_4)_3.6H_2O$, ≥100 g/L	___	pH 1.5-1.7	An amorphous carbide closed to $Cr_{23}C_6$ with inclusions of metallic clusters deposited	[5]
3.	Chromic acid, 250 g/L	Potassium sulfate, 2.5 g/L	Current density 15.5-31.0 A/dm^2, temperature 325 K	Bright electyrodeposit at a high current efficiency, high microhardness, with less porosity	[6]
4.	$CrCl_3.6H_2O$, 0.4M, $Cr_2(SO_4)_3.6H_2O$, 0.2M	H_3BO_3, 0.4M, NaCl 0.4M stabilizing agent, 10 g/L HCOOH 20 ml/L, and urea 2M	pH 1.9-2.3, current density 7-11 A/dm^2	Bright chromium deposits having a thickness 30-40 μm	[8]
5.	Chromic acid	Organic complexing substanc (thiosemicarbazide diaceti acid), 2.7 g/L	___	Best conditions for the chromium reduction on cathode	[11]
6.	Chromic acid	C_1-C_{12} alkanesulfonic o alkanedisulfonic compound and aminoalkanesulfonic acid or salts thereof	___	Reduction in anodic corrosion, improved the covering and penetrating power of the bath, reduced surface tension, bright deposit	[14]
7.	CrO_3, 250-400 g/L	Sulfuric acid, 2.5-4.0 g/L boric acid, 10-15 g/L strontium sulfate, 1-1.5 g/L sodium fluoride, 0.2-2.0 g/L	Temperature about 50°C and current density 15.0-50 A/dm^2	Shiny mirror uniform microcrystalline electroplates	[15]
8.	CrO_3, 250-350 g/L	H_2SO_4, 2.5-3.5 g/L, $SrSO_4$, 2-4 g/L, and SiO_2, 0.5-1 g/L	Current density 10-20 A/dm^2, lead anode alloyed with 10% Sn or 7% Sn and 1% Ag	Alloying the anode decreased it potential and the rate of lea peroxide formation and Cr^3 oxidation.	[16]
9.	Chromium sulfate	Oxalic acid as a ligand and aluminum sulfate as a buffer agent	___	___	[17]
10.	Trivalent electrolytes	Formic acid and methanol	Temperature 25°C and a very gental agitation	An excellent quality of deposit with a deposition rate of 50-100 μm/h	[19]
11.	Chromic acid	CH additive	___	Microcrack chromium electroplating, productivity is doubled, 50% of the electricity is saved	[20]
12.	$Cr_2(SO_4)_3.6H_2O$, 25 g/L	Na_2SO_4, 100 g/L, H_3BO_3, 35-40 g/L, malonic or oxalic acid, 7-10 g/L, sulfur-containing surface active agent, 0.08-0.10g/L	pH 2.2-4.2; an current density 2-A/dm^2	Plastic chromium coatings at a current efficiency of 30-35%	[23]
13.	CrO_3, 50-250 g/L	Sulfate 1%, boric acid, lanthanum oxide	___	___	[25]
14.	CrO_3, 250 g/L	NH_4F, 30 g/L	Temperature 50°C current density 25-60 A/dm^2	Brighter deposits even up to 50 μm thickness	[26]
15.	$CrCl_3.6H_2O$, 0.8 mol/L	NH_4Cl, g/L 26, H_3BO_3, 2 g/L, NaCl, 36 g/L, and dimethyl formamide, 400 g/L, surfactant, 0.01 g/L and wetting agent, 1-2 ml/L	pH 1.1-1.2, temperature 25°C, current density 14 A/dm^2	Current efficiency reached ≥30%	[27]
16.	CrO_3, 200-250 g/L	H_2SO_4, d 1.84, and Cr^{3+}, 2-8 g/L	Temperature 55-60°C, current density 40-60 A/dm^2, and plating duration 2-3 minutes	Surface hardness, abrasion resistance, and decorative property of aluminum workpieces were increased and its service lifetime was lengthened	[30]
17.	CrO_3, 150-170 g/L	$SrSO_4$, 5-7 g/L, NaCl, 0.8-2.0 g/L, 1-(C_{20-35} alkyl)-4,5,6,7-tetrahydro-1H-indene , 2-5 g/L	___	Improved current efficiency	[31]
18.	CrO_3, 100 g/L	Cr-2S, 1-5 g/L	___	Current efficiency up to 20%, high quality bright chromium coatings are obtained	[33]

Table 1: Continued.

Sr No	Major Constituents, Concentrations	Additives, Concentrations	Operating Conditions	Properties	Reference
19.	CrO_3, 250-300 g/L	H_2SO_4, 2.5-3.0 g/L, and Cr^{3+}, 1.0-3.0 g/L	Temperature 48-52°C, current density 20-30 A/ dm^2,	Electroplate is uniformly silver grey, adhesion is good	[34]
20.	CrO_3, 120-180 g/L	H_2SO_4, 0.6-1.2 g/L, and LC additive, 1.5-2 g/L	Temperature 15-50°C, current density 4-30 A/dm^2	Reduction of the amounts of CrO and water used and lowered th operating temperature; th appearance of the electroplate wa good	[35]
21.	CrO_3 industrtial grade, 120-180 g/L	H_2SO_4 (CP), 0.5-0.9 ml/L, Cr^{3+} 0.3-2 g/L, and CS-type additive, a mixture of rare earth compounds	Temperature 20-45°C, cathodic current density 7-30 A/dm^2, tank voltage 3-10 V	Saved starting materials cost of wastewater treatment, (2) saved the electricity and thermal energy, and (3) improved working environment and simplifies production facilities	[36]
22.	Chromic acid	Halo carboxylic acid-rare earth compound mixture	____	Throwing power and cathodic current density were improved, the Vicker's hardness of the electroplate was 980-1100, and the adherence was good	[37]
23.	CrO_3, 160-200 g/L	Cr^{3+}, 1-3 g/L, H_2SO_4, 0.5-1.2 g/L, and RL-3C additive, 4.5-5.5 g/L	Temperature 40 ± 5°C, current density 6-12 A/dm^2	Improvement of throwing power, lowering current density i.e. higher current efficiency, better working environment	[38]
24.	CrO_3	SiF_6^{2-}, BF_4^-, and blackening agents, such as $NaNO_3$	____	____	[40]
25.	Chromic acid	Rare earth additives	____	Better electroplating bath and electric conduction, internal stress, porosity, deposition rate, average power consumption, cost, and pollution was improved	[41]
26.	Chromic acid	H_3BO_3, 5-10 g/L, H_2SO_4	____	Bright chrome electrodepsoit, improved the electrolyte covering power, and also the current efficiency	[44]
27.	CrO_3, 50-180 g/L	CS additives comprising multiple kinds of rare earths	Current density 4~60 A/dm^2 and at Temperature 15~70°C	Throwing power increased by 30~50%, whereas corrosion resistance of the coating by NSS test was 2-3 grades higher and hardness was up to 850~1270 Hv	[45]
28.	Chromic acid	Sulfoacetic acid, iodate, and a N organic compound (glycine)	Temperature ~50-70°C	Bright and smooth functional chromium elecrodeposit, current efficiency ≥ 20%	[47]
29.	CrO_3, 200 g/L	Sulfuric acid, 2 g/L			[50]

introduction of fluoride ions into sulfuric acid solutions of chromium(III) containing oxalic acid substantially increased the chromium current efficiency, up to 43%. It was supposed that fluoride ions affect the composition of film that was formed on the electrode during chromium deposition [9].

Effect of type and concentration of foreign acid anions on the course of stepwise reduction of chromium(VI) oxide was reported. When two types of chromium electroplating catalytic agents were applied: sulfate anions and hexafluorosilicate(IV) anions, the reduction rate of the cathode layer was twice larger than in the case, when only one type of catalytic agent was applied [10]. The action of the organic complexing substance, thiosemicarbazide diacetic acid, on kinetics of chromium electroplating and cathode current efficiency was investigated. The optimum concentration of organic substance of 2.7 g/L was the best conditions for the chromium reduction on cathode. Formation of a stable complex of organic substance with CrO_3 was determined [11].

The kinetics of oxygen, ozone, and Cr(VI) ion for oxidation on platinum and lead, PbO_2, electrodes in chromium(III) sulfate solution with an additive of oxalic acid as the ligand was studied. It

was shown that chrome plating in chromium(III) sulfate solutions proceeded without accumulation of Cr(VI) ions and may be performed without separation of anode and cathode compartments when platinum or titanium-platinum anodes were used [12]. Reduction of chromic acid(VI) to metallic chromium occurred as a result of cathode reduction of surface layer composed of chromium compounds. This reduction was possible only in some defined range of pH in the cathodic diffusion area. pH in the cathodic area was determined by the type and concentrations of foreign acid anions. Their advantage was that they formed with Cr(III) and hydroxide ions the anion complex $[Cr_x^{3+}(H_2O)_y(OH)_w(A)_2]^{n-}$, which prevented excessive alkalization of the cathodic area and enabled metallic chromium deposition [13].

C_1-C_{12} alkanesulfonic or alkanedisulfonic compounds and aminoalkanesulfonic acids or salts thereof, were used as additives in chromium plating baths, to reduce anodic corrosion, improve the covering and penetrating power of the bath, reduce the surface tension and gave a bright deposit [14]. Composition of an electrolyte for hard decorative chromium electroplating was proposed. The electrolyte for hard decorative chromic plating at temperature about 50°C and current density 15.0-50 A/dm^2 contained 250-400 g/L chromic acid, 2.5-4.0 g/L sulfuric acid. Shiny mirror uniform microcrystalline electroplates were obtained in this electrolyte with added 10-15 g/L boric acid, 1-1.5 g/L strontium sulfate and 0.2-2.0 g/L sodium fluoride [15]. The bath comprising CrO_3 250-350, H_2SO_4 2.5-3.5, $SrSO_4$ 2-4, and SiO_2 0.5-1 g/L was used. The current density was 10-20 A/dm^2. The lead anode was alloyed with 10% Sn or 7% Sn and 1% Ag. Alloying the anode decreased its potential and the rate of lead peroxide formation and Cr^{3+} oxidation [16]. A new chromium(III) sulfate solution, containing oxalic acid as a ligand and aluminum sulfate as a buffer agent, was proposed for chrome plating and the properties of chromium deposits were studied [17].

Chromium electrodeposition on nickel and copper after treating their surfaces in pyridine and toluenesulfonic acid was studied. The adsorption layer that forms under these conditions is found to affect the electrode process until the deposit becomes 0.4-0.8 μm thick. The layer has an effect on the formation of the near-electrode film that is typical for the chromium deposition process, on the Cr(VI) to Cr(III) process, and on the metal deposition [18]. The role of formic acid and methanol on speciation rate and quality in the electrodeposition of chromium from trivalent electrolytes was discussed. A successful enhancement of both the quality and the deposition rate has been obtained by the addition of some quantities of formic acid and methanol. The results were obtained by using very conventional conditions such as 25°C, no pH adjustment, low current density and very gentle agitation. An excellent quality of deposit with a deposition rate of 50-100 μm/h was obtained. Sustained deposition up to ~200 μm/h was achieved with prolonged electrolysis [19]. A new type of additive was developed and named CH, was used in Cr electroplating and its performance was evaluated. Micro-crack chromium electroplating coating was obtained by using the plating bath with CH additive. Compared with common chromium electroplating baths, the productivity was doubled and 50% of the electric power was saved [20]. Role of macro-and microdistributions in electrodeposition of chromium and its alloys from electrolytes based on chromic acid was discussed [21]. Influence of organic additives, such as propylene carbonate, saturated mono-carboxylic acids, to a standard chromium-plating electrolyte on the processes of incomplete reduction of chromic acid and chromium electrodeposition was studied. A possible mechanism describing the influence of organic substances on the electrode processes in chromium plating electrolytes was discussed [22].

A sulfate solution with a low content of Cr(III) was developed for obtaining plastic chromium coatings at a current efficiency of 30-35%. The proposed composition of the solution, g/L, and operating conditions were: $Cr_2(SO_4)_3.6H_2O$ 25; Na_2SO_4 100; H_3BO_3 35-40; malonic or oxalic acid 7-10; sulfur-containing surface active agent 0.08-0.10; pH 2.2-4.2; and current density 2-6 A/dm^2 [23]. Results of experiments carried out with nonetching electrolytes but containing sulfate and potassium iodate was reported. Different concentrations of chromic acid, sulfate and potassium iodate were used and current efficiency, rate of build-up, throwing power, deposit nature and microhardness were evaluated [24]. Experiments were carried out with varying concentrations of chromic acid from 50 g/L to 250 g/L in the presence of 1% sulfate by means of Hull cell tests in order to determine the basic solution composition. Current

efficiency and rate of build-up were also determined in the case of selected compositions. The effect of boric acid or lanthanum oxide was investigated [25]. Decorative or hard chromium plating was possible from a bath containing chromic acid 250 g/L and ammonium fluoride 30 g/L at 50°C and current density 25-60 A/dm^2. The bath produced brighter deposits even up to 50 μm thickness [26]. Electroplating of chromium was carried out from a bath containing $CrCl_3.6H_2O$ 0.8 mol/L, NH_4Cl 26, H_3BO_3 2, NaCl 36, and dimethyl formamide 400 g/L, surfactant 0.01 g/L and wetting agent 1-2 ml/L, pH 1.1-1.2, 25°C, 14 A/dm^2. As thick as 80 μm electroplate was obtained and the current efficiency reached ≥30% [27]. Process and mechanism of hard chromium plating from trivalent chromium bath were studied [28].

Decorative chromium plating of powdered metallurgical parts was discussed. The preparation of powdered metallurgical parts involved the steps of washing, degreasing, weak etching, electroplating of copper from a cyanide bath, bright copper electroplating, bright nickel electroplating and electroplating of chromium [29]. ZL-102 aluminum workpiece was electroplated with bright nickel, followed by electroplating of chromium. The electroplating of chromium was carried out from a bath containing CrO_3 200-250, H_2SO_4, d 1.84, and Cr^{3+} 2-8 g/L, under the conditions of 55-60°C, 40-60 A/dm^2, and 2-3 minutes. The surface hardness, abrasion resistance, and decorative property of aluminum workpieces were increased and its service lifetime was lengthened [30]. Chromium electroplating bath with improved current efficiency was reported. It additionally contained, besides CrO_3 and $SrSO_4$, NaCl and a substance from 1-(C_{20-35} alkyl)-4,5,6,7-tetrahydro-1H-indene in the following proportions: indene derivative 2-5, CrO_3 150-170, $SrSO_4$ 5-7, and NaCl 0.8-2.0 g/L [31]. The effect of organic additive on the chromium current yield, structure and properties of electrodeposits was studied. The electric current yield increased with increasing concentration of the organic additive [32]. Chromium plating bath was investigated which contained chromic acid 100 g/L and Cr-2S-solid catalyst. The latter was a mixture of inorganic salts with different solubility products. Maximum current efficiency up to 20% was reached over a broad concentration range of Cr-2S, 1 to 5 g/L, and high quality bright chromium coatings were obtained [33].

The dull chromium electroplating was carried out in a bath comprising CrO_3 250-300, H_2SO_4 2.5-3.0, and Cr^{3+} 1.0-3.0 g/L with the operating conditions of 48-52°C, 20-30 A/ dm^2, 10-20 minutes, Pb-Sn alloy, Sn 4-8%, anode, and area ratio of cathode to anode = 1:2-3. The electroplate was uniformly silver gray color, the adhesion was good, and ≥ 98% of the electroplates were up to standard [34]. Bath comprising CrO_3 120-180, H_2SO_4 0.6-1.2, and LC additive 1.5-2 g/L was used. The temperature, current density, ratio of area of cathode to anode, and anode were 15-50°C, 4-30 A/dm^2, 1:3-4, and Pb-Sn alloy, 8-12% Sn, or Pb-Sn-Sb alloy, Sn 7, Sb 1%, respectively. The use of the additive enabled the reduction of the amounts of CrO_3 and water used and lowered the operating temperature. The appearance of the electroplate was good, the consumption of the anode was reduced and the method was economical [35]. Electroplating of chromium was carried out from a bath containing CrO_3, industrial grade, 120-180, H_2SO_4 (CP) 0.5-0.9, Cr^{3+} 0.3-2, and CS-type additive, a mixture of rare earth compounds, 1-2 g/L, 20-45°C, cathodic current density 7-30 A/dm^2, tank voltage 3-10 V, anode material Pb-Sn alloy, 8-15% Sn, and deionized water for the tank. The use of the CS additive had the advantages of (1) saved starting materials cost of wastewater treatment, (2) saved the electricity and thermal energy, and (3) improved working environment and simplified production facilities. The disadvantage was that when the electroplating was carried out at ≥50°C its advantages did not show up [36]. The electroplating of chromium on bright nickel-electroplated brass was carried out from baths containing halo carboxylic acid-rare earth compound mixture as an additive. The throwing power and cathodic current density were improved, the Vicker's hardness of the electroplate was 980-1100, and the adherence was good [37].

Bicycle parts were electroplated with chromium from RL-3C additive, which was a mixed catalyst of rare earth cations and other composite anions. The bath composition was chromic anhydride 160-200, Cr^{3+} 1-3, H_2SO_4 0.5-1.2, and RL-3C additive 4.5-5.5 g/L and operating conditions were 40 ± 5°C, current density 6-12 A/dm^2, 6 minutes, Pb-Sn alloy anode and area ratio of cathode/anode = 1:2-3. The advantages of using RL-3C were improvement of throwing power, lowering current density i.e. higher current

efficiency, better working environment [38]. The current efficiency of chromium electrodeposition and cathodic polarization curves were determined in halide-chromic acid-sulfuric acid systems. The composition of the cathodic films formed was determined by XPS and AES. The results show that the sulfate is an effective catalyst for the deposition of bright chromium and that the current efficiency of the chromium deposition increases remarkably when F^- and Cl^- were added to the bath, and also that F^- and Cl^- participated in the formation of the films [39]. From microstructure of black chromium electroplate it was concluded that the use of baths containing chromic anhydride, catalyst, such as SiF_6^{2-}, BF_4^-, and blackening agents, such as $NaNO_3$, were ideal. Weighing method was used to study the effect of each factor [40]. The addition of rare earth additives in chromium electroplating resulted in a better electroplating bath and electroplate than ordinary baths and electric conduction, internal stress, porosity, deposition rate, average power consumption, cost, and pollution were improved [41]. Current efficiency of chromium deposition and cathodic polarization curves were determined in halide-chromic acid-sulfuric acid systems. The depth profile curves of film illustrate that halide is distributed in inner layer of the film and SO_4^{2-}. The F^- and Cl^- enter into the surface of the cathode and formed a bridged complex which reduced chromium dichromate, $[Cr^{III}\text{-}X^-\text{-}Cr^{III}]$, in which electron transition is easily carried out [42]. The electrode reaction mechanism of chromium electrodeposition was investigated by cyclic voltammetric, chronoamperometric and coulometric methods. A $Cr(VI)O_4Cr(III)OOHHSO_4^-$ complex film was formed in the 1st CE reaction which decomposed in a following chemical reaction; therefore, the final mechanism of the first step was CES. The HSO_4^- ligand played a catalytic role in the 1st reaction. Metallic chromium was produced in a 2nd electrochemical or chemical reaction. Partial reactions of the film formation were identified [43]. Effect of boric acid in sulfuric acid-based decorative and hard chromium electroplating baths was discussed. A H_3BO_3 content of 5-10 g/L in H_2SO_4-based chromium electroplating baths increased the brightness, of the electrodeposits, improved the electrolyte covering power, and also the current efficiency. In addition, bath tolerance to contamination by Cr(III) and Fe(III) was enhanced [44].

Chromium plating bath containing low concentration of CrO_3, 50~180 g/L, with the addition of so-called CS additives comprising multiple kinds of rare earths was recommended. Electrodeposition was performed at 4~60 A/dm^2 and at 15~70°C. The throwing power increased by 30~50%, whereas corrosion resistance of the coating by NSS test was 2-3 grades higher and hardness was up to 850~1270 Hv [45]. Method of treating a chromium electroplating bath was discussed, which contained an alkyl sulfonic acid to prevent heavy lead dioxide scale build-up on lead or lead alloy anodes used there in [46]. Electroplating bath and process for depositing bright and smooth functional chromium at high efficiencies was reported. The bath comprised chromic acid, sulfoacetic acid, iodate, and a nitrogen organic compound such as glycine. The electrodeposition was carried out at ~50-70°C at current density ~1-10 A/in^2, and the current efficiency was $\geq$ 20% [47].

Make-up of mixed-catalyst bath, sampling of solutions, operation and control of chromic acid/sulfuric acid bath, operation and control of mixed-catalyst systems, hoeing of the bath with a special tool, practical operation limits of chromic acid concentration, temperature, cathodic current density, and CrO_3/SO_4^{2-} ratio for chromium electroplating processes, and improper F^- addition in hard chromium plating were discussed [48]. Improvement of the distribution and brightness of chromium plate by addition of chlorine compounds to a sulfate bath was discussed. Three baths were prepared each having CrO_3 250 and SO_4^{2-} 3.5 g/L. The 2nd bath contained Cl 0.75 and the 3rd Cl 1.5 g/L, in the form of HCl. All 3 baths were operated at 55°C with current density 1 A/in^2 for 5 h. A substantial improvement was noted for all Cl additions [49].

The electrode reactions occurring at carbon, chromium, copper, and nickel cathodes in the standard chromium electroplating bath containing CrO_3 200 and H_2SO_4 2 g/L have been reinvestigated. At chromium, nickel and copper, the potential of the chromium(VI)/chromium(III) couple is determined by the removal of an insulating oxide film which forms spontaneously when the metal is immersed in the bath [50]. A detailed mechanism for the reduction of chromium(VI) solutions to chromium metal was

proposed. To prevent the formation of a stable $Cr(H_2O)_6^{3+}$ complexes, a cathodic film of chromic dichromate was formed with 1 end blocked by complexing with HSO_4^-. Decomposition of the film by reaction with H_3O^+ produced chromous hydroxide, the reduction of which to metallic chromium was catalysed by HSO_4^- [51].

References

1. "The Canning Handbook on Electroplating", 22nd ed., W.Canning Limited, Brimingham (1978), p. 455-456.
2. K. A. Graham,"Electroplating Engineering Handbook", 3rd edition, Van Nostrand Reinhold Company Limited, New York, p. 633-644 (1971).
3. J. K. Dennis and T. E.Such, "Nickel and Chromium Plating", 2nd ed., Butterworths, London, p. 178-179 (1986).
4. I. U. Haque, I. Sadiq and A. Khan, *J. Chem. Soc. Pak.*, **24** (2002), in press
5. E. N. Lubnin, A. A. Edigaryan and Yu. M. Polukarov, *Prot. Met.*, **36**, 301-305 (2000).
6. Rm. Krishnan, S. Sriveeraraghavan, S. Jayakrishnan, J. C. Kennedy, R. Sekar and J. G. Mary, *Bull. Electrochem.*, **15**, 233 (1999).
7. C. Lei, J. Hanying and G. Zhuqing, *Trans. Nonferrous Met. Soc. China*, **9**, 641 (1999).
8. C. Lei, C.Wenmi, G. Zhuqing, T. Fuzhou and J. Hanying, *Cailiao Baohu*, **32**, 1 (1999).
9. A. A. Edigaryan and Yu. M. Polukarov, *Prot. Met.*, **35**, 1 (1999).
10. J. Socha, *Inz. Powierzchni*, (3), 20 (1998).
11. I. N. Korisichuk, Z. I. Bobanova and A. N. Batishchev, *Elektron. Obrab. Mater.*, (5-6), 54 (1995).
12. A. A. Edigaryan and Yu. M. Polukarov, *Prot. Met.*, **34**, 545 (1998).
13. J. Socha, *Inz. Powierzchni*, (2), 38 (1998).
14. L. Frediani and G. Merello, PCT Int. Appl. WO 98 36, 108 (1998).
15. G. E. Grunwald, M. Hekler, C. Marin, C. Iuhos and F. Fazsi, Rom. RO 105, 834 (1992).
16. M. M. Hekler, E. Grunwald, F. Fazai and A. Farkas, Rom. RO 105, 983 (1993).
17. A. A. Edigaryan and Yu. M. Polukarov, *Prot. Met.*, **34**, 95 (1998).
18. I. G. Khomchenko and A. N. Zhuchkov, *Russ. J. Electrochem.*, **33**, 1277 (1997).
19. S. K. Ibrahim, A. Watson and D. T. Gawne, *Trans. Inst. Met. Finish.*, **75**, 181 (1997).
20. F. Huang, J. Li and Z. Wu, *Cailiao Baohu*, **29**, 14 (1996).
21. S. S. Kruglikov and E. S. Kruglikova, *Russ. J. Electrochem.*, **32**, 1179 (1996).
22. I. G. Khomchenko and I. M. Morozova, *Russ. J. Electrochem.*, **32**, 996 (1996).
23. A. A. Edigaryan and Yu. M. Polukarov, *Prot. Met.*, **32**, 461 (1996).
24. J. C. Kennedy, A. Aruna, R. M. Krishnan, S. Jayakrishnan, S. Sriveeraraghavan and S. R. Natarajan, *Bull. Electrochem.*, **12**, 283 (1996).
25. R. M. Krishnan, A. Ramakrishnan, S. Jayakrishnan, S. Sriveeraraghavan, N. Kannan and S. R. Natarajan, *Bull. Electrochem.*, **12**, 278 (1996).
26. S. Sriveeraraghavan, S. Jayakrishnan, R. M. Krishnan, and S. R. Natarajan, *Met. Finish.*, **94**, 68 (1996).
27. D. Du and C. Zhang, *Cailiao Baohu*, **28**, 19(1995).
28. H. Li, S. Duan and X. Zhang, *Diandu Yu Tushi*, **12**, 5 (1993).
29. X. Yang, *Cailiao Baohu*, **27**, 38 (1994).
30. J. Gao, *Diandu Yu Huanbao*, **15**, 35 (1995).
31. V. T. Fomichev, G. P. Gubarevich, E. V. Moskvicheva, E. A. Smirnov and V. S. Ushkov, U.S.S.R. SU 1, 816, 290 (1993).
32. S. V. Vashchenko, L. N. Solodkova and Z. A. Solovèva, *Gal'vanotekh. Obrab. Poverkhn.*, **2**, 15 (1993).
33. M. A. Shluger and E. N. Shuvalova, *Gal'vanotekh. Obarb. Poverkhn.*, **1**, 92 (1992).
34. L. Zhang, *Cailiao Baohu*, **26**, 31 (1993).
35. L. Lu, T. Yu, J. Hon, X. Gao, F. Song and L. Qu, *Cailiao Baohu*, **26**, 32 (1993).
36. Y. Mo, *Cailiao Baohu*, **26**, 33 (1993).
37. G. Fang and Z. Yu, *Cailiao Baohu*, **26**, 26 (1993).
38. D. Yi, *Cailiao Baohu*, **26**, 33 (1993).
39. L. J. Fang, J. N. Wu and W. Z. Wang, *J. Appl. Electrochem.*, **23**, 495 (1993).
40. J. Xie, Z. He and Z. Ni, *Cailaio Baohu*, **25**, 21 (1992).
41. D. Qian, *Cailiao Baohu*,, **25**, 10 (1992).
42. J. Fang, N. Wu and Z. Wang, *Wuji Huaxue Xuebao*, **8**, 266 (1992).
43. C. Dorgai and L. Tomcsanyi, *Magy. Kem. Foly.*, **98**, 63 (1992).
44. M. Constantin, E. Gruenwald, C. Varhelyi and C. Juhos, *Galvanotechnik*, **82**, 3819 (1991).
45. H. Chen, *Daindu Yu Tushi*, **10**, 10 (1991).
46. K. Newby, U.S. US 4, 810, 337 (1989).
47. N. M. Martyak, U.S. US 4, 810, 336 (1989).
48. R. K. Guffie, *Prod. Finish.*, **51**, 88 (1987).
49. G. Dubpernell, D. J. Kenney and K. Komolboon, U.S. US 4, 602, 983 (1986).
50. L. C. Jiang and D. Pletcher, *J. Appl. Electrochem.*, **13**, 235 (1983).
51. J. P. Hoare, *J. Electrochem. Soc.*, **126**, 190 (1979).