



## AGING OF WATERBORNE PAINT BASED ON ACRYLIC RESIN EMULSION AND ORGANIC PIGMENT

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### ABSTRACT

Aging of waterborne paint on the base of acrylic resin emulsion with and without green Luconyl has been investigated by general appearance assessment, adhesion change, FT-IR and discoloration. The obtained results showed that both of paint-formula coatings had no cracks, blisters, flacks and there was no change of adhesion during the aging process. However, IR analysis indicated that there were some changes in chemical structures of coating with and without Green Luconyl during aging process. To be more specific, IR spectrums of initial and aged coating no containing Green Luconyl illustrated aging process led content of O-H and C=C increased significantly but the baseline of spectra was fairly unchanged. For the Green Luconyl-filled coating, the baseline of initial coating's IR spectra exhibited a reduction than that of aged coating while both of coatings (before and after aging) exhibited spectra of similar shape. Moreover, SEM images indicated that the surface morphology of samples changed differently depending on the presence of organic pigment. The surface of aged coating without Luconyl looked rougher than the one with Luconyl after aging process. Hence, the weather aging test had a more significant influence on paint coatings in absence of Luconyl than paint coating in presence of Luconyl. It was explained that the macroradical produced in aging process would attack conjugated double bonds of Luconyl instead of double bonds of AC-261 causing the aged Luconyl coating to become more opaque than initial while coating unfilled Luconyl had significant changes in its chemical structure during the aging process. Although this was a hypothesis, it was suitable with the obtained results. The paint coating with Luconyl illustrated a significant color change, especially, showed the loss of green color while the other paint coating showed slight color change.

*Keywords:* acrylic emulsion, organic pigment, TiO<sub>2</sub>, water based paint, architectural paint.

### 1. INTRODUCTION

Architectural paints have been used as the protective and decorative materials with purpose increasing beauty and being suitable customers' tendency. In the past, architectural paints were mainly solvent-based paints, which contained high level of organic solvents. These solvents were responsible for the strong odor noticeable in buildings that have been freshly painted. They

were also potentially hazardous for both human health and environment which was why concerted efforts are being made to reduce or remove their presence in paints without negatively impacting on paint performance. With the rising environmental awareness, many countries around the world applied law to restrict solvent based binder in architectural paints. As a result, water-based paints become more popular in the architectural paints. According to American Paint Quality Institute, water-based paints make up about 80 percent of household paints sold today. The water-based paints usually include: water-based binders (acrylic binder account a high proportion), rutile TiO<sub>2</sub>, additives and some pigments in the paste form.

For the outdoor applications, polymers will be degradable by weather factors such as UV radiation, humidity, oxygen, temperature change etc. As a result, the paint coatings will be blistering, chalking, losing the adhesion [1-7]. Therefore, research on evaluating weathering resistance of architectural paints are really necessary. In fact, natural testing is used to assess weathering resistance with highly trustful results. However, this method requires a long time period. Although accelerated weathering test simulates just several factors of weather affecting paint coatings, this method can be used to predict the lifespan of coating in certain conditions. Thus, the accelerated weathering test combining with natural test determines rule, degradation mechanism of polymer materials and predicts their lifetime [8, 9].

Published paper indicated that the degradation of polymer material in general and acrylic polymer in particular, due to the UV light. J. Hu and his co-workers studied the ageing behavior of acrylic polyurethane varnish coating in accelerated weathering environments namely a fluorescent UV/condensation weathering device and a xenon lamp exposure and weathering equipment for different time periods. The results illustrated degradation rate in the UV condition is about 1.3 times greater in the Xenon test conditions [10]. The degradation mechanism of polymer material could be explained that under effect of UV rays and humidity, photo-oxidative reactions occurs and macroradical disproportionation will be created leading to hydrolysis, chain scissions, etc. However, some researches showed that when paint coatings were applied natural environment test containing polluted factors which contained large amount of dust, the degradation process of polymer material slowly occurred due to a layer of dust on the samples surfaces would shield UV radiations [11].

M.M. Di Crescenzo and his colleagues reported on the photochemical degradation of 15 artist-grade formulations, including three binders (poly(n-butyl acrylate-co-methyl methacrylate), poly(vinyl acetate-co-vinyl versatate), poly(n-butyl methacrylate-co-styrene-co-2-ethylhexyl acrylate)) and five pigments (titanium white, artificial ultramarine blue, mars yellow, quinacridone red, phthalocyanine green) which have been widely used in the creation of outdoor contemporary murals. Obtained results showed that acrylic and styrene-acrylic samples being more stable than the vinyl ones. Influence of pigments and extenders on the stability of polymers was also evaluated and it was observed that, regardless of binder typology, samples containing artificial ultramarine blue underwent the most evident degradation [12].

The research group at Institute for Tropical Technology, Vietnam Academy of Science and Technology also published some studies on the weathering durability of some kind of acrylic containing UV stabilizers underwent accelerated weathering test [2, 3, 7, 13-15]. We also reported that the degradation of Acrylic emulsion AC-261 underwent the UV/consideration testing by IR, UV-Vis, weight loss, etc. [7, 13]. Results showed that the content of C-H and C-O groups reduced while the content of O-H, C=O acid and C=C (alkene), which were photo-oxidation reaction products, increased during the accelerated weathering test. The degradation of AC-261 coating led to an increase in the coating surface roughness. This result was expected because oxidation and hydrolysis processes are leading to low molecular weight compounds which may be easily removed by the hot water treatment, thus generating micro-cavities and

micro-holes at the surface. After 1152 hours testing, the samples weight was 82% in comparison with initial.

Primal Acrylic Emulsion AC-261 has been widely used for water-based paints fabrication. Degradation of coating based on AC-261 with and without nano TiO<sub>2</sub> was published [7, 13, 15]. However, due to costumers' demand on beauty, paint formula on the base of AC-261 needs to be added with some pigments. Hence, weather durability evaluation of AC-261 with some pigment coating is highly necessary. In this work, we present the results obtained by research on aging AC-261 by UV/consideration equipment through IR analysis, and characterizations of surface morphology, of adhesion as well as weight loss.

## 2. MATERIALS AND METHODS

### 2.1. Materials

- *Binder*: PRIMAL™AC-261, acrylic emulsions having; a solid content of 50 wt%, 1.06 g/mL of density, pH at 9.5, Brookfield viscosity < 300 cps, was supplied by Dow Chemical company (USA).

- *Pigments*:

+ TiO<sub>2</sub> in the rutile form R706, was purchased from DuPont.

+ Luconyl® NG 8730, obtained from BASF (Swiss), was organic pigment having 1.2 g/mL of density, 48 % wt. of solid content, C<sub>32</sub>H<sub>16</sub>CuN<sub>8</sub> of formula.

- *Additives*:

+ Film-forming agent: Texanol (2, 2, 4-trimethyl-1, 3-pentanediol monoisobutyrate) was supplied by Sigma (Germany).

+ pH adjustment agent: AMP95 was obtained from Merk(Germany).

+ Dry retardant agent: Propylene glycol– PG (E1520) was ordered from Dow chemical (USA).

+ Thickening agent: Arysol 2020 was purchased from Dow chemical (USA);

+ Surfactant agent: Strodex TH100 (surfactant 3 in 1);

+ Anti-foaming agent: Foamaster A12;

+ Antifungal Agent: HBRR 250 was supplied by Dow chemical (USA);

+ Preservative agent: Rocima 623 was provided by Rohm & Haas (Germany).

### 2.2. Paint formula preparation

In this work, two paint formulas were prepared which referred as M0 for paint containing no Green Luconyl and M1 for paint filled with organic pigment. The paint formulas were fabricated with constituents as in Table 1.

Paint system preparation: the paint system preparation was conducted via two steps in 120 minutes. Firstly, the AC-261 and R-TiO<sub>2</sub> were added into the paint mill which was followed by adding the additives and some water. The mixture was stirred at high speed (1000-1200 rpm) during 30 minutes. After that, the mixture was grinded with grinding paintball for 60 minutes. In

the next step, thickener (Arysol 2020) and organic pigment were added into the mixture and then the mixture was stirred at high speed for 30 minutes. In this step, water was added to adjust the mixture viscosity.

*Table 1. Constituents of paint system.*

<i>No</i>	<i>Chemicals</i>	<i>M0</i>	<i>M1</i>
		<i>Weight (g)</i>	<i>Weight (g)</i>
1	Latex AC 261	318	318
2	Texanol	10	10
3	Deionized water	32	32
4	R-TiO <sub>2</sub> , R 706	159	159
5	602-N (Dow)	2	2
6	Strodex TH100 (surfactant 3 in 1)	3	3
7	Triton X405, 70 % (Dow)	2.2	2.2
8	Foamaster A12:	1.6	1.6
9	Propylene glycol 99,5 % (Sigma)	3.2	3.2
10	HBRR 250 (Dow)	3.2	3.2
11	AMP 95, 95 % (Sigma)	2.6	2.6
12	Rocima 623 (Rohm & Haas)	3.2	3.2
13	Luconyl® NG (BASF) (if the paint system containing green color)	0	10
<b>Total</b>		540	550

### **2.3. Sample preparation**

#### *2.3.1. Substrate preparation*

- The mortar sheets were fabricated from cement Portland PC 30 provided by Hoang Thach Cement Company and river sand with size < 2 mm and reached 100 mark, having size 150 × 75 × 10 mm, according to the TCVN 8653-1:2012.

- The glass sheets substrates: having 70 mm × 100 mm × 3 mm of diameter, were cleaned with acetone and washed again with water. Finally, they were dried in a heating oven.

- Fibro-cement sheets having size of 70 mm × 150 mm × 3 mm, were washed with deionized water and then dried in an oven.

#### *2.3.2. Sample preparation*

The paint coatings on the substrates, as mentioned above, were applied by using a sprayer (6 kg/cm<sup>2</sup> of pressure). The volume of paint on each substrate was calculated using formula:

$$V_L = \frac{d_{\mu m} \times S_{(m^2)}}{10 \times X_{(\%)}}$$

V: the volume of paint (L); d: the dry paint coating ( $\mu\text{m}$ ); S: the square of paint coating ( $\text{m}^2$ ); X: the solid content (%).

Samples for IR analysis were prepared on glass substrates with 15  $\mu\text{m}$  of dried thickness. After stabilizing at temperature of  $25 \pm 2$  °C and humidity of  $50 \pm 5$  % during 7 days, the paint coatings were removed from glass substrate and attached on aluminum window and then conducted the tests.

Samples for weight loss, morphology and color measurements were fabricated on glass substrates with 150  $\mu\text{m}$  of dried thickness and then conditioned at temperature of  $25 \pm 2$  °C and humidity of  $50 \pm 5$  % during 7 days before tests.

Samples for evaluation of coatings degradation, i.e. cracking, blistering, flacking and chalking, were prepared on Fibro-cement sheets with 150  $\mu\text{m}$  of dried thickness and then conditioned at temperature of  $25 \pm 2$  °C and humidity of  $50 \pm 5$  % during 7 days before doing the tests.

## 2.4. Accelerated weathering test

Accelerated weathering tests were performed in a UV/condensation weathering chamber Atlas UVCON UC - 327 - 2 (USA) equipped with UVB-313 fluorescent lamps and operated under wet-cycle conditions of 8 hrs UV irradiation at 60 °C following by 4 hrs of dark water condensation (CON) at 50 °C (1 cycle consists 8 hrs UV and 4 hrs CON) according to the standard ASTM G154 [18]. The samples before and after testing were dried in vacuum oven at 50 °C for 24 hours before the analysis.

## 2.5. Analysis

### 2.5.1. Morphology

The morphology of sample surfaces before and after the accelerated weathering test were determined by SEM images, which were recorded by SEM Model SM 6510LV (Jeol – Japan) at Institute for Tropical Technology, Vietnam Academy of Science and Technology.

### 2.5.2. IR analysis

The chemical changes occurring upon the UV-B/condensation accelerated aging in exposed coatings were analyzed by FTIR spectrometer NEXUS 670 from Nicolet (detector DTGS - KBr, resolution of  $8 \text{ cm}^{-1}$ ) at the Institute for Tropical Technology.

### 2.5.3. Determination of cracking, blistering, flacking and chalking

Cracking, blistering and flacking were determined in accordance with BS EN ISO 4628-4:2003, BS EN ISO 4628-2: 2003 and BS EN ISO 4628-5: 2003, respectively. The results were evaluated according to the level shown in the illustration in the standards: 0 meaning no defects and 1, 2, 3, 4, 5 meaning towards increasing the quantity and size of defects.

Chalking was determined by the Kempf Chalking Rate Tester (Model 241 - Erichsen) device in accordance with BS EN ISO 4628-6: 2003 at the Institute for Tropical Technology. The chalking rate was classified from the degree 0 (the best) to the degree 5 (the worst).

#### 2.5.4. Adhesion

The adhesion of paint coatings and mortar sheets was determined according to the standard TCVN 2097-1993.

#### 2.5.5. Color measurement

Color measurements on the surfaces of samples were carried out according to ASTM D2244. A Color-Tec PCM+ measures the color in L\*; a\*; b\* coordinates at three locations on each sample using the Commission Internationale' Eclairage (CIELAB 1976 color space) three-dimension color space system. In this system, L\*axis (+L\* for light, - L\* for dark) represents the lightness, a\*(+ a\* is for red, - a\* for green), and b\*(+ b\* for yellow, and - b\* for blue) the chromaticity coordinates. At least four replicates were measured for each formulation to obtain the average values of color. Calculations incorporated the values of lightness and chromaticity coordinates before and after weathering tests to determine the discoloration ( $\Delta E^*$ ) of the weathering exposed samples by using the following equation:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

with  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  as the difference of initial and final values of L\*, a\*, and b\*.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. General appearance assessment

General appearance assessment can provide the initial results of polymer degradation upon the accelerated weathering test. After 800-hour aging, the samples' surfaces were assessed about general appearances using a magnifier having 10 times magnification. Some characteristics of paint coatings after aging were displayed on Table 2. The obtained results showed that there was no difference in the appearance. No crack or blister of the paint coatings were observed (Table 2). Only the samples without Luconyl presented a slight chalking at 1 degree.

*Table 2.* General appearance assessment.

No	Characterizations	M0 (no Green Luconyl)	M1 (containing Luconyl)
1	Cracking (degree)	0	0
2	Blistering (degree)	0	0
3	Flacking (degree)	0	0
4	Chalking (degree)	1	0

The results of adhesion test indicated that there was no difference between the initial and 800-hour aged samples in both of the two paint systems. The adhesion of all samples gained the

2 degree. It may be explained that AC-261 is one of resin having high weathering durability. In addition, coating formula contained R-TiO<sub>2</sub> – as enhancing weathering resistance. Consequently, coating based on AC-261 resin and R-TiO<sub>2</sub> can resist environment factors and thus increasing lifetime of coating [6, 7, 13-15]. On the other side, adhesion is determined by breakpoint of interface between mortar substrate and paint coating being the deepest layer which is, more or less, degraded by accelerated weathering test. Hence, there was similar adhesion of coating with and without Luconyl.

### 3.2. Chemical changes of functional groups during the accelerated weathering test

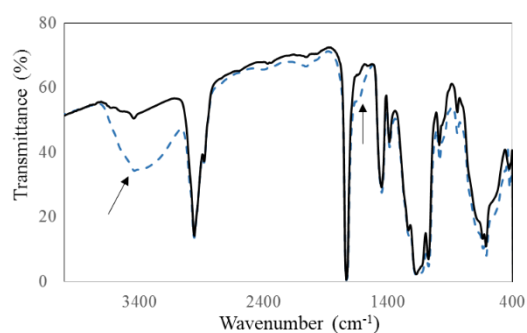


Figure 1. IR spectra of AC-261/TiO<sub>2</sub> before (—) and after 800-hour aging (---).

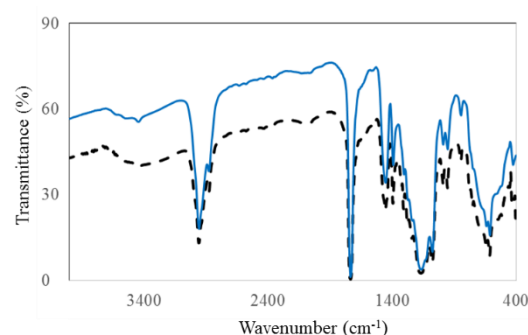


Figure 2. IR spectra of AC-261/TiO<sub>2</sub>/Luconyl before (—) and after 800-hour aging (---).

In aging process of materials, the degradation of material, initially, may not be observed obviously in the appearance of samples but can be detected by chemical changes of functional groups. The chemical changes of functional groups are usually monitored by IR spectroscopy. IR spectra of paint coatings before and after aging process are displayed in Figure 1 and 2.

As can be seen, IR spectra of AC-261/TiO<sub>2</sub> before aging included some characteristic bands: vibration at 3440 cm<sup>-1</sup> corresponds to the O-H group stretching. However, this vibration was small and low intensity. It might be the O-H group of humidity which was contained in the coating. Moreover, alkane C-H, carbonyl group C=O stretching were located at 2946 and 1730 cm<sup>-1</sup>, respectively. Comparing with IR spectra of AC-261/TiO<sub>2</sub>, the IR spectra of AC-261/TiO<sub>2</sub>/Luconyl showed a little difference. It was explained that the characteristic bands of Luconyl might be covered by the characteristic bands of AC-261.

As can be seen from Figure 2, there was a little difference between before- and after-aging sample. However, the peak located at 3440 cm<sup>-1</sup> saw higher intensity, larger square which meant a significant amount of O-H groups produced resulting in appearance of a small shoulder peak at 1640 cm<sup>-1</sup>. It was explained that TiO<sub>2</sub> played a role of a UV-absorber as well as a photocatalyst. During the degradation of polymer, photo-oxidation reactions created O-H and COOH groups [7, 13]. Moreover, the photo-degradation of polymer might be due to chain scissions and macroradical disproportionation, resulting in terminal double bonds [12]. However, the paint coatings in presence of Luconyl spectra showed there was no difference between before and after aging.

It might be explained that macroradical disproportionation can be created due to the TiO<sub>2</sub> acting as a photo-catalyst that undergoes UV rays. This macroradical disproportionation would attack polymer chains to produce O-H and C=C groups. However, for the paint system

containing Luconyl, the macroradicals would attack the conjugated double bonds of Luconyl. Consequently, the paint coatings become more opaque and discolored leading to reduce baseline of 800-hour aging IR spectra. In other words, the organic pigment can act as an UV-absorber. It absorbed UV rays and thus reducing the polymer degradation. Notwithstanding, these were hypothesized and thus needing further studies to investigate.

### 3.3. Morphology of samples' surfaces

SEM images of paint coatings' surfaces initial and 800-hour aging were showed on Fig. 3.

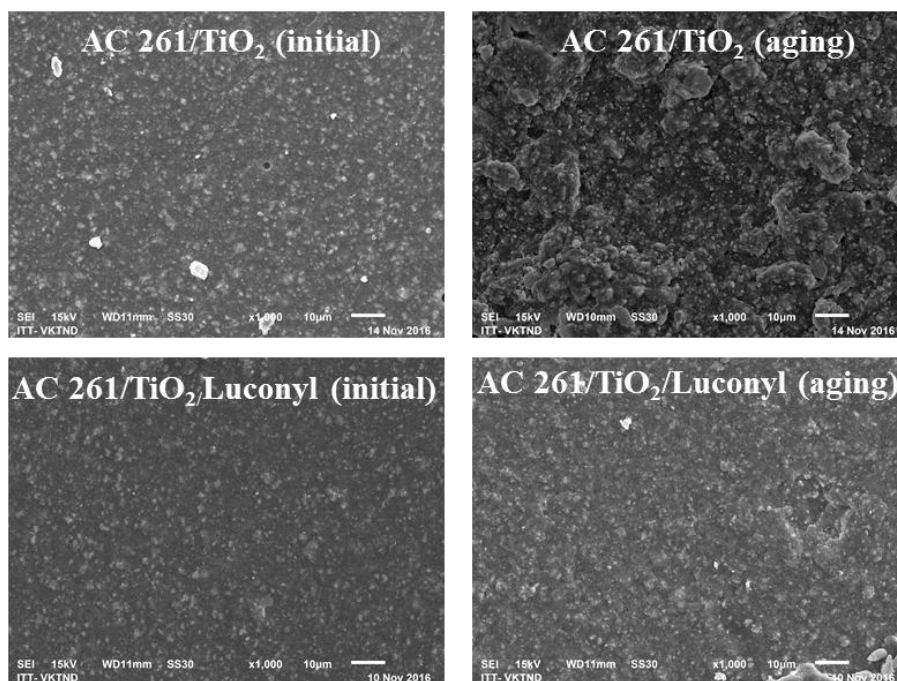


Figure 3. SEM images of paint coatings' surfaces of initial and 800-hour aging samples.

As can be seen from the Fig. 3, no cracks, blisters or changes in the hiding properties of the paints were observed in the other samples. In comparison with initial paint coating in absence of Luconyl, the 800-hour aging sample surface was rougher and the pin-holes appeared. This result was expected because oxidation and hydrolysis processes were supposed to lead to low molecular weight compounds which may easily be removed by hot water treatment, thus generating micro-cavities and micro-holes at the surface as we reported elsewhere [13]. Surface of aged coating seemed to be rougher than surface of initial coating with both of coating formula with and without Luconyl. In comparison with aged neat coating surface, surface of aged Luconyl coating was smoother. This result seemed to be suitable with the hypothesis, as mentioned above.

### 3.4. Color measurement

Color measurement showed a photodegradation degree of materials during artificial weather testing. Assessment of discolorations of samples upon the aging by UV/consideration indicated parameters  $L^*$ ,  $a^*$ ,  $b^*$  and calculated to  $\Delta E^*$ . For the color changes were either



insignificant ( $\Delta E^* \leq 3$ ) or small ( $3 < \Delta E^* \leq 5$ ), the color changes could not be recognized by eyes. These changes can be just determined by equipment [12]. The  $L^*$ ,  $a^*$ ,  $b^*$  and  $\Delta E$  change of coatings during the weather testing were shown on Table 3.

As can be seen from Table 3, the sample in absence of Luconyl is seen with a less color variations in comparison to the other sample. For the sample in the absence of Luconyl, all of parameters  $L^*$ ,  $a^*$ ,  $b^*$  showed a slight change. The  $b^*$  value experienced the largest change, increased from 6.39 to 7.33 (approximately 16 %). As a result, the  $\Delta E^*$  value was small, level off 3.75 for 800-hour aging sample. In the contrast,  $\Delta E^*$  of sample containing Luconyl showed the high value, at 6.69 for 800-hour aging sample. For the sample containing Luconyl, the  $L^*$  and  $b^*$  showed slight change while the  $a^*$  experienced the largest change. The fact that  $b^*$  value slowed down meant the color of Luconyl loss in the aging process. This seemed suitable with the hypothesis as mentioned above.

Table 3. Color variations of paint samples upon aging times.

Aging time (hours)	Parameters			
	$L^*$	$a^*$	$b^*$	$\Delta E^*$
Sample without Luconyl				
0	94.90	1.00	6.39	0.00
200	94.07	1.75	7.69	1.72
400	93.58	1.43	7.34	1.68
600	92.63	1.25	7.71	2.64
800	91.27	1.20	7.33	3.75
Sample with Luconyl				
0	43.52	-38.84	2.09	0.00
200	43.60	-36.64	1.50	2.29
400	44.12	-33.89	1.24	5.06
600	44.90	-32.72	1.03	6.36
800	43.03	-32.19	1.64	6.69

In the aging process, the surface of sample can be rougher and thus scattering light [12]. As a result, parameters indicated a slight change.

#### 4. CONCLUSION

The aim of this study was to compare the stability of different waterborne paints based on the acrylic emulsion,  $TiO_2$ , additives and either in absence of Luconyl or in presence of Luconyl. After 800-hour aging, both of the paint systems showed that there was no significant change in general appearance. The adhesion was stable after aging. However, the results from IR analysis, SEM images as well as discoloration indicated that Luconyl, up to a point, helps paint coating become more stable. The macroradical produced in the aging process may attack the conjugated double bonds of Luconyl instead of double bonds of AC-261, consequently, the polymer

material would be more stable and the color showed the significant change. Color measurement also showed the change of coating with Luconyl was substantial. The color measurement showed that the green color of this coating had significant change. This result might due to the organic pigment absorbs UV light and thus reducing the polymer degradation.

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