Effect of Silane on the Active Aging Resistance and Anticorrosive Behaviors of Natural Lacquer

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ABSTRACT: Environmentally friendly and renewable hybrid lacquer coatings with excellent aging resistant and anticorrosion properties were studied. The coatings were prepared using raw lacquer coupled with the silane agent 3-amino-propyltriethoxysilane or N-(2-aminoethyl)-3-aminopropyltrimethoxysilane via an eco-friendly sol−gel preparation process. The physical−mechanical properties, thermal stability, aging resistance, and anticorrosion properties of the as-prepared coatings were analyzed. Additionally, the surface of the coatings before and after an accelerated aging treatment was studied by scanning electron microscopy and X-ray photoelectron spectroscopy. The results revealed that the hybrid lacquer coating A (with a raw lacquer-to-APTES mass ratio of 1.8:1) resulted in films with a significantly enhanced antiaging effect (e.g., six times higher than that of lacquer at a gloss loss rate of 30%). Besides, this film revealed an exceptional anticorrosion performance (with the lowest corrosion current $I_{\text{corr}} = 2.476 \times 10^{-10}$ A·cm$^{-2}$) and a high protection efficiency (99.99 and 94.10%), as demonstrated by its electrochemical characteristics. Furthermore, all films exhibited a good barrier because of their dense structure, which prevents the corrosive medium from penetrating the coating during the salt spray test analysis after 1000 h. And the coating A relatively layered was distributing any significant cancaves, integrity better than all coatings studied, indicating that the based electrolyte was easier to penetrate it after salt spraying 2000 h.

1. INTRODUCTION

Corrosion can seriously damage energy metal structures, which can lead to potential losses of 1/5 of the total energy produced worldwide and 4.2% of the gross national product on average.1 Thus, the development of effective corrosion inhibition technologies represents a high economic value.2 Polymer organic coatings have various advantages over their metal counterparts. Thus, polymer organic coatings are widely used in numerous industrial applications owing to their low density, easy processing, and superior anticorrosion and mechanical properties against moisture and gases under rough environments.3–6 Several methods are available today for preparing anticorrosive coatings including thermal spray coating, chemical vapor deposition, plasma spraying, electroplating, laser cladding, and sol−gel processes, among others.7,8 As is well-known, raw lacquer is a natural, biodegradable, renewable, and environmentally friendly coating product which is people-friendly, durable, and impermeable and exhibits chemical resistance to corrosive medium.9,10 Because drying raw lacquer involves an enzyme-catalyzed process, this step is slower than for common organic coatings.11 Moreover, enzymatic oxidation requires severe and specific conditions (ca. 80–90% relative humidity at 20–30 °C) for the activation of laccase. Thus, there is a growing interest in developing methods that allow rapid drying of raw lacquer under natural environments. In this sense, urushiol−metal polymers were prepared by the reaction between a metal ion and the phenyl hydroxyl groups of urushiol.12–15 The resultant urushiol−metal polymers can be rapidly dried at room temperature while showing enhanced anticorrosive properties for industrial applications.16,17 Lacquer materials hybridized with organic silanes have demonstrated rapid drying characteristics under natural environments, and
the hybridized coatings have been studied by determining the mechanism of the hybridization reaction. Additionally, basic chemical sol–gel processes have been used to prepare promising protective coatings, allowing further design and control of their compositions and properties. Therefore, sol–gel processes can be a potential alternative to prepare corrosion resistant coatings. Considering the specific properties of hybridized lacquer coatings described in the literature, sol–gel methods can be used to expand the scope of application of these materials.

Herein, an eco-friendly sol–gel method was used to conduct the reaction between lacquer and a silane coupling agent. This reaction resulted in fast-drying lacquer hybrid coatings at low cost and with higher mechanical strength and better thermal stability characteristics. Most importantly, the resultant lacquer hybrid coatings showed significantly enhanced aging and corrosion resistance properties characterized by accelerated aging, electrochemical analysis, and salt spray test analyses.

2. RESULTS AND DISCUSSION

2.1. Measurement of the Physical–Mechanical Properties. Raw lacquer is a natural product whose composition and structure depend on the variety, origin, and condition of the lacquer tree. We measured the drying times of various hybrid lacquer coatings containing suitable organic silane ratios using a drying time recorder, and the results are shown in Table 1.

Table 1. Physical and Mechanical Properties of Film Samples

| entry | organic silane | ratio (wt %) | TF (h) | HD (h) | pencil hardness | gloss |
|-------|----------------|-------------|--------|--------|----------------|-------|
| 1     | L              | <24         | <48    | 4H     | 54.4           |
| 2     | APTES          | 4:1         | <5     | 4H     | 98.6           |
| 3     | 3:1            | <1.5        | <5     | 5H     | 98.6           |
| 4     | 2:1            | <1          | <5     | 5H     | 98.6           |
| 5     | 1:1            | <35 min     | 3      | 5H     | 98.3           |
| 6     | 1:1            | <45 min     | 2      | 4H     | 82.5           |
| 7     | 1:1            | <30 min     | 2      | 6H     | 97.7           |
| 8     | AATMS          | 4:1         | <1.5   | <20    | 99.4           |
| 9     | 3:1            | <3          | <28    | 5H     | 93.6           |
| 10    | 2:1            | <45 min     | 9      | 4H     | 88.3           |
| 12    | 1:1            | <25 min     | 2.5    | 4H     | 99.9           |
| 11    | 1:1            | <40 min     | 9      | 4H     | 92.5           |
| 13    | 1:1            | <35 min     | 6      | 6H     | 98.0           |

*Ratio between raw lacquer and silane coupling agent. aDrying times were determined by the drying time recorder. TF: touch-free dry, HD: hard dry.

As shown in Table 1, the cross-link onset times of the hybridized lacquer coatings (entries 2–13) were shortened to less than half of the drying time of L (entry 1). However, when an excess of 3-aminopropyltriethoxysilane (APTES) (entries 2–7) or N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AATMS) (entries 8–13) was added, the cross-link onset time was advanced remarkably. In these cases, the touch-free (TF) and hard-dry (HD) drying times of the hybrid coatings containing high APTES (entries 6 and 7) and AATMS (entries 12 and 13) decreased. The drying time of the hybridized lacquer was shortened via enzymatic oxidation and autoxidation of the lacquer and the sol–gel reaction of silanes. Moreover, alcoholsy of the urushiol hydroxyl groups and the alkoxy group of the organic silanes took place, leading to oxidative cross-linking polymerization. Thus, the autoxidation of the urushiol unsaturated side chain to form a more complex polymer was confirmed, which promoted fast drying of the lacquer material. Because the pencil hardness and gloss properties of the coatings were excellent, all of the films can be selected for various applications. The hybridized lacquer coatings with the shortest drying times (entries 6, 7, 12, and 13) were further studied.

Among the various measurements concerning coatings, gel content plays a vital role in the characterization of relative structures, especially to those coatings that could not be soluble in any organic solvents or water. The measured values corresponded to the different samples (coatings A, B, C, D, and E) are summarized in Table 2. A gradual decrease in gel content was observed with the increase in exposure time. The main reason is that part of the conjugate and isolated double bond in urushiol long carbon chain did not participate in the polymerization at room temperature and could not completely form the interpenetrating network structure. Obviously, the effect of coating E was the worst, whereas that of A exhibited a better performance, which indicated that coating A relatively completely reacted with a greater degree of gelation.

2.2. Characterization of the Synthesized Hybridized Coatings. Fourier transform infrared (FT-IR) measurements were carried out to investigate and confirm the structures of the hybrid lacquer films and lacquer coatings, and the spectra are shown in Figure 1. The spectra of APTES and AATMS are shown in Figure 1a. The obvious absorption peaks at 1050 and 690 cm⁻¹ were associated with Si−O−C and RC−CRH cis-structure extending vibrations, respectively. In Figure 1b, the spectra of the hybrid lacquers (A, B, C, and D) showed the presence of a stretching vibration peak at 3400 cm⁻¹, which was assigned to the phenolic hydroxyl group (−OH), whereas absorption bands ascribed to −CH₂ and −CH groups were observed at 2925 and 2854 cm⁻¹, respectively. The peak at 1710 cm⁻¹ indicated that more urushiol quinones appeared. The phenolic hydroxyl group in urushiol was replaced by a Si atom, thereby reducing the strength of the absorption peak as compared to lacquer (E). However, the absorption band assigned to −CH₃ at 1460 cm⁻¹ was relatively intense. New absorption peaks at 1120 and 1050 cm⁻¹ were associated with Si−O−Si and Si−O−C extending vibrations, respectively. Moreover, the intensity of the peaks at 1060 and 690 cm⁻¹ (ascribed to trienes) and the peak of the RC−CRH cis-structure increased, suggesting that laccase polymerization took place.

2.3. Thermogravimetric Analysis of Different Coatings. The thermogravimetric (TG) analysis of the hybrid lacquer films (A, B, C, and D) and lacquer (E) is shown in Figure 2 and Table 3. The lacquer films (A, B, C, D, and E) underwent two-stage major weight-loss processes. The weight loss of the A, B, C, and D films started at 319, 327, 305, and
304 °C, respectively, whereas that of lacquer E started at 335 °C. This weight loss resulted from the degradation of the uncompleted cross-linked urushiol oligomers and other constituents such as glycoproteins and polysaccharides. The maximum temperature of the weight loss associated with the decomposition of the polymer for the hybrid films was 10 °C higher than that of raw lacquer. This weight loss was produced by the decomposition of the basic structural framework of Si–O–Si formed by the reaction of lacquer and the silane coupling agent. These Si–O–Si groups have superior chemical stability and heat resistance. In addition, as a result of the electronegativity difference between Si and C atoms, the Si–O bond is more polar than the C–O group. Thus, the Si–O bonds can effectively shield the connected hydrocarbon groups and improve the activation energy for the main chain fracture.\(^{21,22}\)

It is not easy to break the resultant chemical bond between the atoms, thereby improving the thermal stability of the hybrid lacquer films (A, B, C, and D), which showed higher char yields as compared to lacquer (E, 19.19%). In addition, the A films showed good thermal properties.

### 2.4. Aging Resistance Analysis of the Hybrid Lacquer Coatings

After accelerated aging, all coatings were not obviously damaged. On the basis of the surface gloss, films that underwent accelerated aging treatments were analyzed. Gloss was used to illustrate the surface of the film. The film surface gloss decreased with time and under the impact of external conditions.\(^{23}\) In the experiments, the films were placed in a xenon lamp aging box and the gloss of the films was reduced for a long time. The gloss loss rate was calculated using the following equation

\[
P = \frac{P_0 - P_i}{P_0}
\]

where \(P_0\) and \(P_i\) are the gloss before and after aging, respectively.

When exposed to the xenon lamp, the films underwent further cross-linking to form a more dense and smooth structure with the increasing ambient temperature. Therefore, before exposure, the gloss of the coatings declined more slowly or even increased, exhibiting lower and even negative gloss loss performance, such as for coating C. The gloss loss of coatings increased because the coatings may have holes or even cracks to form the rough surface in a relatively higher temperature when continually exposed under the xenon lamp. As shown in Figure 3 and Table 4, the gloss loss rates of the hybrid lacquer films (A, B, C, and D) were less than 40% when exposed to UV irradiation for 192, 288, and 336 h (A and C showed values...
As a whole, the A, B, C, D, and E films revealed the existence of holes. In addition, the C, D, and E films showed more significant changes as compared to the A and B films, indicating that the former were more significantly affected by the UV exposure (a gloss loss rate of 80%). As a result, the A film showed the best aging resistance (six times higher than that of the E film with a gloss loss rate of 30%) among the films tested herein.

Higher film surface UV exposure time and temperatures favored the polymerization of lacquer with APTES or AATMS to form a denser structure which provided the film with improved aging resistance. As a result, the loss rate of the films was relatively low after 240 h of UV exposure. In addition, the good chemical and heat resistance properties of those Si=O−Si and Si−O−C groups resulted in hybrid lacquer films (A, B, C, and D) with superior thermostability as compared to lacquer (E). The phenol hydroxyl (−OH) groups in lacquer favored ionization (oxidation) of H atoms and oxygen anion, with the film surface becoming rough and the gloss significantly changing as a result. Besides, upon increasing the illumination time, the Si−O−CH\textsubscript{3} groups in the structure of the A, B, C, and D films readily ionized −OCH\textsubscript{3} radicals, destroying the molecular branch structure and gradually decreasing antiaging as a result. As shown in Figure 4, the A and B films showed better aging resistances as compared to C and D. These films were not densified because of the higher stereo-hindrance effect of AATMS as compared to that of APTES.\textsuperscript{24,25} The A, B, C, D, and E films showed fracture surfaces before aging, with a, b, c, d, and e images showing diverse morphologies after artificial aging. As shown in Figure 4, before the aging treatment, the surface of the films was relatively smooth and with no cracks, whereas cracks of varying degrees were observed after the artificial aging treatment. The surface of the B and D films also revealed the existence of holes. In addition, the C, D, and E films showed deeper cracks than A and B, indicating that the former were more significantly affected by the UV exposure (a gloss rate of 80%). As a whole, the A film showed the best aging resistance (six times higher than that of the E film with a gloss loss rate of 30%) among the films tested herein.

### Table 4. Effect of Exposure Time on Different Lacquer Coatings

| T/h | GA (%) | GB (%) | GC (%) | GD (%) | GE (%) |
|-----|--------|--------|--------|--------|--------|
| 0   | 0      | 0      | 0      | 0      | 0      |
| 48  | 7.74   | 4.30   | −0.11  | 4.37   | 16.20  |
| 96  | 9.78   | 15.38  | −2.40  | 21.51  | 27.98  |
| 144 | 13.44  | 23.14  | 0.53   | 31.44  | 25.49  |
| 192 | 14.37  | 28.89  | −3.26  | 37.42  | 19.33  |
| 240 | 16.00  | 32.26  | −0.22  | 40.04  | 41.68  |
| 288 | 21.37  | 34.52  | −0.22  | 35.40  | 61.28  |
| 336 | 21.67  | 35.34  | 9.79   | 36.04  | 86.64  |
| 384 | 17.22  | 33.67  | 7.23   | 25.24  |        |
| 432 | 16.44  | 39.90  | 9.15   | 30.37  |        |
| 480 | 22.03  | 38.01  | 61.57  | 43.78  |        |
| 528 | 23.08  | 40.71  | 72.59  | 62.15  |        |
| 576 | 27.63  | 39.49  | 81.48  | 89.32  |        |
| 624 | 33.56  | 58.81  |        |        |        |
| 672 | 41.86  | 80.65  |        |        |        |
| 720 | 80.86  | 86.65  |        |        |        |

Below 21.67 and 9.79%, respectively. The loss rates of the E film were 61.28 and 86.64% after 288 and 336 h, respectively, indicating that the surface of the film may be significantly damaged or peeled off. After exposure for 576 h, the loss rates of the A, B, C, and D films reached 27.63, 39.49, 81.48, and 89.32%, respectively, with the surfaces of the C and D films being seriously damaged. After irradiating for 720 h, the loss rates of the A and B films were 80.86 and 86.65%, respectively, and the films showed no aging resistance. Hence, the data above demonstrated that the A film possessed good antiaging effects (six times higher than those of the E film) at a gloss loss rate of 30%.

### 2.5. XPS Analysis of the Hybrid Lacquer Coatings

To sufficiently understand the chemical reaction taking place on the coating surfaces during the aging process, the surface of hybrid coatings was analyzed by X-ray photoelectron spectroscopy (XPS). The C 1s, O 1s, N 1s, and Si 2p spectra of coatings A, C, and E before and after the accelerated aging treatment are shown in Figure 5, and the results are summarized in Tables S5–10. The C 1s spectra consisted of various components, which were fitted into three Gaussian–Lorentzian peaks corresponding to C−C or C−C (284 eV), C−O−C (286 eV), and O−C−O (288 eV).\textsuperscript{26−29} The N1 and O1 bands were centered at 400 and 532 eV, characteristic of C−N and Si−O−Si species, respectively.\textsuperscript{30} The C 1s, O 1s, and N 1s peaks of coating A before the accelerated aging treatment were observed at 298, 543, and 413 eV, respectively (Figure 5). The C, O, and N elemental contents of coating A before the accelerated aging treatment were 76.84, 16.90, and 0.42%, respectively (Table 5). After the accelerated aging treatments, these values were 67.99, 23.26, and 2.43%, respectively (Table 6). The oxygen-to-carbon (O/C) ratio increased from 0.262 to 0.342 after the aging treatment, indicating that the UV radiation can promote molecular chain scission and degrade the polymer. This loss of carbon may be ascribed to the migration and volatility of the oxidation products obtained via degradation of the carbonaceous compounds.

As shown in Tables 7 and 8, the C and O elemental contents of coating C before the accelerated aging treatment were 76.03 and 16.90%, respectively, whereas these values changed to 51.14 and 30.96% after the aging treatment, respectively. The
Figure 5. continued
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O/C ratio of coating C increased from 0.233 to 0.605 after the aging treatment. Compared to that of coating C, the lower O/C ratio of coating A after aging revealed good radiation damage resistance.

Tables 9 and 10 summarize the XPS spectra and elemental content data of coating E before and after accelerated aging treatment. The C, O, and N elemental contents of coating E before the accelerated aging treatment were 76.54, 15.17, and 3.89%, respectively, whereas these values changed to 40.86, 39.79, and 1.98% after aging exposure, respectively. The O/C ratio of coating C before the aging treatment was 0.198, and this value increased to 0.974 after the aging process. The O/C reduction percentages of coatings A, C, and E after the accelerated aging treatment were 0.342, 0.605, and 0.974%, respectively. Therefore, coating A showed the best antiaging resistance.

**Tables 5. Coating A before Accelerated Aging**

| element | start BE | peak BE | end BE | height | Counts | area (N) | at. (%) | O/C |
|---------|----------|---------|--------|--------|--------|----------|---------|-----|
| C 1s(1) | 298.3    | 284.6   | 279.3  | 38623.2 | 0.66   | 54.20    |         |     |
| C 2s(2) | 298.3    | 286.4   | 279.3  | 13549.5 | 0.23   | 19.15    |         |     |
| C 3s(3) | 298.3    | 288.8   | 279.3  | 3027.7  | 0.02   | 1.51     |         |     |
| O 1s    | 543.3    | 532.9   | 528.3  | 25251.8 | 0.24   | 19.60    |         |     |
| Si 2p   | 113.3    | 102.1   | 98.3   | 3422.0  | 0.06   | 5.12     |         |     |
| N 1s    | 413.3    | 400.1   | 395.3  | 4881.6  | 0.01   | 0.42     |         |     |

**Figure 5. XPS analysis of coatings A, C, and E before and after accelerated aging.**
properties among the three coatings, whereas coating E showed the poorest properties.

2.6. Corrosive Resistance Analysis of the Hybrid Lacquer Coatings. The corrosion resistance ability of bare steel coated with A, B, C, D, and E films was investigated by studying the potentiodynamic polarization curves under a 3.5 wt % NaCl aqueous solution, and the results are shown in Figure 6. The coatings showed a marked shift in both the cathodic and anodic branches of the polarization curves toward lower current densities. The corrosion-related parameters were calculated on the basis of the Tafel potential curves, and the results are shown in Table 11. The polarization resistance (R_p) values were calculated from Tafel plots, in eq 2:

$$R_p = \frac{b_a b_c}{2.303(b_a + b_c)I_{corr}}$$

(2)

where b_a and b_c are the anodic and cathodic slopes, respectively.

The corrosion rate (CR) and protection efficiency (PE) were calculated following eqs 3 and 4:

$$CR (\text{mm/year}) = \frac{I_{corr} (A/cm^2) \cdot M (g)}{D (g/cm^3) \cdot V}$$

(3)

Table 6. Coating A after Accelerated Aging

| element   | start BE | peak BE | end BE | height counts | area (N) | at. (%) | O/C |
|-----------|----------|---------|--------|---------------|----------|---------|-----|
| C 1s(1)  | 298.0    | 284.7   | 279.0  | 28379.5       | 0.53     | 47.78   |     |
| C 2s(2)  | 298.0    | 286.4   | 279.0  | 8260.3        | 0.15     | 12.98   |     |
| C 3s(3)  | 298.0    | 288.2   | 279.0  | 5034.5        | 0.08     | 7.23    | 0.342|
| O 1s     | 543.0    | 532.2   | 528.3  | 24711.0       | 0.26     | 23.26   |     |
| Si 2p    | 113.0    | 101.9   | 98.3   | 3550.6        | 0.07     | 6.32    |     |
| N 1s     | 413.0    | 400.2   | 395.0  | 6051.0        | 0.03     | 2.43    |     |

Table 7. Coating C before Accelerated Aging

| element   | start BE | peak BE | end BE | height counts | area (N) | at. (%) | O/C |
|-----------|----------|---------|--------|---------------|----------|---------|-----|
| C 1s(1)  | 298.3    | 284.5   | 279.3  | 46713.4       | 0.83     | 59.08   |     |
| C 2s(2)  | 298.3    | 286.1   | 279.3  | 11500.3       | 0.19     | 13.38   |     |
| C 3s(3)  | 298.3    | 287.2   | 279.3  | 3571.1        | 0.05     | 3.57    | 0.233|
| O 1s     | 543.3    | 532.7   | 528.3  | 25493.7       | 0.24     | 16.90   |     |
| Si 2p    | 113.3    | 101.9   | 98.3   | 3622.0        | 0.07     | 5.24    |     |
| N 1s(1)  | 413.3    | 400.1   | 395.3  | 6275.7        | 0.02     | 1.25    |     |
| N 1s(2)  | 413.3    | 402.3   | 395.3  | 5560.0        | 0.01     | 0.59    |     |

Table 8. Coating C after Accelerated Aging

| element   | start BE | peak BE | end BE | height counts | area (N) | at. (%) | O/C |
|-----------|----------|---------|--------|---------------|----------|---------|-----|
| C 1s(1)  | 298.0    | 284.6   | 279.0  | 23516.0       | 0.45     | 37.39   |     |
| C 2s(2)  | 298.0    | 286.2   | 279.0  | 6922.5        | 0.11     | 9.19    |     |
| C 3s(3)  | 298.0    | 288.2   | 279.0  | 4403.7        | 0.05     | 4.56    | 0.605|
| O 1s     | 543.3    | 532.5   | 528.3  | 33615.2       | 0.37     | 30.96   |     |
| Si 2p    | 113.3    | 102.6   | 98.3   | 6468.0        | 0.18     | 15.35   |     |
| N 1s     | 413.0    | 400.4   | 395.4  | 5393.1        | 0.03     | 2.55    |     |

Table 9. Coating E before Accelerated Aging

| element   | start BE | peak BE | end BE | height counts | area (N) | at. (%) | O/C |
|-----------|----------|---------|--------|---------------|----------|---------|-----|
| C 1s(1)  | 298.4    | 284.6   | 279.4  | 43038.1       | 0.71     | 52.87   |     |
| C 2s(2)  | 298.4    | 286.0   | 279.4  | 14107.9       | 0.30     | 22.16   |     |
| C 3s(3)  | 298.4    | 288.2   | 279.4  | 3503.6        | 0.02     | 1.51    | 0.198|
| O 1s     | 543.4    | 532.5   | 528.4  | 22441.0       | 0.20     | 15.17   |     |
| Si 2p    | 113.4    | 102.2   | 98.4   | 3092.0        | 0.06     | 4.40    |     |
| N 1s     | 413.4    | 400.2   | 395.4  | 7862.6        | 0.05     | 3.89    |     |

Table 10. Coating E after Accelerated Aging

| element   | start BE | peak BE | end BE | height counts | area (N) | at. (%) | O/C |
|-----------|----------|---------|--------|---------------|----------|---------|-----|
| C 1s(1)  | 297.9    | 284.6   | 278.9  | 17494.4       | 0.33     | 23.34   |     |
| C 2s(2)  | 297.9    | 286.2   | 278.9  | 7729.9        | 0.16     | 11.10   |     |
| C 3s(3)  | 297.9    | 288.4   | 278.9  | 5530.1        | 0.09     | 6.42    | 0.974|
| O 1s     | 542.9    | 532.5   | 527.9  | 4778.7        | 0.56     | 39.57   |     |
| Si 2p    | 112.9    | 106.2   | 97.9   | 8359.9        | 0.24     | 17.37   |     |
| N 1s     | 412.9    | 400.2   | 394.9  | 4992.9        | 0.02     | 1.33    |     |
| N 1s     | 412.9    | 402.1   | 394.9  | 4182.3        | 0.01     | 0.65    |     |
The samples were studied by different coatings on the mild steel substrate surface. The visual microcosmic observation of the coatings is shown in Figure 7 after a 1000 h exposure in a 5.0 wt % NaCl solution in the salt spray test. In addition, this test can be used as an indication of barrier properties in the hybrid matrix. Macroscopic results of anticorrosion coatings before and after the 2000 h salt spray test are shown in Figure 7 and Table 12. They did not obviously change before and after the spray test, in that the coatings show no color change, bubbles, cracks, and rust, as well as no obsession in macroscopic observation. All coatings show no obvious damage on the whole after exposure, as shown in Figure 8, and the corrosion manifest as wide relatively shallow areas, with no deep pitting of localized corrosion. The dense surface of samples A and B was microscopic, integrity better than C, D, and E films. The films were showing the corrosion products, and distribution of numerous pores and pits, bad overall, especially E film. That is the presence of pores and pits based electrolyte is easier to penetrate the corrosive medium of the coatings, accelerating corrosion. In contrast to the entire process, the coating microstructure E determines more rapid corrosion than A, B, C, and D coatings because it loses its electrochemical protection in a relatively weak somewhere, such as pores and pits. Sectional surface of sample E became larger than those of other films after 1000 h of corrosion immersion period. This is attributed to the inner corrosion and/or corrosion product wedging, a process that might be similar to the exfoliation corrosion of metal steel. After spraying for 2000 h, the coatings fell off with different degrees of damage. coatings D and E formed holes which seemed a bit deep. Particularly, the damaged area of coating E was relatively large during complete exposure to the salt spray environment. After the shielding effect of protective coatings during increasing exposure time, the metal steel matrix is completely exposed to the corrosive atmosphere.41 Thus, the apparent resistance to the corrosion of coating A exhibited excellent barrier to the corrosive atmosphere.

### 3. CONCLUSIONS

In this work, renewable hybrid lacquer coatings were prepared. These coatings showed good aging resistance and anticorrosion properties. These coatings were prepared by an eco-friendly process, and no volatile organic compounds were employed, reducing the material costs. The hybrid lacquer coatings with a raw lacquer-to-APTES mass ratio of 1.8:1 showed significantly enhanced antiaging characteristics (six times than that of regular lacquer with a gloss loss rate of 30%). This coating showed the lowest $I_{\text{corr}}$ value ($2.476 \times 10^{-10}$ A/cm²) and highest PE (99.99 and 94.10%), and no obvious damage was observed in the salt spray test when compared to all films.

### Table 11. Corrosion Parameters Determined from Tafel Curves for Bare Metal and Films

| sample | $E_{0}$/V | $I_{0}/(\text{A-cm}^{-2})$ | $R_p$ (Ω) | CR (mm/year) | PE/% |
|--------|-----------|----------------|-----------|-------------|------|
| bare metal (F) | $-0.3013$ | $8.310 \times 10^{-6}$ | $1.456 \times 10^3$ | $8.726 \times 10^{-2}$ | $0^a$ |
| L (E) | $-0.4430$ | $4.200 \times 10^{-9}$ | $7.975 \times 10^{-7}$ | $4.411 \times 10^{-3}$ | $99.94$ |
| A | $-0.5852$ | $2.476 \times 10^{-10}$ | $2.328 \times 10^6$ | $2.650 \times 10^{-4}$ | $99.99$ |
| B | $-0.5769$ | $2.796 \times 10^{-10}$ | $3.106 \times 10^6$ | $2.936 \times 10^{-4}$ | $99.99$ |
| C | $-0.2828$ | $1.257 \times 10^{-9}$ | $3.454 \times 10^8$ | $1.320 \times 10^{-3}$ | $99.98$ |
| D | $-0.2919$ | $1.438 \times 10^{-9}$ | $2.500 \times 10^8$ | $1.510 \times 10^{-3}$ | $99.98$ |

$^a$0—based on this sample; _—excluding this sample.
studied, significantly protecting the metal from the corrosive medium and avoiding penetration issues through surface cracks or pores and pits after 2000 h. Therefore, the hybrid lacquer coatings represent an environmentally friendly coating technology with promising applications in the aging resistance and corrosion protection industries.

4. EXPERIMENTAL SECTION

4.1. Materials. Raw lacquer (L) was collected from the Hubei Province. APTES and AATMS were purchased from Aladdin Industrial Corporation. A cardanol phenolic resin diluent was purchased from the Biological Materials Technology Co. Ltd (Jiangsu, China). Crystalline NaCl (99.2%) was used to prepare a 3.5 wt % NaCl aqueous solution. All chemicals were used as received.

4.2. Preparation of the Hybridized Corrosion Coatings. Raw lacquer (25 g) was stirred in an open glass container at 25−40 °C for 2−4 h until the water concentration decreased to 3−5%.\(^a\) The hybrid coatings were subsequently prepared by adding APTES or AATMS to the raw lacquer at different raw lacquer-to-APTES or raw lacquer-to-AATMS mass ratios (i.e.,

| degree          | A | B | C | D | E |
|-----------------|---|---|---|---|---|
| color           | + | + | + | + | + |
| pulverization   | + | + | + | + | + |
| crack           | + | + | + | + | + |
| blistering      | + | + | + | + | + |
| rust            | + | + | + | + | + |
| obscession      | + | + | + | + | + |

\(^a\)“+” indicates no change in degree.

Figure 7. Macroscopic results of anticorrosion coatings before (a) and after (b) the 2000 h salt spray test.

Figure 8. Results of anticorrosion coatings after the 1000 (a) and 2000 h (b) salt spray test.
4:1, 3:1, 2:1, 1.8:1, 3:2, and 1.3:1). A 20 wt % cardanol phenolic resin diluent was subsequently added to the above mixture. After stirring at room temperature for 0.5 h, the mixture was coated on the surface of dry tinplate and copper pieces previously treated with sandpaper and cleaned with ethanol. The specimens were dried at room temperature. A silane coupling agent-free lacquer coating (denoted as L) was prepared under similar conditions for comparison. In addition, the hybrid coatings of lacquer to APTES or AATMS in different mass ratios (1.8:1 and 1:3:1) formed the films, including L/APTES = 1.8:1, L/AATMS = 1:3:1, L/AATMS = 1.8:1, and L/AATMS = 1:3:1, which are designated as coatings A, B, C, and D, respectively.

4.3. Characterization Experiments. Drying properties of hybrid lacquer coatings were evaluated by a drying time recorder (TaiYu Equipment Co. Ltd., Japan), according to the Chinese standards GB/T1728-1979 and GB/T6739-2006. The gel content method was performed using the following procedure. Gel content is expressed as

\[
\text{Gel content} = \frac{m_f}{m_0} \times 100\%
\]

where \(m_0\) is the initial weight of the film and \(m_f\) is the final weight after extraction with xylene.

FT-IR spectroscopy measurements (KBr) were conducted on an American Nicolet 5700 FT-IR spectrometer. TG and derivative TG analyses were carried out on a DSC822e-type TG analyzer (Mettler-Toledo) at a rate of 10 °C/min within a temperature range from 30–600 °C under a nitrogen atmosphere. Following the Chinese standard GB/T 1865-1997, the aging resistance of all films was tested on an LXD-080 xenon lamp aging box (Shanghai Huitai Instrument Manufacturing Co. Ltd.), with wavelengths ranging from 290 to 800 nm and with an irradiance of 0.51 W/m². The spraying rainfall cycle lasted 24 min and was repeated in intervals of 120 min, with a residual pressure of 10⁻⁸ mbar. An Al Kα monochromatized radiation (photon energy = 1486.6 eV) was employed as the X-ray source. The corrosion resistance of the coatings was investigated via electrochemical measurements on a CHI660E electrochemical workstation with a 3.5 wt % NaCl standard aqueous solution and with a platinum auxiliary electrode and a Pt working electrode. EIS measurements were performed in a salt-spray testing chamber (FQY015 Cyclic Corrosion Tester) with a 5.0 wt % aqueous solution of 0.51 W/m².

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