植酸盐对 16锰钢缓蚀性能影响的研究

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[摘 要] 采用失重法和极化曲线法研究了植酸盐对 16锰钢的缓蚀作用。结果表明,在原油与 3.5%NaCl溶液的混合介质中,植酸盐有较强的缓蚀作用,与十二烷基苯磺酸钠 (SDBS)及聚乙二醇辛基苯基醚 (POPE)复配后,缓蚀效果更佳。其最佳复配使用浓度为 ρ(植酸盐):ρ(SDBS):ρ(POPE) =100 mg/L∶25 mg/L∶25 mg/L。

[关键词] 植酸盐; 缓蚀剂; 缓蚀协同作用; 输油管道; 表面活性剂
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0 前 言

随着石油天然气工业的发展,输油管道的腐蚀防护越来越受到重视。输油管道的内腐蚀主要是由原油的沉积水造成的,目前,我国原油综合含水率日益升高,达到 90%[1],水质特性日趋复杂,有时甚至伴有高浓度 CO_2、H_2S的产生,导致管道的腐蚀问题加剧。而通过添加高效的缓蚀剂可有效地减少腐蚀损失。目前,缓蚀剂技术正向着低毒环保的植物型方向发展。本工作研究了植酸盐在原油介质中对 16锰钢的缓蚀作用,并将其与一些表面活性剂,如十二烷基苯磺酸钠 (SDBS),聚乙二醇辛基苯基醚 (POPE)进行复配,考察了其缓蚀性能。

1 试 验

1.1 原材料及设备

植酸盐 (化学纯) SDBS, POPE,氯化钠,原油 (富含沉积水), 16锰钢试片; SHT型搅拌数显恒温电热套, DT100单盘分析天平,游标卡尺,砂纸等。

试验所用挂片为 16锰钢试片,其组成见表 1。16锰钢材是一种塑性、韧性良好的材料,塑性预加应变量不大于 1.1%[2],其抗冲击、疲劳和断裂性能与原材料的相比变化不大,因此,可用于埋藏式输油管线的设计。试验介质为 3.5%NaCl溶液,抚顺石油二厂储油库提供原油。

表 1 16锰钢组成成分质量分数 %

碳	硫	磷	硅	铬	锰
0.12	≤0.02	≤0.03	0.43	0.12	1.20～1.60

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1.2 试验方法

采用静态挂片失重法对缓蚀剂性能进行评价。试验过程:将 16锰钢片悬在盛有原油和 3.5%NaCl溶液的玻璃烧杯中,烧杯置于恒温加热套中,匀速搅动,放置 24 h后,取出,去除腐蚀产物、水洗、丙酮脱脂、干燥后用分析天平称重。重复多组空白及加缓蚀剂的平行试验,并按式 (1)和式 (2)分别计算腐蚀速率 V和缓蚀率 E。腐蚀速率按试样失重计,每次取 3个样,取其平均值,腐蚀速率的计算公式为:

$$V=\frac{\Delta m}{A\cdot t} \tag{1}$$

式中 V ——腐蚀速率, g/(m^2·h)
Δm ——挂片失重, g
t ——腐蚀时间, h
A ——挂片表面积, m^2

缓蚀率计算公式: $E=\frac{V_1-V_2}{V_1}\times 100\%$ (2)

式中 V_1 ——不加缓蚀剂时的腐蚀速率, g/m^2·h
V_2 ——加缓蚀剂时的腐蚀速率, g/m^2·h

在 8511恒电位仪、TD-3型 X-Y函数记录仪系统上测定各种变化条件下的极化曲线,以铂片为辅助电极,饱和甘汞电极为参比电极[3],电位扫描速度为 0.5 mv/s。根据公式 $(I_0-I_1)/I_0\times 100\%$ (式中 I_0为空白电解液的电流; I_1为加有缓蚀剂电解液的电流)计算缓蚀效率 E。用循环伏安仪测循环伏安曲线,对电极和参比电极同上。工作电极制备方法同上,面积为 0.5 cm^2。测定同一扫描速度下不同浓度缓蚀剂的循环伏安曲线。考虑到实际输油管线的温度,试验中温度保持在 50 ℃左右。

2 结果及讨论

2.1 缓蚀剂用量的选定

在试验温度下,原油和 3.5%NaCl溶液混合介质中添加不同浓度的植酸,反应时间均为 24 h,测得结果见表 2。

表 2 不同植酸盐用量下的缓蚀率

植酸盐用量/(mg·L^{-1})	50	70	80	90	100	110	150	200
缓蚀率/%	24.8	30.3	51.8	72.5	88.6	76.5	61.6	44.3

由表 2可知,在一定用量范围内,加入缓蚀剂的量越大,其缓蚀效果越好,但缓蚀剂的加入量超过某一临界值时,其缓蚀效率变化不大,甚至有下降趋势,当缓蚀剂用量为 100 mg/L时,其缓蚀效果最好。

2.2 协同复配效应

将 SDBS、POPE与植酸盐进行复配,并与植酸盐缓蚀效果进行对比,试验结果见表 3。植酸盐的加入量固定在 100 mg/L。

表 3 加入不同缓蚀剂的平均腐蚀速率及缓蚀率测试结果

缓蚀剂	试样面积/10^{-4}·m^2	试片失重/g	平均腐蚀速率/(g·m^{-2}·h^{-1})	缓蚀率/%
空白	35.02	0.073 1	0.870 3	-
	34.47	0.072 0		
	38.54	0.080 5		
植酸盐	45.38	0.013 4	0.123 6	85.8
	38.87	0.011 5		
	41.01	0.012 2		
植酸盐:SDBS:POPE=4:1:1(质量比)	35.28	0.002 8	0.034 0	96.1
	35.01	0.002 7		
	36.41	0.003 2		

由表 3可知,当植酸盐用量为 100 mg/L时,其缓蚀效果最好,为 85.8%。把植酸盐与 SDBS及 POPE复配使用时,当三者比例为 100 mg/L∶25 mg/L∶25 mg/L时,其缓蚀效果最佳。

2.3 缓蚀机理分析

2.3.1 植酸盐对 16锰钢的缓蚀作用

植酸盐为环己六醇六磷酸钠或钾,分子式为 $X_3C_6H_{15}O_{24}P_6$,X为钠或钾。植酸盐分子中具有能同金属配位的 24个氧原子,9个羟基和 6个磷酸基,含有可解离的氢离子,是一种少见的金属多齿螯合剂。当与金属配位时,易形成多个螯合环,所形成的络合物稳定性极强,植酸根离子对钢有较强的配位能力,形成的配合物在钢的表面形成保护膜,从而抑制了金属的腐蚀,而且在介质中,通过螯合物离解平衡缓慢释放有效的缓蚀成分[4]。另外,由于极性基团数目较多,更易提供电子,使化学吸附增强,缓蚀效果提高。

为验证不同浓度的植酸盐的缓蚀效果,分别做了浓度为 50,100,150,200 mg/L和 250 mg/L的植酸盐在同一条件下的循环伏安曲线见图 1。图 1中从左到右是向负极扫描,返回时是向正极扫描。下方曲线为还原曲线,上方曲线为氧化曲线。从图中可以看出,浓度为 50 mg/L的植酸盐的循环伏安曲线上有较明显的还原峰和氧化峰,说明该浓度的缓蚀剂对锰钢的缓蚀效果较差。当浓度增大时,缓蚀效果明显提高,尤其是当浓度为 100 mg/L时,循环伏安曲线较平滑,还原峰和氧化峰不明显,说明缓蚀效果很好。当浓度再增大时,出现了还原峰,并且随着浓度的增大,还原峰的峰电位变化不大,说明浓度再增大时,对锰钢的缓蚀效果变化不大。

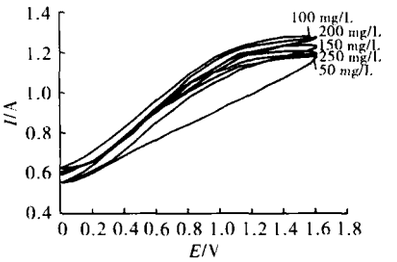

图 1 不同浓度的植酸盐在同一条件下的循环伏安曲线

2.3.2 SDBS和 POPE对 16锰钢的缓蚀作用

SDBS之所以能够起到缓蚀作用,是因为 SDBS在介质中电离出带负电荷的烷基酸根离子,它们易与带正电的钢表面发生静电吸附,且采取亲水基朝钢表面疏水基朝介质的直立吸附方式。但是其单独使用时,缓蚀效果并不好。这是由于它对钢表面发生的孔蚀和缝隙腐蚀起不到太大的缓解作用。POPE为聚氧乙烯醚类非离子表面活性剂,极性基为聚氧乙烯键,故有一定的亲水性,且亲水极性基团带有部分负电荷。在富含沉积水的原油介质中,钢铁表面带有正电荷[5,6],故 POPE的亲水基一端靠静电引力很容易吸附到钢铁表面,而疏水基一端则伸向介质溶液中,有效阻隔了介质和钢表面的直接接触,从而显著减慢其腐蚀速度。POPE在钢铁表面上的吸附基本符合 Frumking吸附模型[7],而且 $f>0$(吸附自由能参数),这说明吸附在钢铁表面上的 POPE分子之间有相互引力,这很可能是以

Van der Waals分子力为主的相互作用力,同时亦说明钢铁表面的吸附活性点极不均匀,在这些条件下,POPE在钢表面上的吸附层就不可能十分均匀致密,因此单独使用 POPE的最大缓蚀率也并不高。

2.3.3 植酸盐与 SDBS及 POPE对 16锰钢的缓蚀协同效应

当三者按 4∶1∶1比例 (质量比)加入介质中时,缓蚀率大大提高,其原因可能是带负电的 SDBS和 POPE共同吸附在带正电的钢表面,两者之间又有相互吸引力 ($f>0$),其结果是使钢表面的吸附层更加完整致密,从而显著加强了缓蚀作用。但当 SDBS和 POPE浓度超过一定值时,它们在溶液中的存在形式可能发生变化,如生成胶团等,而吸附在钢表面的活性剂分子可能形成表面胶团 (半胶团),使部分钢表面裸露出来,缓蚀率则开始有所降低,这种现象在类似体系中常见[8]。

2.4 几种同类用途缓蚀剂的比较

目前用于输油管线的缓蚀剂可大致分为咪唑啉类、铵盐和季铵盐类。它们的共同点是:作为缓蚀剂的有机化合物都由电负性较大的 N、O、S等原子为中心的极性基和 C、H等原子组成的非极性基构成,且能够以某种键的形式与金属表面相结合。咪唑啉作为一种较低毒性的新型缓蚀剂引起了人们的关注,它对铜、铁等具有较好的缓蚀效果。铵盐和季铵盐类缓蚀剂主要通过氮原子吸附来减缓腐蚀。Hackerman[9]指出,对于相同系列的有机缓蚀剂,根据其分子式中杂原子的不同,缓蚀效率一般遵循如下的变化规律,即:P > Se > S > N > O。植酸盐含 P有机物且环保,经过试验表现出了良好的缓蚀性能。

3 结 论

(1)失重法试验和极化曲线测试均表明,植酸盐在原油介质中对 16锰钢有较好的缓蚀效果,它属于螯合型缓蚀剂,且当其与一些表面活性剂进行复配时,缓蚀率显著提高。

(2) SDBS与 POPE单独使用时,效果不理想,但与植酸盐的复配协同效应显著。

(3)植酸盐作为一种混合控制型缓蚀剂,符合环保植物型缓蚀剂的发展趋势,在输油管线缓蚀剂开发方面具有良好的发展前景。

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50万 t/年丝网产品表面处理项目已经备案

近日,河北省发改委同意安平县昊天世博工业产品有限公司 50万 t/年丝网产品表面处理项目备案。

该项目建设地点位于河北省安平县东黄城乡西南侧,建设规模为年产镀锌丝、镀锌网、镀锌件 50万 t(中国采购与招标网编辑整理),项目总投资 18 499.47万元,建设起止年限为 2007年 1月 1日至 2008年 1月 1日。

(据中国采购与招标网)

Language, Qinhuangdao 06000, China; 2. School of Chemical Engineering and Biotechnology, Hebei University of Technology, Tangshan 063000, China). *Cailiao Baohu* 2007,40(02),17~19 (Ch). A series of rotary coupon-hanging tests was performed to screen a novel tungstate-based inhibitor with good corrosion-inhibition capability for carbon steel in seawater treatment. The optimized formulation of the tungstate-based inhibitor for seawater treatment was established, while its corrosion-inhibition mechanisms were primarily discussed in connection with the measurement of the potentiodynamic polarization curve. It was found that the critical concentration of single tungstate corrosion-inhibition agent in seawater was as much as 40 mg/L under the selected test conditions, and the corrosion-inhibition efficiency of the composite tungstate-based corrosion-inhibition agent for carbon steel in seawater was over 90%. Moreover, the titled inhibitor was effective in inhibiting both the anodic and cathodic processes, with the inhibition for the anodic process to be dominant. Moreover, the newly developed inhibitor had the advantages of high efficiency, low toxicity, and environmental acceptance. The optimized formulation for the newly developed inhibitor was suggested to be composed of 40 mg/L of tungstate, 40 mg/L of polyaspartic acid, 10 mg/L of 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), and 3 mg/L of Zn^{2+}.

Key words: seawater; corrosion inhibitor; carbon steel; sodium tungstate; polyaspartic acid; corrosion-inhibition mechanism

Corrosion Inhibition of 16 Mn Steel by Phytic Acid Salt

WANG Qiang, SHI Wei-zhen, LI Xiao-guang (School of Vocational Technology, Liaoning University of Petroleum & Chemical Technology, Fushun 113001, China). *Cailiao Baohu* 2007,40(02),20~22(Ch). The corrosion inhibiting action of phytic acid salt to 16 Mn steel was investigated using weight loss method and polarization curve method. It was found that phytic acid salt had good corrosion inhibiting effect for 16 Mn steel in the mixed medium of crude oil and 3.5% sodium chloride at 50 ℃. More important, the phytic acid salt combined with sodium dodecyl-benzene-sulfonate (SDBS) and polyglycol octyl-phenyl ether (POPE) showed considerably improved corrosion inhibition capability for the Mn steel, owing to a synergistic corrosion inhibition function among the three ingredients. The optimized formulation of the composite corrosion-inhibition agent was suggested to be 100 mg/L phytic acid salt : 25 mg/L SDBS : 25 mg/L POPE.

Key words: phytic acid salt; corrosion inhibitor; surface active agent; corrosion inhibition action

Development of a Novel Additive for Zinc Electroplating in Alkaline Zincate Bath

DENG Nian-chao[1], HU Xia-lin[1], CHANG Xiao-bo[2], XIONG Gang[1], PAN Zhao-ji[1](1. Wuhan Research Institute of Materials Protection, Wuhan 430030, China; 2. Qinghua Machine-Making Factory, Changzhi 046000, China). *Cailiao Baohu* 2007,40(02),23~26(Ch). A novel environmentally acceptable additive for zinc electroplating in a non-cyanide alkaline zincate bath was developed. The performance of the additive was investigated and compared to that of convention additives making use of electrochemical testing, scanning electron microscopic observation, and energy dispersive X-ray analysis. It was found that the newly developed additive had a broad current density range for bright electroplating, good dispersion capability, and good throwing power. The corresponding electroplated Zn coating prepared in the presence of the newly developed additive had a small brittleness and good re-machining performance.

Key words: zinc electroplating; zincate; additive

Pretreatment Processes for Al Electroplating of NdFeB Permanent Magnet in Melted Salt at Room Temperature

HAN Wen-sheng[1], XIE Rui-bing[2], XIAO Yi-de[2](1. Research Center of Machinery Environmental Technology, Guangzhou Electric Apparatus Research Institute, Guangzhou 510300, China; 2. Wuhan Research Institute of Materials Protection, Wuhan 430000, China). *Cailiao Baohu* 2007,40(02),27~29(Ch). The effects of various pretreatments on the electroplating process and performance of electroplated Al coating were investigated and compared, attempting to establish a novel water-free pretreatment process for Al electroplating of NdFeB permanent magnet from a melted salt bath at ambient temperature and hence get rid of the damage to the Al coating by a large number of micropores on the surface of the NdFeB powder metallurgy material. Thus comparative investigations were made among various pretreatment processes such as roasting degreasing and chemical degreasing, sand blasting and acid pickling, sealing and without sealing, and activating and without activating, with respect to the effects of the pretreatment on the adhesion of the Al coating to substrate. And the adhesion of the Al coating to the substrate was evaluated based on scanning electron microscopic observation and chisel-knife test and heat-quench test. As the results, it was suggested to apply the pretreatments including roasting degreasing, rust removal by sand blasting, drying, and electrochemical activation; and carry out cleaning in solvent, rinsing in water, and drying at the end of the electroplating, so as to effectively remove the oxidation film in the surface and bulk of the NdFeB material and hence increase the adhesion of the Al coating to the substrate.

Key words: NdFeB permanent magnet; Al electroplating in melted salt bath at ambient temperature; water-free pretreatment; adhesion

Development of Novel Environmentally Acceptable Formula of Electrolyte for Micro-Arc Oxidation of Mg Alloy

HUANG Jing-hao, ZHANG Yong-jun (School of Mechanical Engineering, South China University of Technology, Guangzhou 510640, China). *Cailiao Baohu* 2007,40(02),30~31(Ch). Orthogonal tests were carried out to optimize the composition of the electrolyte for the micro-arc oxidation of AZ91D Mg alloy and improve the corrosion protection capability of the micro-arc oxidation coating. Thus the optimized environmentally acceptable electrolyte formula was established, and the effects of various ingredients in the electrolyte on the corrosion-prevention capability of the micro-arc oxidation coating on Mg alloy were investigated. As the results, it was suggested that the optimized electrolyte bath be composed of 1.10 mol/L NaOH, 0.04 mol/L silicate of alkali metals, and 0.50 mol/L oxyacid salt of alkali metal; or be composed of 1.10 mol/L NaOH, 0.04 mol/L silicate of alkali metals, and 0.30 mol/L oxyacid salt of alkali metals. The micro-arc oxidation coatings on the Mg alloy prepared using the optimized electrolyte baths showed good corrosion-prevention capability and could have promising application in engineering.

Key words: Mg alloy; micro-arc oxidation; electrolyte; orthogoral test

Study of a Fluorocarbon Paint for Anodizing Protection of Aluminum Alloy

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Key words: fluorocarbon protecting paint; aluminium alloy anodising; coating; insulation protection

Study of Plasma Carburizing Process for Stainless Steel and Ni-