# Preparation and Performance Optimization of Two-Component Waterborne Polyurethane Locomotive Coating 

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#### Abstract

This paper reports the effects of different formulas on the performance of waterborne polyurethane (WPU), including two-component WPU and curing agent, wetting dispersant, defoaming agent, and wetting agent. The optimization of rheological additives selection, through the optimization of coating physical properties and chemical properties, can make the film show uniform color and appearance without pinholes, bubbles, or wrinkles, and have a long probation period. Through the analysis of performance after a 1000-h quick ultraviolet (QUV) aging test, the light reduction rate is $23.19 \%$, and the color difference is 1.9 . As can be seen from the scanning electron microscope (SEM) image and the three-dimensional stereomicroscope, the film shows relatively uniform dispersion, good compactness, and smooth surface. The two-component WPU topcoat is found to have high gloss $87.1\left(60^{\circ}\right)$ and high weather resistance, which provides a positive indication for the modulation and production of waterborne locomotive paint.


Keywords: two-component; waterborne polyurethane paint; locomotive topcoat

## 1. Introduction

Waterborne polyurethane (WPU) is environmentally friendly comparing to traditional solvent coatings, which contains low volatile organic compounds (VOC) and harmful air pollutants (HAPs) [1-3]. WPU reduces the risk of explosion and poisoning during the coating production process, and increases human health and safety [4]. Nowadays, environmental protection requirements on coatings are becoming more and more strict. Coatings are required to produce less pollution and consume less power [5]. As a water-based locomotive topcoat, WPU shows excellent mechanical properties, good compatibility, good moldability, and easy modification to meet the performance and application requirements [6,7]. WPU can be widely used in coatings, adhesives, wood processing, automotive manufacturing, medicine, and other fields [8-10]. In recent years, WPU modification and long-term reliability evaluation have attracted much attention. The reliability tests include QUV aging test, salt spray resistance test, temperature cycling test, damp heat test, accelerated weathering test, etc. [11-14]. Aznaret al. [15] used $50 \%$ WPU and acrylic compound formula to achieve 70 gloss. After accelerated aging test, the relative gloss change amount was lower than that of solvent-based acrylic and polyurethane paint. Gao et al. [16] analyzed the effects of sunlight, humidity, temperature,
and wind speed on aging performance in theoretical simulation experiments. The effects of sunlight radiation and temperature were 0.492 , and the effect of humidity was 0.474 , respectively. After ultraviolet irradiation, Zhu et al. [17] analyzed the infrared spectrum of polyurethane composite coatings and concluded that the failure mechanism was caused by the conversion of acetamide to primary amides, and the $\mathrm{C}-\mathrm{N}$ bond was easily broken. Boubakriet al. [18] pointed out that the cross-linking density of thermoplastic polyurethane gradually increased, and there was competition between the chain fracture and cross-linking mechanism. Xia et al. [19] prepared a polyurethane coating by applying ultraviolet light curing, added fluoro-acrylic monomer and mercaptan, and achieved a luster of $86.9 \pm 0.9$, which improved the hydrophobicity, mechanical properties, and yellowing properties of the coating. Haase et al. [20] found that the water-based coating turned yellow at 3024 h with fewer defects after plasma modified coating, while the solvent-based coating began to show defects at 1008 h after accelerated weathering.

However, water as a solvent shows several disadvantages, including poor dispersion ability, high surface tension, foaming, poor light and color retention, poor weather resistance, unstable performance of large areas of coating, easy to flow hanging, and other defects [21]. In order to obtain a reliable and stable coating, we refer to the tests performed by relevant experts and compare the tests with different formulas, focusing on the comparison of QUV aging reliability properties. For WPU modification, the appearance of the painting film on a large area of the locomotive, the mechanical properties, the trial period, and storage stability during the construction are comprehensively analyzed [22]. The comparison and analysis of a 1000-h QUV aging test show that the topcoat has a high gloss, and the gloss and color difference change little, which solves the problem of poor weather resistance of WPU [23,24]. These properties are closely related to chemical structure and microscopic morphology [25]. Finally, the optimized formulation of WPU to pcoat with high gloss and weather resistance is obtained. WPU has become one of the most important candidates in the development of rail transit locomotive coatings. It has been recognized and developed all over the world, and its industrial products have formed a large market scale at a very high speed.

## 2. Experimental Section

### 2.1. Materials

The formulations of raw materials are shown in Table 1.
Table 1. Raw material varieties, additions, and specifications.

| Number |  | Component | wt.\% |
| :---: | :---: | :---: | :---: |
| Part A | 1 | Deionized water, A.S. Watson Group Ltd., Hong Kong | 15-17 |
|  | 2 | Wetting and dispersing agent D1 Disper BYK-190, high molecular block copolymer of pigment affinity group, $40 \mathrm{wt} . \%$, acid index: 10 mg $\mathrm{KOH} / \mathrm{g}$, solvent: water, BYK Additives \& Instruments, Wesel, Germany Wetting and dispersing agent D2 BYK-P104S, polysiloxane copolymer, $50 \mathrm{wt} . \%$, acid index: $150 \mathrm{mg} \mathrm{KOH} / \mathrm{g}$, solvent: xylene/di-isobutyl ketone, 1:1, BYK Additives \& Instruments, Wesel, Germany | 0.5-2 |
|  | 3 | Defoamer F1 TEGO Airex 902W, organic polyetherester, $99 \mathrm{wt}$. . , TEGO, Berlin, Germany | 0.05-0.1 |
|  |  | Defoamer F2 BYK-028, mixture of hydrophobic solids and polysiloxane in polyglycol, $98 \mathrm{wt} . \%$, BYK Additives \& Instruments, Wesel, Germany | 0.1-0.2 |
|  | 4 | DuPont-R706 Rutile, Titanium Dioxide, DuPont, Midland, MI, USA | 22-24 |
|  | 5 | Hydroxy acrylate aqueous dispersion A1 Bayhydrol ${ }^{\circledR}$ 2470, $45 \mathrm{wt} . \%$, acid index: $10 \mathrm{mg} \mathrm{KOH} / \mathrm{g}$, solvent: water, Covestro Polymers Company Ltd., Leverkusen, Germany <br> Hydroxy acrylate aqueous dispersion A2 Bayhydrol ${ }^{\circledR}$ 2646, 50 wt. $\%$, acid index: $10 \mathrm{mg} \mathrm{KOH} / \mathrm{g}$, solvent: water, Covestro Polymers Company Ltd., Leverkusen, Germany | 54-55 |

Table 1. Cont.

| Number |  | Component | wt.\% |
| :---: | :---: | :---: | :---: |
|  | 6 | Wetting leveling agent L1 BYK-378, polyether modified dimethylpolysiloxane, 100 wt. \%, BYK Additives \& Instruments, Wesel, Germany <br> Wetting leveling agent L2 BYK-349, polyether modified siloxane, 100 wt. \%, BYK Additives \& Instruments, Wesel, Germany | 0.1-0.6 |
|  | 7 | Flash inhibitor NALZIN ${ }^{\circledR}$ FA 179, organic zinc chelates, $100 \mathrm{wt} . \%$, Elementis Chemical Co., Ltd., London, UK | 0.2-0.5 |
|  | 8 | Rheology additive R BYK-425, modified urea polyurethane solution, $50 \mathrm{wt} . \%$, solvent: water, BYK Additives \& Instruments, Wesel, Germany | 0.7-1.5 |
|  | 9 | Ultraviolet light absorber UV1 100F, nanoscale Titanium Dioxide, $40 \mathrm{wt} . \%$, solvent: water, Beijing THK SCI Co., Ltd., Beijing, China Ultraviolet light absorber UV2 200F, nanoscale Zinc Oxide, 40 wt. \%, solvent: water, Beijing THK SCI Co., Ltd., Beijing, China | 0.2-0.6 |
| Part B | 10 | Aqueous isocyanate curing agent B1Bayhydur ${ }^{\circledR}$ XP 2655, $100 \mathrm{wt} . \%$, Covestro Polymers Company Limited, Leverkusen, Germany Aqueous isocyanate curing agent B2Bayhydur ${ }^{\circledR}$ XP 2487, 100 wt.\%, Covestro Polymers Company Ltd., Leverkusen, Germany | 16-18 |

### 2.2. Characterization Methods

The raw materials of deionized water, wetting and dispersing agent D1Disper BYK-190, wetting and dispersing agent D2 BYK-P104S, defoamer F1 TEGO Airex 902W, defoamerF2 BYK-028, and DuPont-R706 were added into the grinding tank according to the formula. Firstly, the basket sander (FTM-L, Shanghai Farfly Energy Technology Co., Ltd., Shanghai, China) was used to grind and disperse at the speed of $1500-2000 \mathrm{rpm}$ until the fineness was no more than $20 \mu \mathrm{~m}$. Then hydroxy acrylate aqueous dispersion A1 Bayhydrol ${ }^{\circledR} 2470$ or A2 Bayhydrol ${ }^{\circledR}{ }^{\circledR} 2646$, wetting leveling agent L1 BYK-378, wetting leveling agent L2 BYK-349, flash inhibitor NALZIN ${ }^{\circledR}$ FA 179, Rheology additive R BYK-425, ultraviolet light absorber UV1 100F or UV2 200F were adjusted to the A component according to the formulation amount, which was dispersed uniformly by a dispersing machine (SFJ-400, Shanghai Modern Environmental Engineering Technology Co., Ltd., Shanghai, China) at 400-500 rpm, and packaged by a 100 mesh copper mesh. A component was used in combination with aqueous isocyanate curing agent B1Bayhydur ${ }^{\circledR}$ XP 2655 with the ratio of $6: 1$. The viscosity was adjusted by water in order to achieve the spraying conditions. According to the requirements of the testing standards, the test plate was first sanded with a sandpaper and then wiped with alcohol. The topcoat reached the required thickness by spraying. After the film was completely dried for 7 days, the film performance test was performed [26].

Paint film test: The fineness test used the hegman fineness gauge (QXD, Tianjin Jingkelian Material Testing Machine Co., Ltd., Tianjin, China). The measuring range was $0-50 \mu \mathrm{~m}$. The test was repeated three times and the closest two values were taken to calculate the arithmetic mean, which was the final fineness. The international standard was adopted ISO1524:2013 [27]. Drying time test: Surface drying used the finger contact method. Inside drying used the filter press method. The international standard was adopted ISO 1517:1973 [28]. The bending performance test used a film elasticity tester (QTX, Shanghai Modern Environmental Engineering Technology Co., Ltd., Shanghai, China). The paint film was observed visually or used a $4 \times$ magnifying glass for damage such as texture, cracks, and peeling etc. The flexibility of the paint film was represented by the smallest shaft rod diameter that did not cause the paint film to break. The international standard was adopted ISO 1519:2011 [29]. The cross-cut test used a paint film scriber (Shanghai Modern Environment Engineering Technology Co., Ltd., Shanghai, China). The international standard was adopted ISO 2409:2013 [30]. The gloss test used a gloss meter (AG446, BYK, Wesel, Germany). The international standard was adopted ISO 2813:2014 [31].

QUV aging test: Xenon lamp aging machine (H. J. Unkel Limited, Shanghai, China) was used. The light source is a UVA-340 UV lamp, and its radiance is $0.89 \mathrm{~W} / \mathrm{m}^{2}$. One cycle applies a UV light time of 4 h , a room temperature spray of half an hour, and then keeping at $60^{\circ} \mathrm{C}$ for 3.5 h . The test was performed for 1000 h . It was tested with international standard ISO 4892-2016 [32]. Samples were taken out at regular intervals for performance evaluation of the coating film.

Performance Characterization: SEM was performed using a scanning electron microscope (SEM, Hitachi S-4800, Hitachi Company, Tokyo, Japan). The sample was adhered to the specimen holder with conductive adhesive, and gold spraying was performed. The observations were taken in SE mode. The stereomicroscope morphology was observed using a Digital Microscope (KH7700, Seika Corporation, Tokyo, Japan).

### 2.3. Major in Performance Test of Topcoat

The technical indicators and performance tests of WPU topcoat are shown in Table 2.
Table 2. Topcoat technical indicators and performance test.

| Projects | Technical Indicators | Test Results | Experiment Method |
| :---: | :---: | :---: | :---: |
| Fineness $(\mu \mathrm{m})$ | $\leq 20$ | 15 | ISO 1524:2013 [27] |
| Applicable period $(\mathrm{h})$ | $\geq 2$ | 7 | ISO 9514:2005 [33] |
| Surface drying time $(\mathrm{h})$ | $\leq 4$ | 2.5 | ISO 1517:1973 [28] |
| Inside drying time $(\mathrm{h})$ | $\leq 24$ | 16 |  |
| Paint film color and appearance | Uniform, no particles, pinholes, | Pass | Visual inspection |
| Bending performance $(\mathrm{mm})$ | bubbles and wrinkles | 1 | ISO 1519:2011 [29] |
| Cross-cut test level | $\leq 2$ | ISO 2409:2013 [30] |  |
| Luster $\left(60^{\circ}\right)$ | $\leq 1$ | ISO 2813:2014 [31] |  |
| Pencil hardness | $\geq 85$ | ISO 15184:2012 [34] |  |
| Heat resistance $\left(150^{\circ} \mathrm{C} 1 \mathrm{~h}\right)$ | $\geq$ HB | ISO 3248:2016 [35] |  |
| Solvent resistance (butanone 50 times) | Basically unchanged | Pass | Pass |
| Water resistance $(24 \mathrm{~h})$ | Basically unchanged | Pass | GB/T 17399:2009 [36] |
| Artificial accelerated aging test $(1000-\mathrm{h}$ level $)$ | Basically unchanged | $\leq 1$ | Pass |
| VOC content $(\mathrm{g} / \mathrm{L})$ | $\leq 300$ | ISO 4892:2016 [37] |  |
|  |  |  | Pass |

## 3. Results and Discussion

### 3.1. Choice of Waterborne Resin and Curing Agent

In view of the technical difficulties of high weather resistance, high gloss, and high weather resistance of locomotive topcoat, two different waterborne hydroxy acrylic resins, hydroxy acrylate aqueous dispersion A1 Bayhydrol ${ }^{\circledR} 2470$ and A2 Bayhydrol ${ }^{\circledR} 2646$, are selected in this experiment to investigate the effect of different hydroxy acrylic resins on the properties of the paint film. Their performance parameters are compared in Table 3.

Table 3. Performance comparison of two waterborne hydroxy acrylic resins.

| Hydroxy Acrylate <br> Aqueous Dispersion | Solid Content [\%] | Viscosity [mPa $\cdot \mathbf{s ]}$ | -OH Content <br> [wt.\%] | pH Value [-] |
| :---: | :---: | :---: | :---: | :---: |
| A1 | 45 | 2000 | 3.9 | 7.8 |
| A2 | 50 | 1800 | 3.8 | 7.7 |

The curing agent selected in this study is aqueous isocyanate curing agent B1 Bayhydur ${ }^{\circledR}$ XP 2655 and B2 Bayhydur ${ }^{\circledR}$ XP 2487. By comparison, it is found that the gloss of paint film made by B1 was higher than that of B2, and thus the curing agent B1 was selected. It does not need a co-solvent and it is hydrophilic, as well as being easy to disperse evenly and stirred by hand. The paint film of the formulated paint shows high hardness and good chemical resistance. The effect of different waterborne hydroxy acrylic resins on the properties of the paint film is shown in Table 4.

Table 4. Performance comparison of two waterborne hydroxy acrylic resin paint films.

| Paint | Bending <br> Performance $(\mathbf{m m})$ | Luster <br> $\left(\mathbf{6 0} \mathbf{0}^{\circ}\right)$ | Impact Resistance <br> $($ front $/ \mathbf{b a c k})(\mathbf{k g} \cdot \mathbf{c m})$ | Cross-Cut Test <br> (Level) | Pencil Hardness |
| :---: | :---: | :---: | :---: | :---: | :---: |
| A1+ B1 | 1 | 90 | $50 / 50$ | 0 | 2 H |
| A2 + B1 | 1 | 80 | $50 / 40$ | 0 | 2 H |

Comparing the two resins from Table 4, the coating gloss of the coating prepared from A1 +B 1 is better than that of A2 + B1. Finally, the aqueous hydroxy acrylic resin A1 and the aqueous isocyanate curing agent B 1 are used together.

### 3.2. Optimization of Additives

### 3.2.1. Selection and Effects of Wetting and Dispersing Agents

The wetting dispersant is helpful to disperse the color filler. The full wetting of the color filler can reduce the surface tension of the material and make the color paste form stable homogeneous particles. When grinded paste and emulsion are mixed, their compatibility and stability after mixing are the decisive factors of uniform non-settling and non-floating color [39].

In this study, wetting and dispersing agent D1Disper BYK-190 and D2 BYK-P104S are used to study the influence of different dosage on dispersion, storage stability, and the appearance of the coating film, as shown in Table 5.

Table 5. Effect of wetting and dispersing agent on slurry and coating film.

| Properties | Null | Wetting and Dispersing Agent Content (wt.\%) |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathbf{0 . 5} \mathbf{D 1}$ | 1 D1 | 1.5 D1 | 0.8 D1 + 0.4 D2 |
| Dispersion effect | Difficult to disperse | Ok | Ok | Ok | Ok |
| Storage at room temperature $(24 \mathrm{~h})$ |  |  |  |  |  |
| Coating appearance |  |  |  |  |  |

The results can be seen in Table 5. When the amount of wetting and dispersing agent is insufficient, the relatively low-density component moves upwards and the high-density component moves downwards. The paint film appears to be floating and the slurry settles. An excessive amount of wetting dispersant will cause the drawback of shrinkage holes to affect the gloss of the topcoat. Therefore, it is essential to coat the slurry with the proper amount of wetting and dispersing agent for the stability of the slurry and the smoothing of the coating. D2 additive contains polysiloxane copolymer, which is more effective in preventing floating. It contains silicone, which helps to prevent Bernard vortex and streaks, which improves the surface smoothness [40]. When the wetting and dispersing agent D 1 with an amount of $0.8 \%$ and D 2 with an amount of $0.4 \%$ are added, the surface of the paint film is most uniform and smooth.

### 3.2.2. Effect of Defoamer on Slurry and Coating Film

The bubbles are mainly attributed to the processes of grinding, dispersing, and stirring, roller coating or spraying, and construction on porous substrate, as well as the side reaction between isocyanate group and water in curing agent [41]. To solve this problem, defoamer F2 BYK-028 and F1 TEGO Airex 902 W are selected to investigate the influence of different dosage and proportion on the grinding process and the appearance of the coating film, as shown in Table 6. With the increase of F1, bubbles generated in the grinding process significantly decrease, but the coating film is always concave. Finally, the appearance of coating film is improved by the slightly weaker defoaming agent F2. When the amount of defoaming agent is less sufficient, pinholes, dark bubbles, uneven surface, and other defects will arise. However, it can reduce the surface tension of the coating. When the amount added is excessive, the surface tension difference in the system will increase, leading to shrinkage
cavity. The surface tension of antifoaming agent is smaller than that of the coating, and it should have good dispersibility in the coating system and incompatibility with the coating system, but it cannot produce a negative effect [42]. When the final defoamers F2 BYK-028 and F1 TEGO Airex902W are used with the amount of $0.15 \%$, the paint film state is smooth and even, as shown in Table 6.

Table 6. Effect of defoamer on slurry and coating film.

| Properties | Defoamer Content (wt.\%) |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Null | 0.05 F1 | 0.1 F1 | 0.2 F1 | 0.15 (F1 + F2) |
| Grinding process | A lot of bubbles | More bubbles, still exist after standing for 24 h | A small amount of bubbles, disappeared after standing for 24 h | A small amount of bubbles, disappeared after standing for 24 h | A small amount of bubbles, disappeared after standing for 24 h |
| Coating appearance | More pinholes, dark bubbles, etc. | Uneven and defective | Individual depression | More shrinkage holes on the surface | Smooth |

### 3.2.3. Effect of Wetting Leveling Agent on the Coating Film

In this study, wetting leveling agents L1 BYK-378 and L2 BYK-349 are used to control the appearance of paint film through different addition amounts, as shown in Table 7.

Table 7. Effect of wetting leveling agent on coating film.

| Properties | Wetting Leveling Agent (wt.\%) |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Null | $\mathbf{0 . 3}$ L1 | $\mathbf{0 . 3}$ L2 | $\mathbf{0 . 1 5 ~ L 1 ~ + ~ 0 . 1 5 ~ L 2 ~}$ | $\mathbf{0 . 6}$ L1 | $\mathbf{0 . 6}$ L2 | $\mathbf{0 . 3} \mathbf{~ L 1 ~ + ~ 0 . 3 ~ L 2 ~}$ |
| Coating <br> appearance | Roughness | Individual <br> shrinkage holes | Light orange peel | Smooth | Shrinkage <br> holes | Fisheye <br> defect | Shrinkage <br> holes and <br> fisheye defect |

According to our study, increasing the surface aid L2 reduces the surface tension and improves the wettability of the substrate. However, the additive does not improve the smoothness of the coating surface. Through the secondary surface additive L1, the surface tension is lowered to a high degree and the foam is stabilized. The surface smoothness is increased, and the compatibility is excellent [43]. When the surface additives L1 with an amount of $0.15 \%$ and L2 with an amount of $0.15 \%$ are added, the appearance of the coating film is most improved.

### 3.2.4. Effect of Rheological Additives on the Coating Film

Rheology additive R (BYK 425) is added to the formulation, whose amounts are $0,1 \%, 2 \%, 3 \%$, and $4 \%$ for analysis and comparison, as shown in Table 8.

Table 8. Effect of rheological additives on coating film.

| Rheology Additive <br> R Content (wt.\%) | Viscosity/KU | Effects |
| :---: | :---: | :---: |
| 0 | 53 | floating color, placed on the bottom of the sinking and spray sag |
| 1 | 59.8 | placed with less floating color and sinking |
| 2 | 69.2 | Ok |
| 3 | 75.7 | uneven film and wrinkles |
| 4 | 94 | paint film has more pinholes |

As can be seen from Table 8, as the rheological additive R BYK-425 increases, the viscosity of the system increases. Additive R is used to control the water-based and water-soluble resin systems. It endows WPU with the pseudoplastic flow to improve the storage viscosity and anti-sag of the system. The mechanism of action is that the hydrogen bond in the urea modifier generates a reticular structure to enhance the rheological property, so that the system is in a gelatinous state with larger viscosity. The network structure formed by the additive R in the latex paint prevents the recombination of the
pigment particles and prevents floating coloration and sedimentation. However, as the amount of addition increases, the appearance of the coating film may also be disadvantageous such as unevenness and wrinkles [44]. Finally, by comparison, it is found that when the additive R is added in an amount of $2 \%$, the sedimentation floating color is improved, and the surface state is flat. The color is improved with the surface state being flat.

### 3.3. Effect of Topcoat $n-N C O / n-O H$ on Performance

In the preparation of the two-component WPU, the $n-\mathrm{NCO} / n-\mathrm{OH}$ ratio plays a significant role in the film properties. During the preparation process, the side reaction between isocyanate root and water eventually generates urea polymer, which can improve the degree of polymerization of film-forming material and the performance of paint film. Therefore, the amount of curing agent should be excessive, which can not only guarantee the complete curing reaction with the hydroxyl group, but can also cause a side reaction with water. However, the main reaction will be affected if the amount of curing agent is too high, which will affect the characteristics of the film. The side reaction will also produce carbon dioxide, which will lead to pinholes, bubbles, and other defects in the appearance of the film, resulting in poor performance of the film [45]. The influence of different ratios of $n-\mathrm{NCO} / n-\mathrm{OH}$ on the performance of paint film is shown in Table 9.

Table 9. Effect of different ratios of $n(-\mathrm{NCO} /-\mathrm{OH})$ on the properties of paint film.

| Properties | $n(-\mathrm{NCO} /-\mathrm{OH})$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{1 : 1}$ | $\mathbf{1 . 2 : 1}$ | $\mathbf{1 . 4 : 1}$ | $\mathbf{1 . 5 : 1}$ | $\mathbf{1 . 6 : 1}$ | $\mathbf{1 . 8 : 1}$ | $\mathbf{2 : 1}$ |
| Exterior | Smooth | Smooth | Smooth | Smooth | Smooth | Smooth | Smooth |
| Gloss $\left(20^{\circ}\right)$ | 78.4 | 81.3 | 81 | 79.7 | 78.8 | 76.6 | 71.8 |
| Gloss $\left(60^{\circ}\right)$ | 87.4 | 90.2 | 89.4 | 89.1 | 88.4 | 88.9 | 88.1 |
| Gloss $\left(85^{\circ}\right)$ | 98 | 98 | 96.9 | 96.3 | 94.6 | 96.2 | 96 |
| pencil hardness | $<\mathrm{HB}$ | HB | 2 H | 2 H | $<\mathrm{HB}$ | $<\mathrm{HB}$ | $<\mathrm{HB}$ |
| impact resistance (front/back) $(\mathrm{kg} \cdot \mathrm{cm})$ | $40 / 40$ | $50 / 40$ | $50 / 50$ | $50 / 50$ | $50 / 50$ | $50 / 40$ | $50 / 40$ |
| bending performance $(\mathrm{mm})$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| cross-cut test (level) | 1 | 0 | 0 | 0 | 0 | 1 | 1 |

It can be seen from Table 9 that when the ratio of $n-\mathrm{NCO} / n-\mathrm{OH}$ is less than 1.4 , the degree of crosslinking of the film formation is small, and the gloss is lowered. When it is more than 1.5 , the basic structure of the resin is broken. The smooth state of paint film is not good, which affects the gloss performance. A ratio that is too high or too low will affect the properties of hardness, back impact, and adhesion. In summary, the final choice of $n-\mathrm{NCO} / n-\mathrm{OH}$ ratio is 1.4-1.5.

### 3.4. Weather Resistance of Topcoat

The microstructure of the coating can effectively absorb ultraviolet rays in sunlight. After absorbing the light energy, chemical bonds are broken and free radicals are generated. The aging process is accompanied by photooxidation reaction, among which the existence of singlet oxygen, ozone, and ground oxygen is the key to the occurrence of this process, and alkyl hydrogen peroxide and free radicals are important substances for the continuous photooxidation and photodegradation. UV absorbent is a kind of additive which can dissolve or disperse in water, or dissolve in water with the help of a solvent. It is necessary to add UV absorbent in a waterborne coating system due to its good emulsifying ability and good light retention [23]. Liu et al. [11] analyzed artificial aging tests on alkyd and polyurethane systems. After 720 h , SEM coating surface morphology was analyzed and obvious defects appeared. Rashvand et al. [46] conducted an artificial aging test for polyurethane coating. The nanometer ZnO was added to the system to improve the performance. After 720 h , the color difference reached 10 and the light degradation rate reached $100 \%$. By comparing and optimizing the polyurethane system, we have made a great improvement.

In this study, waterborne polyurethane is used as the film forming material. Under the quick ultraviolet aging test, the formulation has been discussed and studied in the following experimental groups. The No. $1^{\#}$ sample is a mixture of hydroxy acrylate aqueous dispersion A1 and hydroxyacrylate aqueous dispersion A2, and the resin content is $60 \%$. The No. $2^{\#}$ sample uses $60 \%$ hydroxy acrylate aqueous dispersion A1. The No. $3^{\#}$ sample uses $55 \%$ hydroxyacrylate aqueous dispersion A1. The No. $4^{\#}, 5^{\#}, 6^{\#}, 7^{\#}$, and $8^{\#}$ samples are hydroxy acrylate aqueous dispersion A1 with $55 \%$ resin content, and then added with additives of $0.3 \%$ UV1, $0.5 \%$ UV1, $0.3 \%$ UV2, $0.5 \%$ UV2, and $0.5 \%$ (UV1 + UV2), respectively (UV1 and UV2 are ultraviolet light absorber UV 100F and 200F). Their dry film thickness and gloss are shown in Table 10.

Table 10. Thickness and gloss of sample $1^{\#}-8^{\#}$ coatings.

| Properties | Formulation |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{1}^{\boldsymbol{\#}}$ | $\mathbf{2}^{\boldsymbol{\#}}$ | $\mathbf{3}^{\boldsymbol{\#}}$ | $\mathbf{4}^{\boldsymbol{\#}}$ | $\mathbf{5}^{\boldsymbol{\#}}$ | $\mathbf{6}^{\boldsymbol{\#}}$ | $\mathbf{7}^{\boldsymbol{\#}}$ | $\mathbf{8}^{\boldsymbol{\#}}$ |  |
| Film thickness $(\mu \mathrm{m})$ | $56-63$ | $59-62$ | $53-61$ | $50-55$ | $60-61$ | $56-61$ | $53-63$ | $51-61$ |  |
| Luster $\left(20^{\circ}\right)$ | 85.6 | 82.6 | 80.7 | 81.6 | 83.7 | 73.1 | 14.7 | 69.7 |  |
| Luster $\left(60^{\circ}\right)$ | 92.1 | 90.2 | 88.4 | 88.7 | 90.4 | 87.1 | 51.7 | 86.4 |  |
| Luster $\left(85^{\circ}\right)$ | 101 | 101 | 101 | 101 | 101 | 101 | 95.7 | 100 |  |

As can be seen from the data, when the thickness of each sample is the same, ultraviolet light absorber UV1 100F has almost no influence on the gloss, while ultraviolet light absorber UV2 200F has a great influence on the gloss. As can be seen from the data, when the thickness of each sample is the same, the additive J has almost no effect on the gloss. When the additive amount of additive UV2 reaches $0.5 \%$, the $60^{\circ}$ gloss has decreased by $41.5 \%$ compared to the control group without UV absorbent. It has a great effect on gloss. The QUV aging test is then performed to verify the coating properties.

As can be seen from Figure 1 and Table 11, sample No. $1^{\#}$ has the highest original luster, but also has the highest light reduction rate after aging experiment. The performance of sample No. $2^{\#}$ is better than that of sample No. $3^{\#}$, indicating that when the resin content is low, the performance becomes worse after QUV aging test, and the chemical bond is seriously damaged. The formula of additive UV1 has little effect on the gloss, but the weather resistance is almost not improved. The additive UV2 has a great influence on the reduction of gloss, but the performance of gloss retention is stable. Under the condition of $60^{\circ}$ gloss test, the luminous reduction rate of No. $7^{\#}$ sample is only $10.25 \%$.


Figure 1. (a) The change of gloss with time in $1^{\#}-8^{\#}$ sample aging test under $20^{\circ}$ gloss angle; (b) the change of gloss with time in $1^{\#}-8^{\#}$ sample aging test under $60^{\circ}$ gloss angle; (c) the change of gloss with time in $1^{\#}-8^{\#}$ sample aging test under $85^{\circ}$ gloss angle.

Table 11. The rate of light reduction after 1000-h aging test.

| Gloss Reduction Rate | Formulation |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{1}^{\boldsymbol{\#}}$ | $\mathbf{2}^{\boldsymbol{\#}}$ | $\mathbf{3}^{\boldsymbol{\#}}$ | $\mathbf{4}^{\boldsymbol{\#}}$ | $\mathbf{5}^{\boldsymbol{\#}}$ | $\mathbf{6}^{\boldsymbol{\#}}$ | $\mathbf{7}^{\boldsymbol{\#}}$ | $\mathbf{8}^{\boldsymbol{\#}}$ |  |
| $20^{\circ} \%$ | 88.08 | 66.10 | 78.83 | 78.31 | 85.42 | 73.51 | 36.05 | 75.04 |  |
| $60^{\circ} \%$ | 50.16 | 27.27 | 37.44 | 37.77 | 47.56 | 23.19 | 10.25 | 35.42 |  |
| $85^{\circ} \%$ | 38.61 | 19.70 | 31.68 | 31.58 | 40.20 | 9.21 | 9.09 | 20.90 |  |

The color difference calculation was performed based on CIE $L^{*} a^{*} b^{*} 1976$ color difference equation:

$$
\begin{equation*}
\Delta E^{*}=\left[\left(L_{2}^{*}-L_{1}^{*}\right)^{2}+\left(a_{2}^{*}-a_{1}^{*}\right)^{2}+\left(b_{2}^{*}-b_{1}^{*}\right)^{2}\right]^{\frac{1}{2}} \tag{1}
\end{equation*}
$$

where $L^{*}$ characterizes the lightness value and varies between 100 (white) and 0 (black); $a^{*}$ and $b^{*}$ are the chromaticity coordinates; $a^{*}$ indicates the red and green terms; a positive value of $\Delta a$ indicates that the sample is redder than the standard, and a negative value indicates that the sample is greener than the standard; $b^{*}$ indicates yellow and blue terms; and a positive value of $\Delta b$ indicates that the sample is yellower than the standard, and a negative value indicates that the sample is bluer than the standard [46]. Here, a colorimeter (SP60, X-rite, Grand Rapids, MI, USA) was used for measurements.

As can be seen from Table 12, the whole area turns black and yellow. Compared with unadded UV absorbers, UV absorbents have a certain role in weather resistance. Sample $1^{\#}$ has the largest variation in color difference to WPU system, and sample $6^{\#}$ has the smallest variation in color difference.

Table 12. Variation of color difference after 1000-h aging test.

| Aberration | Formulation |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{1}^{\boldsymbol{\#}}$ | $\mathbf{2}^{\boldsymbol{\#}}$ | $\mathbf{3}^{\boldsymbol{\#}}$ | $\mathbf{4}^{\boldsymbol{\#}}$ | $\mathbf{5}^{\boldsymbol{\#}}$ | $\mathbf{6}^{\boldsymbol{\#}}$ | $\mathbf{7}^{\boldsymbol{\#}}$ | $\mathbf{8}^{\boldsymbol{\#}}$ |  |
| $\Delta L$ | -2.3 | -1.6 | -2 | -2.4 | -1.5 | -0.2 | -1.1 | -1.0 |  |
| $\Delta a$ | -0.1 | -0.2 | -0.2 | -0.4 | -0.1 | -0.2 | 0 | -0.1 |  |
| $\Delta b$ | 1.6 | 1.7 | 1.6 | 0.4 | 1.8 | 1.9 | 2.0 | 1.9 |  |
| $\Delta E$ | 2.8 | 2.4 | 2.6 | 2.4 | 2.3 | 1.9 | 2.3 | 2.2 |  |

This rating is based on the ISO 4892:2016 [32] aging rating method. Light loss and discoloration are measured with a gloss meter and a colorimeter, and the rest are visually inspected.

From the comprehensive rating from Table 13, No. $2^{\#}, 6^{\#}$, and $7^{\#}$ can reach the primary level in comprehensive rating. The No. $2^{\#}$ sample added $60 \%$ resin, which is high cost, and can easily cause coating porosity, blister, and other problems in the large-area process. Sample No. $7^{\# 1}$ shows the smallest gloss change in the group. It has stable light retention performance. But the gloss is very low, which cannot meet the high light requirements of locomotives. It can be further developed and applied on matte paint. To summarize, the best performance is No. $6^{\#}$, which can meet the requirements of high gloss and weather resistance on the locomotive. Moreover, from SEM images (Figure 2a-c), the sample $6^{\#}$ paint film shows uniform dispersion and good compactness without any agglomeration. From the stereo microscope morphology (Figure 2d), the maximum height difference of the surface is $12.146 \mu \mathrm{~m}$, and the coating is smooth.

Table 13. Topcoat comprehensive aging performance rating.

| Properties | Formulation |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathbf{1}^{\boldsymbol{\#}}$ | $\mathbf{2}^{\boldsymbol{\#}}$ | $\mathbf{3}^{\boldsymbol{\#}}$ | $\mathbf{4}^{\boldsymbol{\#}}$ | $\mathbf{5}^{\boldsymbol{\#}}$ | $\mathbf{6}^{\boldsymbol{\#}}$ | $\mathbf{7}^{\boldsymbol{\#}}$ | $\mathbf{8}^{\boldsymbol{\#}}$ |
| Comprehensive level | 3 | 1 | 2 | 2 | 2 | 1 | 1 | 2 |
| Loss of light | 4 | 2 | 3 | 3 | 3 | 2 | 2 | 3 |
| Discoloration | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 |
| Powdering | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Pan-gold | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Spot | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Contamination | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cracking | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Foaming | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Mildew | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Peeling off | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Rusty | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |



Figure 2. (a) SEM surface topography at $2 \times 10^{3}$ to $20 \mu \mathrm{~m}$; (b) SEM surface topography at $5 \times 10^{3}$ to $10 \mu \mathrm{~m}$; (c) SEM surface topography at $1 \times 10^{4}$ to $5 \mu \mathrm{~m}$; (d) Three-dimensional topography map by a volumetric microscope.

### 3.5. Determination of the Trial Period of the Topcoat

As can be seen from Figure 3, the viscosity changes slightly in 520 min. Samples are made by spraying paint within $90,160,320$, and 500 min . It can be seen from Table 14 that the luster was almost unchanged for 320 min and slightly decreased for 500 min . The change of viscosity and gloss is comprehensively considered, which meets the requirement of probation period.


Figure 3. Time dependence of the viscosity of the topcoat during the trial period.

Table 14. The gloss of the topcoat during the trial period changes with time.

| Time (min) | Gloss |  |  |
| :---: | :---: | :---: | :---: |
|  | $\mathbf{2 0}^{\circ}$ | $\mathbf{6 0}^{\circ}$ | $\mathbf{8 5}^{\circ}$ |
| 0 | 82.9 | 90.5 | 102 |
| 90 | 81.4 | 90.4 | 99.4 |
| 160 | 81.4 | 89.9 | 101 |
| 320 | 81 | 89.6 | 100 |
| 500 | 71.2 | 85.3 | 97 |

## 4. Conclusions

In this study, hydroxy acrylate aqueous dispersion A1 Bayhydrol ${ }^{\circledR} 2470$ and aqueous isocyanate curing agent B1 Bayhydur ${ }^{\circledR}$ XP 2655 were selected and used together. The ratio of $n-\mathrm{NCO} / n-\mathrm{OH}$ was selected to be 1.4-1.5, the amount of wetting and dispersing agent D1Disper BYK-190 was $0.8 \%$, the wet dispersant wetting and dispersing agent D2 BYK-P104S was $0.4 \%$, the defoamer F1 TEGO Airex 902W and F2 BYK-028 were $0.15 \%$, and the wetting leveling agents L1 BYK-378 and L2 BYK-349 were both $0.15 \%$. When the rheology additive R BYK-425 is $2 \%$, the prepared two-component WPU locomotive topcoat shows a smooth surface. According to the study on weather resistance of the topcoat, it is concluded that by adding $0.3 \%$ ultraviolet light absorber UV2 200F, the first level of artificial accelerated aging resistance is achieved, and a WPU locomotive topcoat with high gloss and high weather resistance is also obtained. Moreover, the test of viscosity and luster during the probation period meets the performance requirements of the 4 h probation period. The coating test was carried out in Tangshan Vehicle Factory, which met the requirements of perfect performance. The $20^{\circ}$ high gloss and longer aging stability need to be further studied and discussed.

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