

植酸在金属防护中的应用现状及展望

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[摘要] 介绍了植酸的分子结构、生产方法和特殊性质。阐述了目前植酸的主要研究和应用现状,如在金属防护中充当阴极型缓蚀剂、用于电镀或化学镀的配位体、用作成膜型的金属钝化剂、在磷化及水性涂料中用作多功能助剂以及其他金属防护领域中的应用,并指出了目前存在的主要问题和今后发展和研究的方向。

[关键词] 金属防护; 植酸; 无铬钝化

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0 前言

传统的金属钝化多采用物美价廉的铬酐或铬酸盐^[1]等六价铬化合物,其对基体金属具有良好的保护作用。但铬类化合物毒性较大且又具有强烈的致癌作用^[2],目前世界各国对其使用和废水排放都做出了严格的限制,禁止使用铬类化合物已成必然趋势。因此,采用环境友好的有机或无机物来取代铬类化合物已迫在眉睫^[3-5]。目前,国内外关于无铬钝化的研究已取得一定的进展,并提出了一些可能作为铬类化合物的安全环保的替代物,如有硅酸盐或聚硅酸盐^[6]、稀土元素^[7-9]、钼酸盐^[10]或钨酸盐^[11]、纳米硅溶胶^[12]及其他有机物^[13,14]等。这些替代物对金属材料都具有一定的钝化作用,但大部分研究仍停留在试验阶段,存在着种种难以解决的困难而无法工业化应用。植酸具有特殊的分子结构和很强的螯合作用及一定的成膜性,且无毒无污染,因而引起了关注。国内在20世纪90年代开始植酸应用于金属防护技术的研究^[15,16],至今已经获得了一定的研究成果^[17-19]。

1 植酸分子结构

1872年 Preffer 发现植酸,直到1969年才由 Graf E等确定其分子结构^[20-22]。植酸学名为环己六醇六磷酸酯,全称为1,2,3,4,5,6-二氢磷酸肌醇(LUPAC),分子式为 $C_6H_{18}O_{24}P_6$,分子量为660.08,室温下为无色或淡黄色液体,其结构式见

图1。植酸分子中含有12个未反应磷羟基,故易溶于水,且水溶液具有较强的酸性。此外,它能同金属配位的24个氧原子,12个羟基和6个磷酸酯基。因此,植酸可以在较宽的pH值范围内与金属离子形成多个螯合环,得到化学性质很稳定的配合物。对各金属离子的具体配位常数见表1^[19]。因为植酸分子中的6个碳原子的空间构型为椅型,6个磷酸基只有一个处在a位,即与对称轴平行,其他5个均在e位上,与对称轴成 109.5° ,呈平伏状(见图1),为了便于描述,对植酸中的6个磷酸基进行了编号, P_1 即是处于a位的磷酸基,这样一来,就有 P_1, P_2, P_4 以及 P_6 所代表的4个磷酸基处于同一平面上,所以,植酸在金属表面与金属发生配位反应时,易在金属表面形成一层致密的单分子保护膜,能有效地阻止腐蚀介质渗入金属表面,从而起到防护作用。同时,经植酸处理后的金属表面形成的单分子有机膜层同有机涂料具有相近的化学性质,而且,膜层中含有的磷羟基和酯基等活性团可与有机涂料中的极性基团形成氢键或发生化学反应,故植酸处理过的金属表面与有机涂层黏接

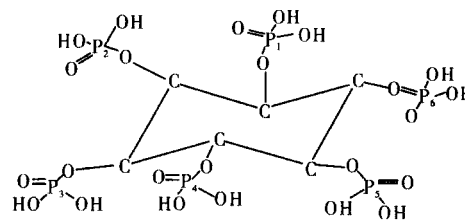


图1 植酸结构图

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性更好。

表 1 不同 pH 值下植酸对金属离子配位常数 $\lg k$

pH 值	金属离子						
	Mg ²⁺	Ca ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
1	8.47	8.63	16.45	1.38	2.59	9.21	15.50
2	10.28	8.23	16.30	2.66	2.98	9.83	15.43
3	9.56	9.73	16.84	2.12	2.05	10.41	15.50
4	10.85	10.02	17.21	7.17	3.89	10.43	15.85
5	10.77	10.05	17.35	15.54	13.49	10.85	14.96
6	10.55	10.87	17.63	15.27	14.92	10.91	15.05

植酸广泛存在于各种动植物体中,以脱脂米糠中含量较高^[20,21],一般为 10%~11% (质量分数)。日本于 1979 年公开的昭 54-81309 提出的米糠法实现了植酸的工业化生产,随后国内杜志政^[22]和李艺等^[23]分别采用不同的方法制备植酸,但仅能提取其中含量的 1/4~1/2,且浓度仅为 40% 左右。由于国内米糠来源较少,吕广宇^[24]研究了以棉籽为原料生产植酸的方法,并已初见成效。植酸毒性极低,小白鼠口服半致死量 (LD_{50}) 为 4 192 mg/kg,高于食盐的半致死量 ($LD_{50} = 4 000$ mg/kg)^[25],使用不会造成任何环境污染。

2 应用及研究现状

2.1 缓蚀剂

植酸易溶于水且对金属离子有极强的螯合性,因而国外很早将其应用于热交换器冷凝水的缓蚀剂^[26],Notoya 等^[27]还研究了植酸盐对铜管的缓蚀机理。早在 1985 年就表明^[28],热交换器的冷凝水中加入 5×10^{-6} (质量分数) 的植酸可以有效地延缓铜质换热管的腐蚀。对于钢质材料的换热器,植酸盐与苯甲酸盐适当复配的缓蚀作用也非常好^[29]。在国内,雷学军等^[30]研究发现,在冷凝水中加入植酸,不但可以延缓设备的腐蚀,而且可有效地“软化”硬水。王林等^[31]采用 XPS 研究了植酸钙和植酸镁对铜在饮用水中的缓蚀行为,其缓蚀效率分别达到 93.7% 和 92.2%。熊金平等^[32]研究发现,植酸对碳钢材料而言是一种阴极型缓蚀剂,它在碳钢表面的吸附层抑制了氧气在界面上的传质。张洪生^[33]和齐勇^[34]采用植酸作为气相缓蚀剂,缓蚀效果已优于目前广泛采用的亚硝酸二环己胺,但使用量一定要恰当,过量的植酸反而会加速腐蚀。植酸很有可能作为新一代的性能优异且

环境友好的缓蚀剂。

2.2 配位体

植酸可以在较宽的 pH 值范围内与各种金属离子形成稳定的配合物。日本专利昭 55-164067 报道了将植酸应用于电镀锌的配位体以替代氰化物的研究成果。国内陈自然等人^[35,36]研究了植酸在电镀锌和铁镍合金中的应用,发现植酸不但可以代替氰化物作为配位体,而且将其用于镀前处理还可以提高镀层的结合力。在镀锌液中加入植酸,可以获得具有宽广的光亮电流密度范围和工作温度范围及极强的走位能力(深镀能力)的镀液^[37]。同样,植酸也可以应用于各种化学镀。侯新初^[38]采用植酸与柠檬酸的复配作为化学镀镍的配位体,获得了稳定的化学镀镍液。徐瑞东^[39]等人研究了植酸作为镍磷合金抗蚀防变色剂,其抗变色能力优于苯甲酸钠、钼酸钠和 EDTA。但不同的 pH 值和温度对植酸的配位能力有一定的影响^[40],应该根据镀液情况调节合适的 pH 值,尽可能提高植酸的使用效率。

2.3 成膜型金属钝化剂

植酸分子可以同时与多个金属离子配位,未反应磷羟基之间可通过氢键或脱水反应而连接,进而形成高交联密度的空间网状植酸(盐)钝化膜,有效地阻止腐蚀介质渗入金属表面,从而减缓金属的腐蚀。Shimakura 等^[41,42]采用植酸盐复配作钝化剂和硅烷偶联剂作附着力促进剂,研究了无铬钝化得到的植酸钝化膜的耐蚀性接近于低铬钝化。Wippmann^[43]和 Manov^[44]等采用电化学测量的方法,研究了植酸对镀锌层的钝化作用和机理。国内对植酸应用于金属钝化剂的研究也比较多,朱传方^[45,46]等研究发现:对于镀锌层表面的钝化,植酸钝化效果抗腐蚀能力优于其他羟基磷酸;植酸是替代无铬钝化比较有实际应用意义的途径之一。采用植酸对钢质传热管进行表面处理,同样可以在金属表面形成致密的钝化层,获得良好的防蚀性能^[47]。经过植酸处理的铁片腐蚀率为 0.031 mm/a,远小于磷酸盐和亚硝酸盐钝化处理的铁片(腐蚀率 0.473 mm/a)^[48]。最近,田冰^[49]研究的植酸钝化技术已应用于钢轨的防腐蚀,赵家文^[50]研究的植酸盐转化膜技术以及肖国华^[51]和李金泉^[52]分别研制的植酸作为金属防锈处理剂也先后获得了国家专利,这些会为我国植酸钝化技术的推

广泛应用和工业化进程奠定基础。随着更多的研究,植酸钝化将会成为替代铬酸盐钝化的最主要方法之一。

2.4 金属磷化多功能助剂

由于植酸及植酸盐特殊的空间网状结构及配位物的高稳定性,其在金属磷化中也得到了推广和应用。Seidel^[53]在磷化液中加入植酸,提高了磷化膜的耐蚀性和成膜性。陈洪希^[54]亦发现,在低温磷化液中加入植酸,不但可提高磷化膜的耐蚀性和成膜性,而且还能克服低温磷化液所需添加剂多、工艺复杂的缺点。余取民专利^[55]提到,在磷化液中加入适量的植酸可以提高磷化膜的耐蚀性和机械强度。一直以来,金属磷化因为能耗大、工艺复杂和环境污染较严重而受到限制,适当引入植酸及植酸盐,可较好解决上述问题。

2.5 水性涂料多功能助剂

植酸具有水溶性,且具有成膜性和缓蚀作用,所以在水性防腐涂料研发中备受“青睐”。Yasuhike^[56]以钛酸酯和钛酸盐作成膜剂,植酸作缓蚀剂,有效地解决了水性涂料孔隙高的问题。采用反应性乳化剂,并在水性涂料中加入植酸,不但可以提高涂料的钙离子稳定性和涂层的耐蚀性,还可以有效抑制水性涂料施工时对金属底材的“闪蚀”^[57]。杨昌柱等^[58]在水性涂料中加入植酸,不但可以与金属表面的氧化层配位,与底层金属形成配位物薄膜,同时还可使得 $K_4Fe(CN)_6$ 转化形成的多孔疏松的膜层更加致密,从而更增强了整个膜层在钢铁表面的附着力以及防锈防蚀的能力。在目前的防腐蚀领域,水性涂料的防护能力与油性涂料相比,差距还比较大,作为多功能助剂的植酸有望缩小差距。

2.6 其他方面

植酸在其他金属防护领域中的应用也十分广泛,如作为金属表面清洗剂中的多功能助剂^[59],不但起缓蚀作用,还可以形成含磷羟基钝化膜提高与环氧底漆的结合力^[60]。王有林等^[61]将植酸应用于金属表面抗氧化剂也取得很好的效果。

3 存在问题及展望

目前,国内对植酸应用于金属防护的研究并不多,特别是关于机理方面的研究,如植酸配位金属的作用过程及机理等,而且绝大部分的观点和机理还只是推测,缺乏明确的试验数据。研究植酸钝化

镀锌层的过程发现,植酸钝化膜很薄,估计只有几百纳米左右,机械强度较差。虽然植酸钝化膜的耐蚀性已经接近于低铬钝化,但由于植酸钝化膜不具备自修复性能,钝化膜一旦被破坏,其防护性能将会大幅减弱。目前这方面的问题主要有:(1)植酸的生产成本比较高,市场价高达 96 000 元/t;(2)植酸钝化膜的厚度和机械强度的提高;(3)植酸配位和钝化过程及机理的研究;(4)植酸钝化膜组成结构的研究;(5)与钼酸盐、钨酸盐和硅溶胶等钝化剂的复配,提高使用效果;(6)植酸与有机涂层的兼容性研究。

综上所述,植酸可以应用于阴极型缓蚀剂、宽适用范围金属离子的配位体、成膜型的金属钝化剂、磷化及水性涂料的多功能助剂等,而且其环境友好性在金属防护领域中具有广阔的应用前景,值得大力推广和应用。希望科学工作者能够投入更多的热情和精力,解决上述问题,为环境友好的金属防护技术的研究贡献一份力量。

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传统低铬钝化的改进

低铬钝化以其节能、环保等诸多优点, 已成为当今主流的钝化工艺。但和传统的高铬钝化相比, 还存在着钝化膜结合力不好, 钝化液调整频繁以及钝化膜颜色不够鲜艳的缺点。

为此, 我厂研制出了 KH-CD 彩钝稳定剂, 改善了低铬钝化的不足。本产品外观为棕红色, 由硫酸盐、冰乙酸和高锰酸钾等组成, 工艺配方如下: 铬酐 5 mL/L, KH-CD 5 mL/L, 硝酸 3 mL/L, pH 值 0.8~1.3, 室温, 时间 5~8 s。

各成分及参数作用:

(1) pH 值 pH 值低, 成膜速度快, 膜层结合力好, 但易发雾, 膜层表面好象罩着一层塑料布, 感觉不清亮; pH 值高, 成膜速度慢, 膜层光亮, 但结合力不好。

(2) 铬酐 含量高、成膜速度快, 但膜层结合力不好, 钝化膜容易呈现暗黄色; 含量低、成膜速度慢且钝化膜色彩偏浅, 不鲜艳。

(3) 硝酸 在钝化液中有两个作用, 第一起化学抛光作用, 可提高膜层光亮度; 第二可调整并稳定钝化液 pH 值。

(4) KH-CD 彩钝稳定剂 硫酸盐在钝化液

中会解析出硫酸根离子, 促进钝化膜的生成和提高钝化膜的结合力。由于它是一种中性盐, 因此它的加入不会对钝化液的 pH 值产生影响; 冰乙酸在钝化液中起缓冲 pH 值的作用, 有利于保持钝化液 pH 值的稳定, 减少钝化液的调整频度; 高锰酸钾能将钝化液中的三价铬氧化成六价铬, 在钝化液中三价铬呈绿色, 六价铬呈红色, 加入高锰酸钾能使钝化膜外观偏红, 色彩更鲜艳; 钝化液中的硫酸含量高, 钝化膜结合力好。因为硫酸根能促进钝化膜中三价铬化合物的生成, 从而在钝化膜中生成“骨架”效应, 增强了膜层的结合力。相应的钝化膜中三价铬含量高, 膜层呈绿色。而硝酸能较好地结合钝化液中的六价铬, 相应地提高硝酸的含量, 钝化膜较多地呈红色。

基于以上的理论, 在给出的配方中以中性的硫酸盐取代了硫酸, 在保持低铬钝化工艺正常 pH 值的前提下, 较大限度地提高了硝酸的含量, 同时与配方中的高锰酸钾作用相协同, 提高了钝化膜中六价铬化合物的含量, 使钝化膜突出鲜艳的红色。

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plated TiN, Ti(Ce)N, (Ti, Cr)N, (Ti, Cr, Ce)N, and CrN coatings were prepared by introduction of 0.5% (mass fraction) cerium in the cathodic target. The morphologies of the coatings were observed using a scanning electron microscope and the action of the rare earth cerium in improving the particle conformation and compactness of the coatings was explored. It was found that the coatings were mainly composed of cobblestone-like and circular particulates, and a little amount of ash inclusions originated from the electric-arc furnace also existed as impurities in the coatings, which was much harmful to the quality of the coatings. Moreover, the introduction of the rare earth contributed to greatly decrease the amount of liquid-dripping particles and increase the compactness of the coatings and hence led to increased compactness of the coatings.

Key words: arc ion plating; alloy coating; particle; Ce

Influence of Heat-Treatment in Vacuum on the Oxidative and Electrochemical Corrosion Resistance of Uranium Surface Overlaid with Graphite

ZHANG Guang-feng, YANG Wei-cai, WANG Xiao-lin, LUO Wen-hua (China Academy of Engineering Physics, Mianyang 621900, China) *Cailiao Baohu* 2005, 38(12), 20~22 (Ch). The corrosion resistance of uranium surface overlaid with graphite after vacuum heat-treatment was studied making use of weight gain method and electrochemical method. The oxidation kinetics curves ($m-t$) of the treated sample were recorded at 100 and 150 °C. Thus the thermal-oxidation behavior of the heat-treated samples in atmosphere containing certain amounts of O₂ and H₂O (gas) and their resistance to chemical corrosion in 50 μg/g Cl⁻ solution were investigated. It was found that heat-treatment of the graphite coated uranium surface contributed to greatly increase its resistance to thermal and chemical corrosion. Namely, at a constant heat-treatment duration of 5 h, the graphite coated uranium surface after heat-treatment at 600 °C in vacuum had better corrosion resistance than the one heated at 500 °C. At the same time, the electrochemical corrosion resistance of the heat-treated uranium depended on the heating duration (2.5~10.0 h) and temperature (500~650 °C), and the one heated at 600 °C in vacuum for 5 h had better corrosion resistance to chemical attack.

Key words: vacuum heat-treatment; oxidation corrosion behavior; graphite coating; uranium

Electroplating Technology for Amorphous Ni-P/Nano-SiC Composite Coating

WANG Yu^a, GUO Jin-biao^a, HE Jian-ying^{a,b}, LI Lei^a, LI Hui-qin^a, SUN Dong-bai^{a,b} (a Corrosion and Protection Center, b Engineering-Research Center for Surface Nano-Technology, University of Science and Technology Beijing, Beijing 100083, China) *Cailiao Baohu* 2005, 38(12), 23~25 (Ch). Hard and wear-resistant nanoparticles of SiC were introduced in the electroplating bath for amorphous Ni-P coating so as to prepare Ni-P/nano-SiC composite coating. The influences of the technological parameters such as bath temperature, current density, and SiC concentration in the plating bath on the P content and distribution of nano-SiC in the composite coating were investigated. The morphologies of the composite coatings were observed using a scanning electron microscope, while the hardness of the coatings was determined using a nano-microhardness instrument. It was found that the content of nano-SiC in the composite coating increased with increasing electric current and the concentration of SiC in the plating bath. Moreover, the incorporation of nano-SiC contributed to greatly increase the hardness of the Ni-P coating prepared at a bath temperature of 60 °C, with the maximum hardness of the Ni-P-SiC composite coating to be as much as 7.4 GPa, which is much larger than that of the amorphous Ni-P coating.

Key words: electroplating; Ni-P amorphous coating; nano-SiC composite coating; technology

Effects of Technological Parameters on Composition and Corrosion Resistance of Electroplated Fe-Ni-Cr Alloy Coating

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was investigated, and the optimized plating parameters were determined so as to prepare bright and compact Fe-Ni-Cr alloy coating of excellent corrosion resistance. As the results, it was suggested to prepare the desired alloy coating at optimized plating conditions, i.e., cathode current of 14 A/dm², bath temperature of 30 °C, bath pH of 2, and concentration of CrCl₃·6H₂O of 25 g/L. The target Fe-Ni-Cr alloy coating was bright and compact and had excellent corrosion resistance. Moreover, the corrosion resistance of the alloy coating increased with increasing chromium content, and the Cr and Fe contents of the target alloy coating were 6% (mass fraction) and 54%, respectively.

Key words: electroplating; Fe-Ni-Cr alloy coating; corrosion resistance; technological parameter;

Effect of Technological Parameters on Composition and Structure of Electrodeposited Calcium Phosphate Coatings

XIAO Xiu-feng, TANG Xiao-lian, GAO Yan-jiao, XU Yi-zhan, LIU Rong-fang (College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350007, China) *Cailiao Baohu* 2005, 38(12), 29~32 (Ch). The effects of cation to anion concentration ratio $n(\text{Ca})/n(\text{P})$ in the electrolyte solution, the current density, and the temperature and pH value of the electrolyte solution on the composition and structure of electrodeposited calcium phosphate coatings were investigated by means of X-ray diffraction, Fourier transformation infrared spectroscopy, and scanning electron microscopy. The results showed that the compositions and structures of the electrodeposited calcium phosphate coatings were highly dependent on the plating parameters. The electrodeposited calcium phosphate coatings deposited at Ca(NO₃)₂ concentration of 0.042 mol/L, NH₄H₂PO₄ concentration of 0.0084~0.0420 mol/L, pH value of 4.0~6.0, current density of 0.4~20.0 mA/cm², and temperature of 0~90 °C consisted of CaHPO₄·2H₂O (DCPD), Ca₈H₂(PO₄)₆·5H₂O (OCP), and Ca₁₀(PO₄)₆(OH)₂(HA). The thermodynamically unstable DCPD transformed to more stable OCP and HA with increasing temperature, current density, pH value, and $n(\text{Ca})/n(\text{P})$ in the electrolyte, which led to an increase of $n(\text{Ca})/n(\text{P})$ in the coatings. Moreover, the crystalline HA coating preferentially oriented along the (002) plane.

Key words: electrodeposition; calcium phosphate; hydroxyapatite; technological parameters; composition and structure

Current State and Trend in Study of Electrochemically Deposited Copper for Interconnects of Ultra-Large-Scale Integrate Circuits

ZHANG Wei-li^a, CHENG Dan-hong², WANG Jian-yong^{1b}, YU Zu-zhan³ (1a Department of Chemistry, 1b School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200044; 2. Department of Training, China Executive Leadership Academy Pudong, Shanghai 201204; 3. Department of Chemistry, Fudan University, Shanghai 200433, China) *Cailiao Baohu* 2005, 38(12), 33~38 (Ch). A review, with respect to the plating bath composition, the application of pulsed electric current, the electrodeposition device, and the properties of the electrodeposited copper coating, was given on the current state and trend in the research of electrochemically deposited copper used for interconnects of ultra-large-scale integrate circuits (ULSI). It was pointed out that the conventional interconnects made of aluminum in ULSI manufacturing have been replaced by that made of copper at a fast pace, which could be attributed to the lower resistivity and better electromigration resistance of copper than aluminum. At the same time, it would be worth noting that the replacement of conventional Al interconnects is greatly contributing to reduce the RC delays and improve the reliability of the ULSI, which is also beneficial to drive the development of various novel technologies and materials concerning copper interconnection. Specifically, electrochemical deposition of copper can be thought of as one of the representative novel key technologies for copper-interconnect fabrication.

Key words: electrochemically deposited copper coating; pulsed electrodeposition; ultra-large-scale integrate circuits; interconnects

Current State and Prospect of the Application of Phytic Acid in Metal Protection

HU Hui-li^{1,2}, CHENG Jin-ning², LIN Jing^{1,2}, WANG Ya-fen² (1. Department of Chemistry, Harbin Institute of Technology, Harbin 150001; 2. Department of Oceanology, Harbin Institute of Technology-Weihai, Weihai 264209, China) *Cailiao Baohu* 2005, 38(12), 39~43 (Ch). The molec-

ular structure, production method, and special properties of phytic acid were briefed. Then a review was given on the current state of research and application of phytic acid with respect to its application as cathodic inhibitor for metal and alloy, complexing agent of electric and chemical plating, film-forming passivant for metal, multifunctional additive in phosphorizing bath and water-based paint, and other metal protection field. Moreover, the issues to be resolved concerning the application of phytic acid were summarized, and the directions for future research and development of phytic acid application were suggested.

Key words: metal protection; phytic acid; chromate-free passivation

Role of Complexant in Trivalent Chromium Plating Baths

LI Guo-hua¹, LAI Huan-wen², HUANG Qing-an² (1. Wannuo Electronics Co. Ltd. of Guangzhou City, Guangzhou 510630; 2. Guangzhou Ultra Union Chemicals Co. Ltd. of Guangzhou City, Guangzhou 510250, China) *Cailiao Baohu* 2005, 38 (12), 44 ~ 46 (Ch). With a view to the significant effect of the complexant in trivalent chromium plating bath on the stability of the bath and plating rate, the roles of the complexants (e.g., carboxylic acid, hydroxyl substituted carboxylic acid, amino substituted carboxylic acid and their salts) in the trivalent chromium bath were summarized. It was pointed out the roles of the complexing agents could be briefed as follows. First, they were capable of increasing the electrodeposition rate by way of forming active complexing ions. Secondly, they were able to retard the hydroxo-bridge polymerization reaction. Thirdly, they were able to shelter metallic impurities and hence decrease the effects of the metallic impurities on the quality of the electroplating and maintain smooth ongoing of the electroplating process. Finally, they were capable of increasing the stabilities of the electroplating solution. Specifically, it was imperative to select proper complexing agent capable of forming active complexed ions so as to ensure smooth chromium electroplating and obtain quality and thick chromium electroplating.

Key words: chromium electroplating; trivalent chromium plating bath; complexant; role

Study on Corrosion Resistance of BTESPT Coatings on Aluminum Alloy Substrate

GUO Zeng-chang, WANG Yun-fang, WANG ru-min (Department of Chemical Engineering, Northwestem Polytechnical University, Xi'an 710072, China) *Cailiao Baohu* 2005, 38 (12), 47 ~ 50 (Ch). The surface treatment of aluminum alloy by chromate is harmful to environment and toxic to human being, therefore it is imperative to develop novel and feasible "green" surface treatment technique so as to replace the conventional chromate-based surface-modification technique. Thus bis-[3-(triethoxysilyl)propyl]tetra-sulfide (BTESPT) was hydrolyzed in the presence of acid catalyst to generate the hydrosol as a surface treatment liquid for the aluminum alloy. The BTESPT hydrosol was then dip-coated on the aluminum alloy surface to form an environmentally benign coating as the potential replacement of conventional chromate conversion coating. The BTESPT dip-coating was cured at 100 °C for 12 h and then subjected to salt-spray test in 3% ~ 5% (mass fraction) NaCl solution. The corrosion behavior of the cured coating was evaluated making use of potentiodynamic polarization and electrochemical impedance spectroscopy techniques and compared with that of the conventional chromate conversion coating. As the results, the BTESPT coating had good anti-corrosion properties and could be used to replace chromate conversion coating.

Key words: bis-[3-(triethoxysilyl)propyl]tetra-sulfide; coating; corrosion resistance; aluminum alloy

Development of Novel Bisphenol A - Phenolic Resin Modified with Epoxy Resin

ZHENG Yi-an, YANG Ying, LI Ke (College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China) *Cailiao Baohu* 2005, 38 (12), 51 ~ 53 (Ch). Traditional phenolic resin synthesized from phenol and methanol contains a great amount of free phenol, which limits its application as the material for food packaging. Thus a novel bisphenol A-based (BPA) phenolic resin was synthesized via the condensation polymerization of bisphenol A as the major raw material, aiming at replacing the conventional phenolic resin. The target resin of 3-dimensional net structure and excellent properties of both the phenolic resin and epoxy resin was thus prepared via the etherifying of n-butanol, modifying with epoxy, and the most setting. The structural features and curing temperature

of the modified phenolic resin were studied by means of infrared spectroscopy and thermogravimetry and differential thermal analysis. The content of free phenol and aldehyde in the immersion solution of the resin coating was measured. It was found that all the epoxy resin had participated in the curing process and the final target resin coating had excellent thermal stability (with the thermal decomposition temperature to be as high as 386 °C) and resistance to acid and sulfur. At the same time, the newly developed phenolic resin coating had a free phenol content as low as 0.0472 mg/L, which is much smaller than the limit (0.1000 mg/L) specified in GB 4805-94 and GB/T 5009.69-2003.

Key words: epoxy resin; phenolic resin; food cans; bisphenol A; inner-wall material

Research on Structure and Properties of Micro-Arc Anodic Oxidation Film on TC4 Titanium Alloy

XING Ze-kuan¹, TANG En-jun¹, DUAN Rui¹, YAN Ming-hua¹, XU Tao² (1. Institute of Aeroengine Overhaul, Airforce of People's Liberation Army, Chengdu 611937; 2. Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China) *Cailiao Baohu* 2005, 38 (12), 54 ~ 57 (Ch). The relationship among the thickness of micro-arc anodic oxidation coating on TC4 titanium alloy and the voltage, electric current density, and processing duration in a sulfuric acid bath was investigated with respect to the excellent wear- and corrosion-resistance of the coating. The process to remove the anodic oxidation coating was explored. The morphology, structure, and composition of the oxidation coating were analyzed by means of scanning electron microscopy and X-ray diffraction. The hardness, corrosion-resistance, friction and wear properties of the coatings were evaluated. It was found that the micro-arc anodic oxidation coating on the Ti alloy substrate was uniform, compact, and stable. The results showed that the coating was 3.5 ~ 11.0 μm thick and was composed of anatase TiO₂ as the major phase and a small amount of rutile TiO₂. Moreover, the micro-hardness, corrosion-resistance to sulphuric acid (30% solution), and friction coefficient of the anodic oxidation coating was higher than that of the Ti alloy substrate by 70%, 50%, and 100%, respectively, but its wear rate was only 10% of that of the substrate. Besides, the coating-removing liquid had a hydrogen-permeation of about 80 mg/L for the Ti alloy substrate coated with the micro-arc anodic oxidation coating. Therefore the micro-arc anodic oxidation coating on the Ti alloy substrate had excellent wear- and corrosion-resistance.

Key words: micro-arc oxidation coating; titanium alloy; technology

Development of Copper-Based Highly Conductive Composite Coating

LI Zheng-li, WANG Xuan-jun, LIU Xiang-xuan, ZHANG You-zhi (Section 503, the Second Artillery Engineering Institute, Xi'an 710025, China) *Cailiao Baohu* 2005, 38 (12), 58 ~ 61 (Ch). The copper powders pretreated using complexant A were used as the raw material to prepare copper-based highly electric conductive composite coating. The effects of curing agent, the content and performance of the copper powders, and the processing technics on the performance of the copper-epoxy conductive composite coating were investigated. It was found that the introduction of antioxidants contributed to effectively prevent the copper powders from oxidation during the formation of the conductive coating. The optimized formulation for the conductive composite coating was suggested to be composed of E51 epoxy resin 50 (mass), polyamide 50, copper powders (400 mesh) 300, titanate coupling agent 2 ~ 3, antioxidant 20 ~ 40, and sedimentation-inhibiting agent 2 ~ 3. Moreover, the target copper-epoxy conductive composite coating had good comprehensive properties. Namely, it had an average surface resistivity of $2.0 \times 10^2 \Omega/\text{cm}^2$ and the appearance and resistivity kept almost unchanged after being stored in atmosphere for 30 days.

Key words: conductive composite coating; copper powders; epoxy resin; conductance

Development of Polyester Acrylate Luminous Paint and Its Properties

CAO You-ming, ZHENG Shi-yuan (Department of Chemistry and Environmental Science, Chongqing University of Arts and Sciences, Chongqing 402168, China) *Cailiao Baohu* 2005, 38 (12), 62 ~ 64 (Ch). The methods to prepare polyester acrylate resin and SrAl₂O₄:Eu²⁺ luminous mate-