

Raman Spectroscopic Study on Mechanism of Aluminum Triphosphate Pigment

GU Zhi-jun^{*}, LIAO Yong-gui, ZHANG Zhi-gang, GUO Qi-long, SU Fang-teng
(Fujian Institute of Research on the Structure of Matter,
Chinese Academy of Sciences, Xiamen 361012, China)

Abstract : The painted steel sample whose coating contained anticorrosive pigment has been investigated by Raman spectroscopy. The protective mechanism of aluminum triphosphate pigment for A3 steel is proposed as follows: Aluminum triphosphate can be dissolved and arrive at the surface of the steel. The dissolved triphosphate ions can complex with ferric ions. And the new products, namely ferric triphosphate, can strongly adhere at the surface of the steel by chemical bonds slowly. At last, a compact protective film, which effectively separates the steel substrate from the aggressive media, is formed at the steel surface.

Key words : Raman Spectroscopy, Mechanism, Pigment, Sodium chloride

CLC number : O TG 172, O 646

Document Code : A

1 Introduction

In 1995, the cost on corrosion of metal in the United States has reached \$ 300 billion or so per year. In order to reduce the loss of corrosion, many protection methods have been used. Organic coating is one of the most effective, economical and popular methods as yet. The various pigments in anticorrosive coatings protect the metal substrates by different mechanisms, either by creation of alkaline environments, by passivation of the active centers originating from geometrical or structural defects, by decreasing the oxygen permeation from the environment or the metal ion diffusion through the coating, or by buffering the formation of hydrogen ions, or by sacrificial metal powders in the coating^[1]. A small amount of inhibitors can obviously retard corrosion, so inhibitors have been considered more and more important. Although some traditional anticorrosive pigments, such as lead- and chrome-based pigments, have good inhibitive performances, but they

Received date: 11 Oct. 2001

^{*} To whom correspondence should be addressed, Tel: 86 - 592 - 6013060, E-mail: zhjgu@ms.fjirsm.ac.cn
Foundation item: Project supported by State Key Lab. for Phys. Chem. of Solid Surface(9703)

have high toxicity too. They are strictly limited, or prohibited to use in many countries and regions. Thus the application and research of new anticorrosive pigments are bound to focus on the highly effective, multifunctional and environmentally friendly pigments. Aluminum triphosphate is an anticorrosive pigment with good inhibitive performance when it is mixed in the epoxy-polyamide resin on A3 steel coupon^[2], however, its mechanism is not clear yet.

There have been lots of studies that have tried to determine the nature of corrosion species, especially on copper and iron, in the presence of active inhibitors in solutions by Raman spectroscopy^[3~11]. Raman spectroscopy has been used to investigate corrosion under paint, but without anticorrosive pigment was in the coating^[12~14]. Therefore, we report here using Raman spectra for studies of the corrosion species at the artificial defect in the coating, in the presence of anticorrosive pigment. It is helpful to better understand the mechanisms of anticorrosive pigments.

2 Experimental

2.1 Preparation of two ferric compounds

To synthesize ferric phosphate^[15], 0.02 mol ferric chloride (FeCl_3), 0.02 mol sodium hydrogen phosphate (Na_2HPO_4), and 0.025 mol sodium acetate (CH_3COONa) were dissolved in 100 mL distilled water respectively, mingled, filtered, dried.

To synthesize ferric triphosphate, 0.05 mol FeCl_3 and 0.03 mol sodium triphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) were dissolved in 100 mL distilled water respectively, mingled, filtered, dried.

2.2 Materials

To prepare the coated coupon, the surface of the A3 steel coupon (200 × 100 mm) was abraded with 60 #, 80 # sand cloth in succession, cleaned, degreased with ethanol, covered by the epoxy-polyamide resin containing aluminum triphosphate pigment, air dried in ambient temperature for one week, placed a plastic tube (inner diameter = 90 mm) on the coated coupon with 704 binder, air dried. The solution was made of distilled water and sodium chloride (NaCl , AR), and the concentration was 3.5 % (wt %).

2.3 Micro-Raman spectroscopy

—Raman spectra were obtained by LabRam I confocal microscopic Raman spectrometer (Dilor) with a He-Ne laser (632.8 nm) in the pore covered with 1 mm solution at ambient temperature and air-open system. (The Raman spectra of ferric phosphate and ferric triphosphate were obtained from their powder samples directly.)

3 Results and Discussion

3.1 Two ferric compounds

Fig. 1 and Fig. 2 show micro-Raman spectra of synthetic ferric phosphate and ferric triphosphate, respectively. In figure 1, the characteristic peak is at $1\,010\text{ cm}^{-1}$. Additional features are observed at 270 , 541 , $1\,444\text{ cm}^{-1}$, and a shoulder peak of 439 and 478 cm^{-1} . In figure 2, the char-

acteristic peak is $1\ 107\ \text{cm}^{-1}$. Additional features are observed at $412, 704, 928$ and $994\ \text{cm}^{-1}$.

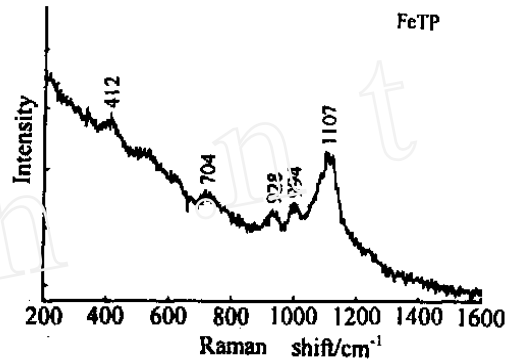
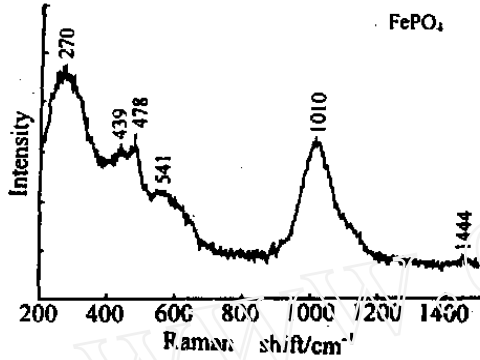


Fig. 1 Micro-Raman spectrum of ferric phosphate (FePO_4)

Fig. 2 Micro-Raman spectrum of ferric triphosphate (FeTP)

3.2 Characterization of painted blank A3 steel coupon

Table 1 summarizes the Raman shifts and corrosion species for painted blank A3 steel coupon

Tab.1 Nominal Raman frequencies (cm^{-1}) of corrosion species observed with exposure time (day) for painted blank painted steel coupon immersed in 3.5 % NaCl solution. The underlined peaks exhibit strong intensities

1 day		2 days		6 days		Assignment	
inner	outer	Inner of yellow	Outer of yellow	black	yellow		black
					220		- Fe_2O_3
		<u>252</u>	<u>256</u>		<u>256</u>	251	- FeOOH
				295			Fe_3O_4
			<u>282</u>		296		- Fe_2O_3
314			314		311	311	$\text{FeCl}_3(\text{s})$ *
351			345		347		- Fe_2O_3
		377			<u>377</u>	<u>377</u>	- Fe_2O_3
<u>382</u>							- FeOOH + - Fe_2O_3
			<u>527</u>		<u>529</u>		- FeOOH
<u>528</u>				538		534	Fe_3O_4
			<u>652</u>		<u>655</u>		- FeOOH
<u>658</u>	<u>668</u>	<u>668</u>		<u>664</u>		<u>670</u>	Fe_3O_4
<u>1304</u> ^{br}			<u>1293</u> ^{br}		<u>1302</u> ^{br}		- FeOOH
- FeOOH + Fe_3O_4	Fe_3O_4	Fe_3O_4	- FeOOH + Fe_3O_4	Fe_3O_4	- FeOOH	Fe_3O_4	Corrosion species
+ - Fe_2O_3		+ - FeOOH	+ - Fe_2O_3		+ - Fe_2O_3	+ - Fe_2O_3	
+ - FeOOH		+ - Fe_2O_3	+ - Fe_2O_3		+ $\text{FeCl}_3(\text{s})$	+ - FeOOH	
+ $\text{FeCl}_3(\text{s})$			+ $\text{FeCl}_3(\text{s})$		+ Fe_2O_3	+ $\text{FeCl}_3(\text{s})$	

*^{br} represents broad wave. * Without illustrated particularly, the location measured was the inner point.

that was exposed in 3.5 % NaCl solution with immersion time. At different points, the corrosion species are different. Namely, the special distribution of corrosion species is inhomogeneous. The corrosion species for painted blank A3 steel coupon are iron oxides and iron oxyhydroxides.

Immersion 1 day, the corrosion species at inner point are mainly -FeOOH , Fe_3O_4 , $\text{-Fe}_2\text{O}_3$, -FeOOH , and scarce FeCl_3 in solution. Although $\text{-Fe}_2\text{O}_3$ exhibits mode in the 1 300 to 1 310 cm^{-1} range, no peak is observed at the frequency that its most intense mode (290 cm^{-1}) is expected. It indicates that this species is not present in detectable concentration. The corrosion species at outer point is mainly Fe_3O_4 . Figure 3 shows their Raman spectra. Immersion 2 days, yellow and black spots can be observed by naked eyes. Only Fe_3O_4 can be detected at the black. However, -FeOOH , Fe_3O_4 and $\text{-Fe}_2\text{O}_3$ at the inner of the yellow, -FeOOH , Fe_3O_4 , $\text{-Fe}_2\text{O}_3$ and scarce $\text{-Fe}_2\text{O}_3$ and FeCl_3 in solution at the outer of the yellow, can be detected. Immersion 6 days, -FeOOH , $\text{-Fe}_2\text{O}_3$, $\text{-Fe}_2\text{O}_3$ and scarce FeCl_3 in solution at the inner of the yellow, Fe_3O_4 , $\text{-Fe}_2\text{O}_3$ and scarce -FeOOH , $\text{-Fe}_2\text{O}_3$, FeCl_3 in solution at the inner of the black, can be detected. Figure 4 shows the micro-Raman spectra of corrosion species for painted blank A3 steel coupon immersed in 3.5 % NaCl solution for 6 days at inner of yellow point (a), and at inner of black point (b).

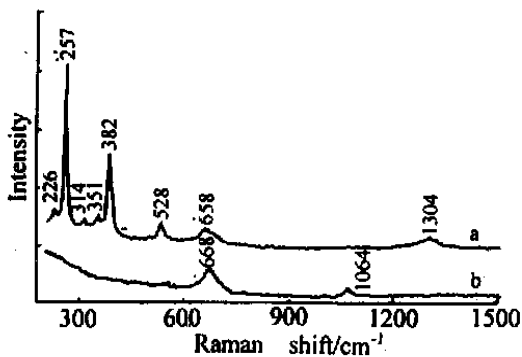


Fig. 3 Micro-Raman spectra of corrosion species for painted blank A3 steel coupon immersed in 3.5 % NaCl solution for 1 day at inner point (a), and at outer point (b)

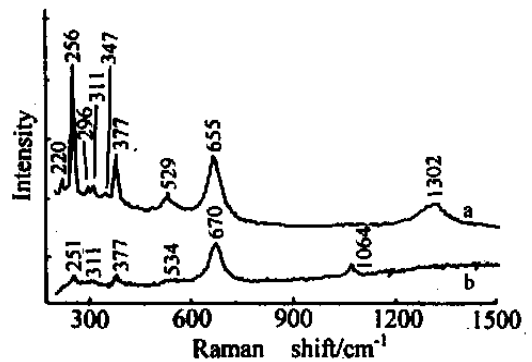


Fig. 4 Micro-Raman spectra of corrosion species for painted blank A3 steel coupon immersed in 3.5 % NaCl solution for 6 days at inner in yellow point (a) and at inner in black point (b)

Because of the artificial defect, "large cathode, little anode" is formed, the defective area becomes the anode relative to the other. When the blank painted A3 steel coupon is immersed in 3.5 % sodium chloride solution, the corrosion occurs at the surface of the defect. Furthermore, at the surface of the defect, geometrical and physical structures are different. Different points have different activities. Their corrosion rates are different too. The points whose corrosion rates are quicker grow quicker because the volume of iron corrosion species is larger than that of the metal. The corrosion species immersed can be oxidized with time, and the stable species can be formed. So

the special distribution of corrosion species is inhomogeneous, and the corrosion species for the painted blank A3 steel coupon are iron oxides and iron oxyhydroxides.

3.3 Characterization of the painted A3 steel coupon whose coating contained aluminum triphosphate pigment

Table 2 shows the Raman shifts and corrosion species for the painted A3 steel coupon, exposed in 3.5 % NaCl solution, whose coating contained aluminum triphosphate pigment, with immersion time. Figure 5 shows the micro-Raman spectra of corrosion species for the sample immersed in 3.5 % NaCl solution for one day (a), and for two days (b) at inner points.

Tab. 2 Nominal Raman frequencies (cm^{-1}) of corrosion species observed with exposure time (day) for the painted steel coupon whose coating contained aluminum triphosphate pigment immersed in 3.5 % NaCl solutions. The underlined peaks exhibit strong intensities

1 day	2 days	19 days	21 days	assignment
		<u>225</u>		- Fe ₂ O ₃
251	<u>245</u>		<u>247</u>	- FeOOH
272				FePO ₄
		<u>288</u>		- Fe ₂ O ₃ + - Fe ₂ O ₃
376			<u>377</u>	- Fe ₂ O ₃
	<u>376</u>			- Fe ₂ O ₃ + - FeOOH
		<u>408</u>		- Fe ₂ O ₃
		499		- Fe ₂ O ₃ + FeCl ₂
534				- FeOOH
		<u>611</u>		- Fe ₂ O ₃
<u>642</u>				- Fe ₂ O ₃
		<u>658</u>		- Fe ₂ O ₃ + Fe ₃ O ₄
	<u>710</u>		<u>715</u> ^{br}	Fe TP *
840				PO ₄ ³⁻
	990-1100	1090 ^{br}	<u>1077</u> ^{br}	Fe TP *
			1309	- FeOOH
		<u>1314</u> ^{br}		- Fe ₂ O ₃
	<u>1342</u> ^{br}			Fe(OH) ₃
<hr/>				
- Fe ₂ O ₃ + - FeOOH	- FeOOH	- Fe ₂ O ₃ + - Fe ₂ O ₃ +	- FeOOH + - Fe ₂ O ₃	Corrosion species
+ FePO ₄	+ - Fe ₂ O ₃ + Fe TP	Fe ₃ O ₄ + FeCl ₂ + Fe TP	+ Fe TP	

* ^{br} represents broad wave. * Fe TP represents ferric triphosphate.

* Without illustrated particularly, the location measured was the darker point.

Immersion 1 day, the mode at 272 cm^{-1} is exhibited; although the mode at 1010 cm^{-1} cannot be distinguished obviously, it can be regarded to be covered by the very broad wave in the 900

to $2\ 700\ \text{cm}^{-1}$ range. Moreover, the oxides and hydroxides of iron have not characteristic peaks at $270\ \text{cm}^{-1}$ or so. So the mode at $272\ \text{cm}^{-1}$ can be regarded as the mode of ferric phosphate. Immersion 2 days, an intense peak at $710\ \text{cm}^{-1}$, a broad wave in the 990 to $1\ 100\ \text{cm}^{-1}$ range, and no peak at $270\ \text{cm}^{-1}$ are exhibited. So they can be regarded as the modes of ferric triphosphate. Immersion 19 days, the centric wave number that the ferric triphosphate is at $1\ 107\ \text{cm}^{-1}$ moves to the lower frequency, $1\ 090\ \text{cm}^{-1}$. Immersion 21 days, it moves to $1\ 077\ \text{cm}^{-1}$ continuously. (See figure 6)

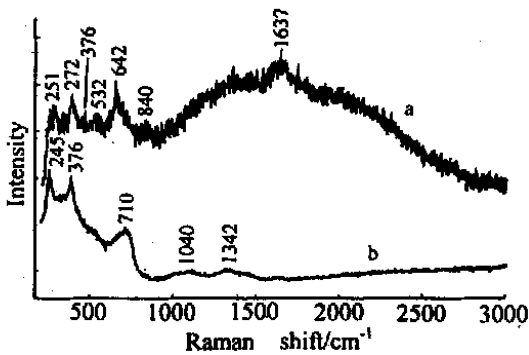


Fig. 5 Micro-Raman spectra of corrosion species for the painted A3 steel coupon whose coating contained aluminum triphosphate pigment immersed in 3.5% NaCl solution for one day (a), and for two days (b) at inner points

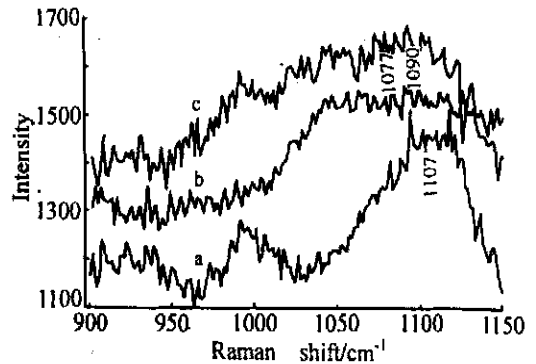


Fig. 6 Micro-Raman spectra of corrosion species for the painted A3 steel coupon whose coating contained aluminum triphosphate pigment immersed in 3.5% NaCl solution for 19 days (b) and 21 days (c), contrary to ferric triphosphate powder (a)

The corrosion species for the painted A3 steel coupon whose coating contained aluminum triphosphate pigment are iron oxides and oxyhydroxides, besides ferric phosphate at first and ferric triphosphate which strongly adheres at the surface of the iron by chemical bonds.

Aluminum triphosphate can dissolve and reach the surface of the steel. The triphosphate ions can be hydrolyzed, so the phosphate ions are formed. The latter can react with iron corrosion products, e. g., Fe^{2+} and Fe^{3+} , so the ferric phosphate can be detected by Raman spectroscopy initially. With the increase of triphosphate ions and iron corrosion products at the surface, the triphosphate ions cannot be hydrolyzed in time, and they can complex with the latter. Furthermore, the product, ferric triphosphate can strongly adhere at the surface of the iron by chemical bonds slowly. So the centric wave number of ferric triphosphate moves to the lower frequencies. At last, a compact protective film, which effectively separates the steel substrate from the aggressive media, is formed at the steel surface.

4 Conclusions

(a) The corrosion species for the painted metal, such as A3 steel, whose coating contained an-

ticorrosive pigment ,can be obtained ,and much information for mechanism of anticorrosive pigment can be provided by Raman spectroscopy study.

(b) The special distribution of corrosion species is inhomogeneous.

(c) The corrosion species for painted blank A3 steel coupon are iron oxides and iron oxyhydroxides. The corrosion species for painted A3 steel coupon whose coating contained aluminum triphosphate pigment are iron oxides and oxyhydroxides ,besides ferric phosphate at first and ferric triphosphate.

(d) The protective mechanisms of aluminum triphosphate pigment for A3 steel are as follows. aluminum triphosphate can dissolve and arrive at the surface of the steel. The dissolved triphosphate ions can complex with ferric ions. And the new products ,namely ferric triphosphate , can strongly adhere at the surface of the iron by chemical bonds slowly. At last ,a compact protective film ,which effectively separates the steel substrate from the aggressive media ,is formed at the steel surface.

References :

- [1] Th Shoulivdis ,et al. Correlation between protection of steel from corrosion and the conductivity of n-semiconductor pigments[J]. Corrosion ,1998 ,54(5) :386.
- [2] Yong-gui Liao ,et al. Electrochemical impedance spectroscopy studies on inhibitive performance of aluminum triphosphate pigment[J]. Electrochemistry ,2001 ,7(1) :126.
- [3] Bunding K A ,et al. Surface-enhanced raman scattering by pyridine on a copper electrode[J]. J. Electroanal. Chem. ,1985. 184 :405.
- [4] Thierry D ,et al. Simultaneous raman spectroscopy and electrochemical studies of corrosion inhibiting molecules on copper[J]. J. Electrochem. Soc. ,1985 ,132(5) :1 009.
- [5] Da Costa S L F A ,et al. Inhibiting action of benzotriazole on copper corrosion in deaerated sulfuric acid containing ferric ions by the rotating disc electrode ,fluorescence ,and raman spectroscopies[J]. Corrosion ,1987 ,43 (3) :149.
- [6] Youda R ,et al. A SERS study on inhibition mechanisms of benzotriazole and its derivatives for copper corrosion in sulphate solutions[J]. Corrosion Science ,1988 ,28(1) :87.
- [7] Aramaki K ,et al. A SERS study on adsorption of some organic compounds on iron[J]. J. Electrochem. Soc. , 1989 ,136(5) :1 299.
- [8] Youda R ,et al. SERS and impedance study of the equilibrium between complex formation and adsorption of benzotriazole and 4-hydroxybenzotriazole on a copper electrode in sulphate solutions[J]. Electrochim. Acta , 1990 ,35(6) :1 011.
- [9] Aramaki K ,et al. In situ raman spectra of pyridinium chloride adsorbed on iron in K_2SO_4 and H_2SO_4 solutions [J]. J. Electrochem. Soc. ,1992 ,139(6) :1 525.
- [10] Oblonsky L J ,et al. Adsorption of octadecyldimethylbenzylammonium chloride to two carbon steel microstructures as observed with surface-enhanced raman spectroscopy[J]. Corrosion ,1995 ,51(12) :891.
- [11] Aramaki K ,et al. Surface-enhanced raman scattering spectroscopy studies on the inhibition mechanisms of

- propargyl alcohol for iron corrosion in hydrochloric acid[J]. Corrosion, 1996, 52(2):83.
- [12] Thierry D, et al. In situ determination of corrosion species formed on painted galvanized steel by raman spectroscopy[J]. J. Electrochem. Soc., 1991, 138(3):879.
- [13] Bernard M C, et al. Underpaint corrosion of zinc-coated steel sheet studied by in situ raman spectroscopy[J]. Corrosion Science, 1993, 35(5~8):1339.
- [14] Bernard M C, et al. In situ Raman study of the corrosion of zinc-coated steel in the presence of chloride[J]. J. Electrochem. Soc., 1995, 142(7):2167.
- [15] Shou-chun Chen. Some Important Inorganic Reactions[M]. Shanghai: Shanghai press of science and technology, 1963:380.

防锈颜料三聚磷酸铝的拉曼光谱研究

辜志俊*, 廖永贵, 张志刚, 郭琦龙, 苏方腾

(中国科学院福建物质结构研究所, 福建 厦门 361012)

摘要: 应用拉曼光谱研究了含有防锈颜料涂装特性的钢样,在此基础上探讨了三聚磷酸铝防锈颜料对 A3 钢的保护机理. 三聚磷酸铝溶解后能到达钢样表面,其离子可与铁离子化合形成三聚磷酸铁. 三聚磷酸铁能缓慢地通过化学键牢固地附着在钢样表面,最终在钢表面形成一层隔绝腐蚀介质和钢样的紧密保护膜阻止了腐蚀的继续发生从而达到保护的目的.

关键词: 拉曼光谱;机理;颜料;氯化钠