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Effect of Nano-TiO_2 Additives on the Corrosion Performance of Lubricating Oil on Steel 45 Substrates

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An oleic acid modified TiO_2 nanoparticles were synthesized by chemical co-deposition method. The surface morphology, size distribution and structure of the nanoparticles were analyzed by transmission electron microscopy, fourier-transform infrared spectroscopy and laser particle analyzer. The anticorrosion performance of oleic acid-TiO_2 was examined by electrochemical techniques. It was found that the TiO_2 nanoparticles with average diameter of 44 nm and combined with oleic acid by covalent bonds, were capable of being dispersed stable in oil, which enabled the nanoparticles to be used as additives in lubricating oil. The results of polarization curves and electrochemical impedance spectroscopy indicated that the addition of oleic acid-TiO_2 nanoparticles in lubricating oil decreased the corrosion current density and increased the corrosion resistance of oil film on steel 45 substrates.

Key Words: Nano-TiO_2, Oleic acid, Modification, Corrosion resistance, Electrochemical impedance spectroscopy.

INTRODUCTION

The application of lubricating oil are the most widespread approach nowadays used for corrosion protection of metallic mechanical parts either in storage or during application by forming effective barrier against corrosive species present in different environments[1]. It is well-known that lubricating oils consist of a mixture of base oil and different additives. Many oil-soluble organic compounds (such as petroleum sulfonates, synthetic alkylbenzene sulfonates, carboxylic acid derivates, oxidized paraffins, alkylated succinic acids, lanolin and 4-nonylphenoxyacetic acid)[1,2] were found to effectively improve the protection efficiency of lubricating oil and used as anti-corrosion additives. However, lead, zinc and barium in petroleum sulfonates[3] and synthetic alkylbenzene sulfonates[4] caused great harm to the environment and human health. In addition, some of these traditional additives had poor thermo-oxidative stabilities and showed oxidative degradation tendencies under severe conditions of high temperature, extreme pressure and high sliding speed[2]. So researchers keep striving to develop an anticorrosion agent with environment-friendly characteristic and high thermo-oxidative stability.

Nanoparticles had been intensively investigated because of their distinctive physical and chemical properties. Specially TiO_2 nanoparticles showed high thermo-oxidative stablility together with good environment-friendly property (without toxic heavy metal element). In addition, Shen's studies had indicated that TiO_2 nanoparticle coatings exhibited an excellent corrosion resistance due to a ceramic protective barrier on metal surface and the electrochemical impedance spectroscopy (EIS) measurements provided an explanation to the increased resistance of TiO_2 nanoparticles coated 316 L stainless steel against corrosion[5,6]. Similar results were also obtained by Sathiyanarayanan *et al.*[7], Zubillaga *et al.*[8] and Shi *et al.*[9]. Recently, Padhy *et al.*[10] evaluated the corrosion resistance of sputter deposited TiO_2 on austenitic 304 L stainless steel in the oxidizing medium of 1 and 8 M nitric acid and showed that an increase in corrosion potential in both test solutions for TiO_2 coated specimens. All these results suggest that TiO_2 nanoparticles can improve the anticorrosion property by replacing traditional organic anticorrosion additives in lubricating oil.

This study synthesized oil-soluble TiO_2 nanoparticles and investigated its effect on the corrosion resistance properties of lubricating oil, thus to evaluate the feasibility of TiO_2 nanoparticles as anticorrosion agent. It is expected that this work will be helpful to expanding the range of application of nano-TiO_2 and improving lubricating oil for corrosion protection of metallic mechanical parts.

EXPERIMENTAL

The reagents in the experiments such as oleic acid, tetrabutyl titanate [$Ti(OBu)_4$], acetone and ethanol were analytical pure reagents. 45# Transformer oil as the base oil of lubricating oil was purchased from Lubricant Company, SINOPEC (China Petroleum & Chemical Corporation) and used without further treatment. The steel 45 (80 mm × 60 mm × 3 mm) was used as the substrate of oil film.

Synthesis of nano-TiO_2: The synthesis procedure of oleic acid-TiO_2 were as follows: $Ti(OBu)_4$ was added to an amount of oleic acid in a closed vessel under vigorous stirring at room temperature. Then deionized water was dropped slowly into the mixtures while stirring. After reaction was conducted for 4 h at 60 ºC, the reaction mixtures were centrifuged and the deposition were washed repeatedly three times with acetone, ethanol and deionized water to remove excess acid. Then the productions was dried in an oven at 60 ºC for 12 h. Finally the pale yellow powder was the expected oleic acid-TiO_2 nanoparticles.

Preparation of test sample oil with oleic acid-TiO_2: The nanoparticles were added to the base oil under the condition of stirring and ultrasonic wave ,and then the base oil with oleic acid-TiO_2 additives used as test sample oil.

Characterization of oleic acid-TiO_2: The FT-IR analysis was performed on an spectrometer (Model Equinox55 from Brucker). TiO_2 nanoparticles were dried in an oven at 40 ºC for 12 h and then KBr pellets were prepared with the dried TiO_2 nanoparticles. The spectra were collected in the range from 4000-500 cm^{-1}. The morphology and size distribution of the TiO_2 nanoparticles was studied by SEM(Model H-9000 from Hitachi) and laser particle analyzer (Model Mastersizer 2000 from Malvern Instruments Ltd., UK).

Evaluation of corrosion resistant properties of oleic acid-TiO_2: The anticorrosion performance of TiO_2 on steel 45 substrates was examined by electrochemical analyzer (Model LK2006A from Tianjin Lanlike electrochemical technology Co., Ltd.). The test were carried out in a three-electrode cell including a saturated calomel electrode (SCE), a platinum auxiliary electrode and working electrodes.The working electrodes were steel 45 substrates and were pretreated by the test sample oil (45# transformer oil with 5 wt. % oleic acid-TiO_2) as follows: electrodes immerged in the sample oil at room temperature for 5 min, then took out and stored in ambient conditions for 16 h.

The electrolyte was 3.5 wt % NaCl aqueous solution (pH = 4.8). The Tafel polarization curves were measured at a sweeping rate of 1 mV/s in the range from -1.5 V to 0.4 V. The applied frequencies of EIS were ranged from 10^{-2}-10^{4} Hz at the steady open circuit potential (OCP). The experimental data were analyzed by ZSimpwin software and the equivalent circuits were described.

RESULTS AND DISCUSSION

The untreated TiO_2 nanoparticles with many hydroxyl groups were hardly dispersed in lubricating oil. Compounds with a long alkyl chain and polar head such as aliphatic acids[11-14], coupling agent[15] and surfactant[16] could effectively improve their dispersion capacity in lubricating oil. Herein we used oleic acid to modify nano-TiO_2 surface, which was designated as oleic acid-TiO_2.

Fig. 1 showed the FTIR spectra of oleic acid and oleic acid-TiO_2 nanoparticles. Absorptions at 2924, 2856 and 3007 cm^{-1}, corresponding to the stretching vibration of $-CH_3$, $-CH_2-$ and =CH-, showed that there were the abundance of long alkyl chain and double bond between carbon atoms.This revealed that oleic acid was successfully modified on the surface of TiO_2 nanoparticles[13]. The characteristic band of carbonyl at 1716 cm^{-1} in carboxylic acid disappeared and the symmetrical and asymmetrical vibrations of COO^- shifted from 1459 and 1400 to 1553 and 1452 cm^{-1} in Fig. 1b, which indicated that the modifier oleic acid reacted with TiO_2 nanoparticles and formed carboxylic acid salt in the nanoparticles. Namely, the surface-modifier film modified on TiO_2 nanoparticles not by physically adsorption, but by covalent bonds. In addition, the absorptions of water or hydroxyl groups near 3400 cm^{-1} is not found in Fig. 1b. It was subsequently concluded that the modifier film could prevent the adsorption of water or hydroxyl groups on the surface of TiO_2, which contributed to controlling the particle size and improving the dispersion capacity of nanoparticles in lubricating oil.

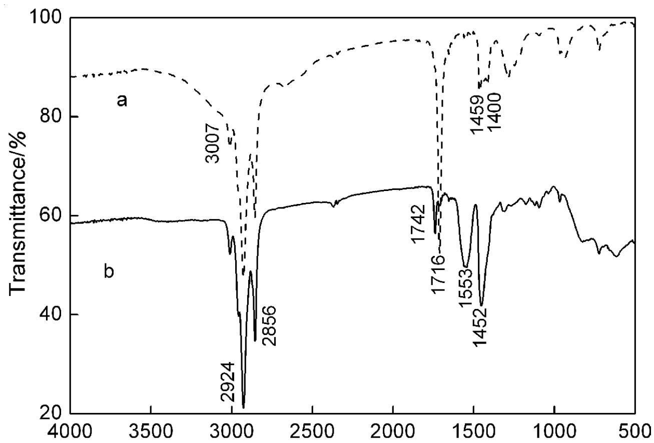

Fig. 1. FTIR spectra of: (a) oleic acid, (b)oleic acid-TiO_2

The TEM image in Fig. 2 clearly showed that the single particles were spherical or close to spherical in shape with the average diameter of 44 nm. The maximum size of oleic acid-TiO_2 particles was also found within 200 nm. After dispersed into base oil, oleic acid-TiO_2 particles showed Gaussian distribution, with the average particle diameter of 60 nm (Fig. 3). These indicate that the existence of surface-modifier oleic acid could effectively prevent the agglomeration and make nanoparticles have an excellent dispersion capability in oil, which enables us to study the effects of oleic acid-TiO_2 nanoparticles as a potential oil additives on the corrosion performance of lubricating oil.

Fig. 4 showed the influence of nano-TiO_2 on corrosion protection of base oil on steel 45 substrate and corresponding electrochemical parameters were given in Table-1. The cathodic Tafel curves of the both oil had few changes, which suggested that the cathodic corrosion process was not affected by the presence of oleic acid-TiO_2 nanoparticles.The corrosion potential (E_{corr}) showed a little cathodic shift with adding TiO_2 nanoparticles and there are obvious passivation region in anodic curves due to the formation of passive film. It could be attributed to oleic acid-TiO_2 which is able to inhibit anodic reaction of corrosion process on substrate. From Table-1, the oleic acid-TiO_2 nanoparticles as additives decreased the corrosion current density (I_{corr}) of oil film from 78.523 to 9.258 $\mu A/cm^2$

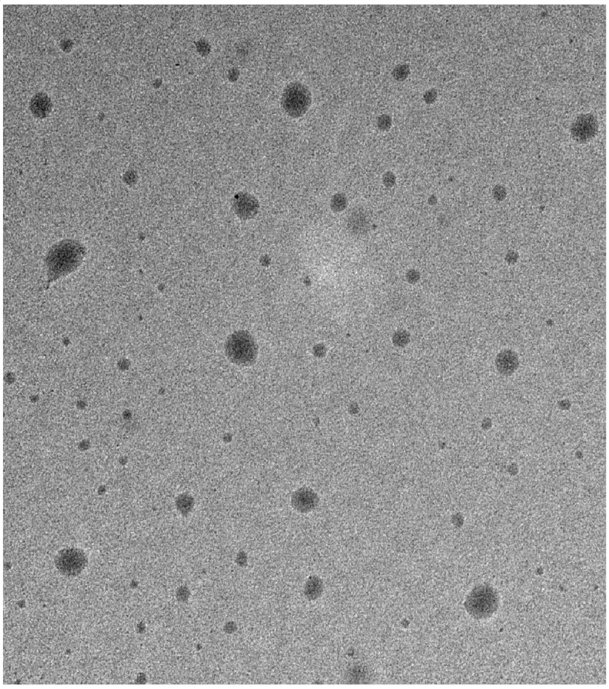

Fig. 2. TEM image of oleic acid-TiO_2 nanoparticles

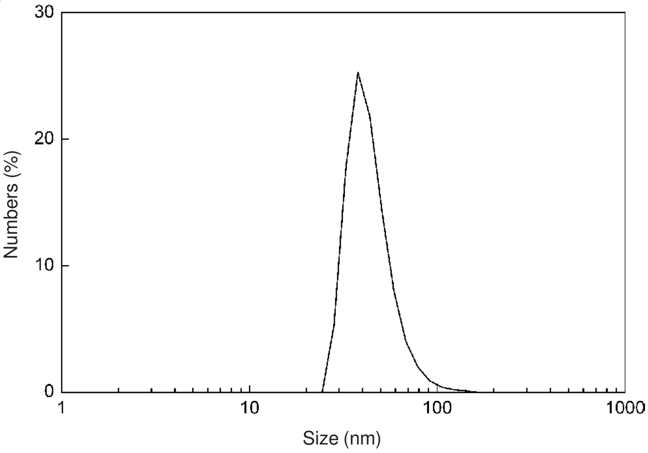

Fig. 3. Size distribution of the oleic acid-TiO_2 in base oil

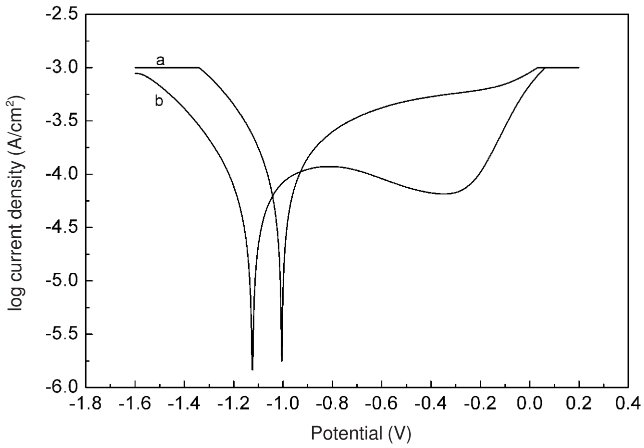

Fig. 4. Tafel polarization curves of (a) base oil and (b) sample oil

and the obtained the corrosion resistance (R_p) for oil film increased from 12544 to 122596 Ω cm^2 after adding TiO_2 nanoparticle. The reduction in the I_{corr} by nine times and

TABLE-1
ELECTROCHEMICAL PARAMETERS
OBTAINED FROM TAFEL CURVES[a]

	I_{corr} (μA/cm^2)	E_{corr} (V)	R_p (Ω/cm^2)
Base oil	78.523	-0.985	12544
Sample oil	9.258	-1.134	122596

Notes: (a) the base oil is 45# transformer oil. Sample oil is 45# transformer oil with 5 wt. % oleic acid-TiO_2.

improvement in R_p by ten times implied that oleic acid-TiO_2 have good corrosion protective proformance to steel 45 substrate as additives of the lubricating oil.

The EIS measurements had also been carried out on the both oil in 3.5 % NaCl solution (Fig. 5). Impedance parameters and the equivalent circuit were given in Table-2 and Fig. 7, respectively. In the Nyquist plots (Fig. 5), there was a RC loop in both plots. But the semicircle diameter of capacitance loop in plot(b) was larger than that in plot(a). The capacitance loop with a large value of the resistance(real axis) illustrated that the oil with 5 % oleic acid-TiO_2 nanoparticles had an excellent corrosion resistance, which were in accordance with those polarization curves. The Bode diagram of the base oil without oleic acid-TiO_2 (Fig. 6a) evidently contained one time constant which could be associated with oil film and two time constant were apparently observed in Bode diagram (Fig. 6b). The one in high frequency (HF) range was related with resistance and capacitance of oil film. The other in low frequency (LF) range was affected by double-layer capacitance associated with the TiO_2 particle-rich layer. Fig. 7 showed the equivalent circuit of impedance spectra of the both oil. In this equivalent circuit, Rs represented the solution resistance. R_f and CPE1 are the oil lm resistance and capacitance, respectively. CPE2 and R_{ct} were the double layer capacitance and the charge transfer resistance at the metal/TiO_2 film interface. Corresponding impedance parameters were obtained by fitting the EIS spectra with the equivalent circuits and listed in Table-2. The corrosion resistance for the oil without TiO_2 was 2343 Ω cm^2, while that for the oil with oleic acid-TiO_2 was 15530 Ω cm^2. This means that the corrosion resistance of the base oil has been significantly improved by oleic acid-TiO_2 nanoparticles.

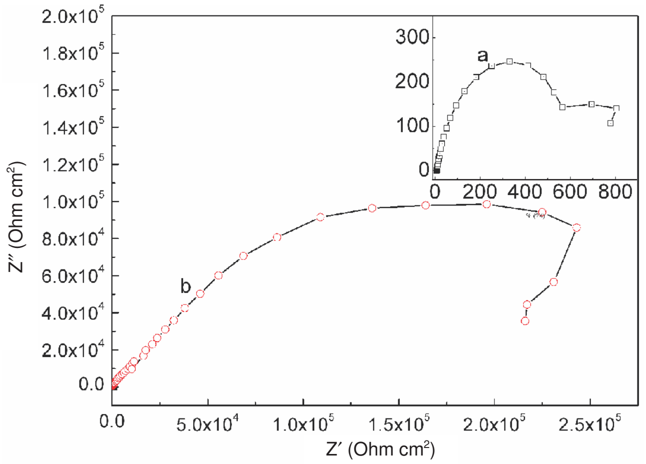

Fig. 5. Nyquist plot for (a) base oil and (b)sample oil

TABLE-2
EQUIVALENT CIRCUIT PARAMETERS DETERMINED BY MODELING IMPEDANCE SPECTRA IN FIG. 5[a]

	Rs (Ω cm^2)	CPE1 (F cm^{-2})	n1	Rf (Ω cm^2)	CPE2 (F cm^{-2})	n2	Rct (Ω cm^2)
Base oil	7.265	3.491×10^{-5}	1.000	2343	–	–	–
Sample oil	10	3.456×10^{-7}	0.740	15530	1.304×10^{-6}	0.5878	368100

Notes: (a) the base oil is 45# transformer oil. Sample oil is 45# transformer oil with 5 wt. % OA-TiO_2.

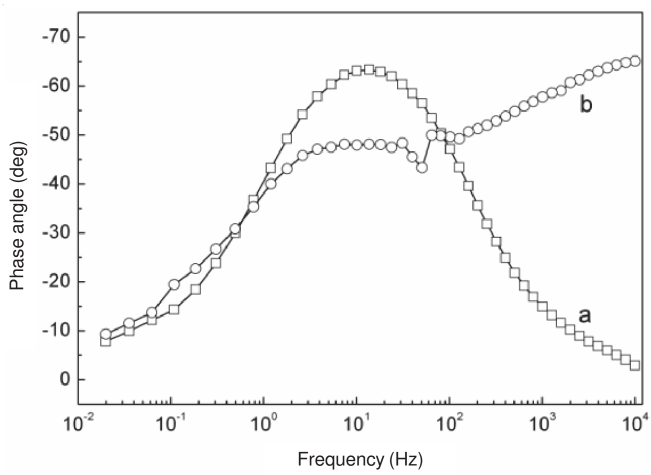

Fig. 6. Bode diagram (a) base oil and (b)sample oil

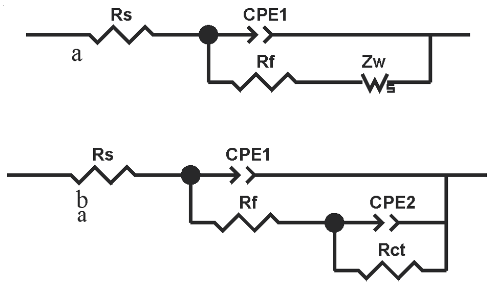

Fig. 7. Equivalent circuit of impedance spectra (a) base oil; (b) sample oil

Conclusion

TiO_2 nanoparticles modified by oleic acid were successfully prepared by the chemical co-deposition method. The covalent bonds between the surface-modifier film and TiO_2 nanoparticles were contributed to preventing agglomeration of nanoparticles and controlling the particle size in lubricating oil. The synthesized nanoparticles with an average diameter of 44 nm could be well dispersed in base oil, which enabled the TiO_2 to be used as additives in lubricating oil. The electrochemical measurement showed that because of the formation of passive film, the corrosion potential positively shifts, I_{corr} decreases nine times and R_p increases above ten times after applying nano-TiO_2 as additives of lubricating oil, which suggested the anticorrosive properties of oil film was improved evidently by adding 5 % TiO_2. The EIS test also confirmed that the oil-soluble TiO_2 nanoparticles had excellent corrosion resistance for metal surface.

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