Sensors and Materials, Vol. 36, No. 9 (2024) 3843–3849
MYU Tokyo

S & M 3770

System Solution for Waterborne Wood Paint Discoloration

Wen-Cheng (Agingu) Shih

Neogeneration Biotech Co., Ltd.,
3F, No. 431, Dadun S. Rd., Nantun Dist., Taichung 408024, Taiwan

(Received July 8, 2024; accepted August 26, 2024)

Keywords: waterborne wood paint, discoloration, tannin staining, titanium dioxide

The transition from solvent to low volatile organic compound and eco-friendly paint is a megatrend in the Asia Pacific region, and waterborne wood paint is still in the early stage of this transition. The most challenging technical problem is paint discoloration that can serve as a sensor for the malfunction of the paint system caused by tannin staining. This is a brownish or tan discoloration on the paint surface owing to the migration of tannin from the wood substrate through the paint film. A typical remedy is to apply an oil sealant in the presence of a tannin-inhibiting agent or a cationic resin in a base coat. This may lead to the constraints of multiple paint applications constraints, additional paint makeup steps, and unwanted chemical substance management. The described waterborne wood paint that is formulated with alumina surface-coated TiO_2 (Al–TiO_2) in combination with an anionic acrylate resin system demonstrates exceptional tannin stain resistance in comparison with silica/alumina surface-coated TiO_2 (Si–Al–TiO_2). A good compatibility with an acrylate resin system and a strong affinity toward tannin for alumina on a pigment surface are instrumental in mitigating waterborne wood paint discoloration.

1. Introduction

The Asia Pacific region has seen the fastest growth in the global wood paint market. This growth is mainly attributed to intensive investments on building and construction industries to accommodate the growing population, per-capita income, and improved life quality.

The global wood paint market continues to be dominated by the solvent-borne system at 40% and the high-solid solvent-borne paint system at 23% (solvent-borne system up to 60% in total), whereas waterborne systems and radiation-curable paints are both at 18% (close to 40% in total). However, the waterborne conversion ratio in the China market is considered far below 10% in comparison with the global ratio of 18%. Therefore, there is a strong momentum toward eco-friendly products with the Chinese government's strong push to reduce volatile organic compound emission and PM 2.5 air pollution with the attempt to promote up to 60% green paints, such as a waterborne paint system.

*Corresponding author: e-mail: agingu.shih@gmail.com
https://doi.org/10.18494/SAM5230

ISSN 0914-4935
https://myukk.org/

In comparison with a solvent-borne system, the technological challenges of a waterborne system include limitations on paint application conditions under considerably strict atmospheric humidity/temperature, paint film deformation by grain raising caused by moisture contamination, the expansion/contraction of the wood substrate, and an additional sealing layer to inhibit the migration of tannin/other chromophore extractives that cause paint discoloration.

Wood is a complex natural organic material that is mainly composed of two groups of compounds: carbohydrates such as cellulose and hemicelluloses (65–75%) and phenols such as lignin (20–30%). Wood also consists of small amounts of extractives in the form of inorganic minerals at 0.1–1% and organic extractives at 1–30%, which are chromophores such as tannins, flavonoids, essential oils, fats, resin, wax, gum, and starch.

Tannins, e.g., tannic acid, are water-soluble, polyphenolic, and high-molecular-weight molecules that are found in many types of wood, including western red cedar, redwood, and oak. The brownish color is caused by their conjugated chemical structure, and their water solubility arises from their polyphenolic structure. The above-mentioned facts about tannins lead to the potential causes of the waterborne wood paint discoloration.[1]

The pH of the waterborne wood paint system is commonly controlled to be slightly alkaline; therefore, tannins with a pKa of 4.2 are prone to deprotonate and form anionic species. This characteristic sheds some light on blocking tannin stain migration through the paint film via electrostatic adsorption by a cationic resin system and/or the addition of chelating additives to produce a water-insoluble tannin-containing complex.

Paint discoloration by tannin staining may occur when tannins dissolve in water, diffuse to the interface of the wood and paint film, and then further migrate to the painted surface, resulting in an unsightly yellow or brown discoloration.

The wood bleeding through white paint is a brownish or tan discoloration on the paint surface, especially on knot holes. This color change on a white paint surface serves as a sensor for the malfunction of the paint system that cannot effectively mitigate the tannin migration from the wood substrate through the paint film, i.e., tannin bleed-through.

There are two effective approaches to inhibiting tannin stain formation: the barrier approach and the chemical approach.

The waterborne wood paint discoloration, i.e., tannin stain, can be effectively mitigated by preventing tannin migration from the wood substrate to the paint film surface through (1) the barrier approach by improving the paint film integrity to eliminate crack formation in the dry film and (2) the chemical approach by the interaction/chelation with a tannin to produce a water-insoluble complex, which would not bleed through a waterborne paint film.

As for the barrier approach, two component solvent-borne primers or sealers are typically used. These primers/sealers require hazardous isocyanates for curing. Thus, they are not preferred because of safety, health, and environmental concerns related to the solvent and isocyanate cross-linker. Furthermore, the paint film integrity caused by the well-dispersed TiO_2 in a resin system, as shown in Fig. 1(a),[2–6] can effectively eliminate the crack formation in the dry film by producing a resin-pigment composite that contributes to tighter film formation and prevent tannin migration from the wood substrate to the paint film surface as shown by the red arrows in Fig. 1(b).

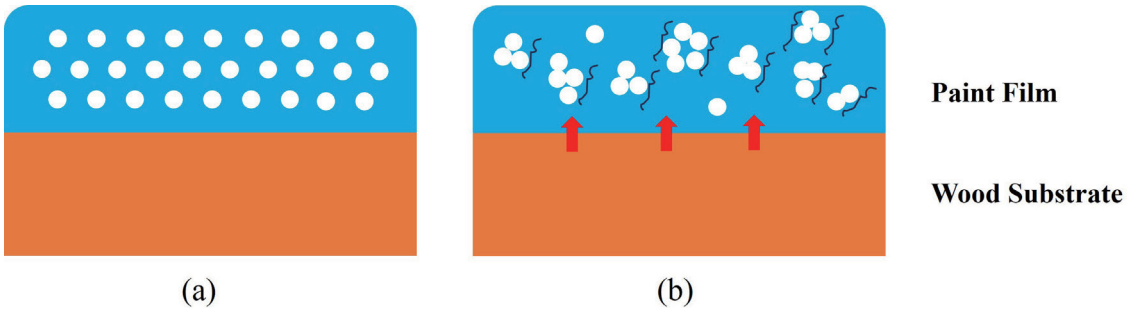

Fig. 1. (Color online) Barrier approach via better pigment spacing and its effect on tannin stain resistance.

With regard to the chemical approach, two alternatives are adopted in relation to the interaction with tannin as described below.

(1) Inorganic chelating metals, which are slightly water-soluble metal cations, such as Ba^{2+}, Zn^{2+}, Al^{3+}, and Zr^{4+}, react with hydroxyl groups on the phenolic rings of tannins.[7]
(2) Cationic resins can cause water-insoluble complex formation, since most of the water-soluble extractives in wood are anionic in nature.[8,9]

However, these two approaches suffer from some limitations that most paint producers avoid, which include heavy odor, poor shelf life, comparatively high paint makeup cost with the addition of a metal-chelating agent, and spray gun blockage with the use of a cationic resin during paint application. Therefore, an existing anionic acrylate resin system in the presence of minimum tannin-inhibiting additives and the optimized TiO_2 pigment is a potential alternative to achieve the maximum benefits in terms of both paint performance and paint makeup cost.

2. Data, Materials, and Methods

Exceptional paint performance in terms of whiteness, hiding power, and gloss with additionally improved tannin stain resistance was achieved through a unique synergistic effect between Al–TiO_2 and a compatible resin system. The paint formulated with alumina surface-coated TiO_2 (Al–TiO_2) in combination with an anionic acrylate resin system (NeoCryl® XK-85 from DSM is a small-particle-size styrene anionic acrylic emulsion designed for coatings requiring outstanding corrosion, water, and humidity resistances) demonstrates prominent tannin stain resistance in comparison with silica/alumina surface-coated TiO_2 (Si–Al–TiO_2) as shown in Fig. 2. The specified ingredients for the testing formulation include water, a dispersant, a white TiO_2 pigment, resin, a coalescing agent, and a thickener in the absence of a tannin-inhibiting agent (HALOX BW-100 from ICL).

3. Results and Discussion

The paint with controlled film thickness and viscosity was applied by a spray technique on an oak substrate. After aging indoors for 1145 h, the delta E (ΔE) of the paint was evaluated. Furthermore, the paint system made from Al–TiO_2 in combination with an anionic acrylate resin

system can approximately meet the required tannin stain resistance that was formulated with a cationic resin system (NeoCryl® XK-350 from DSM is an acrylic cationic copolymer emulsion designed for primers against knot bleeding), as shown in Fig. 3. As mentioned earlier, a cationic resin is commonly used to prevent tannin migration. Here, ΔE is calculated to indicate the change in paint color after aging indoors for 1145 h as measured in the Hunter Lab color space

Fig. 2. (Color online) Discoloration of paints made from (a) Si–Al–TiO_2 and (b) Al–TiO_2 in anionic acrylate systems on an oak substrate.

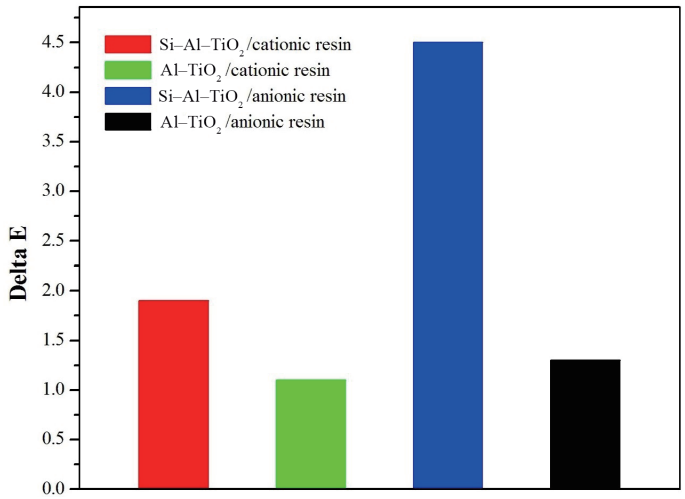

Fig. 3. (Color online) Tannin stain resistance defined by ΔE for Si–Al–TiO_2 and Al–TiO_2 in cationic and anionic resin systems.

on a 3D axis at L^*, a^*, and b^*. A low ΔE indicates a small difference between the measured color after 1145 h and the original paint color, and it stands for a higher tannin stain resistance. The method strictly followed ASTM D6686 for the "Standard Test Method for Evaluation of Tannin Stain Resistance of Coatings."

Two determining factors for achieving the prominent tannin stain resistance for the paint that was formulated using Al–TiO_2 in an anion acrylate resin system include a good compatibility between Al–TiO_2 and an acrylate resin system and an effective interaction with tannin through alumina on a pigment surface.

Regarding the interactions between an acrylate resin and Si–Al–TiO_2/Al–TiO_2 pigments, Zaman *et al.*[10] investigated the bonding type and absorption strength of polyacrylic acid (PAA) on silica, alumina, and kaolin. They found that the PAA adsorption on the surface of alumina was found to be approximately 10 times stronger than that on kaolin particles, and there was no adsorption of PAA on the surface of silica particles, i.e., PAA adsorption strength: Al > kaolin >> Si. The carboxylate oxygens ($R\text{-}COO^-$) can bridge an Al^{3+}-octahedral dimer, which consists of Lewis acidic heteroatoms to accept the electrons from carboxylate groups.[11,12] The strong adsorption of the acrylate resin with carboxylate functional groups on an Al surface-coated TiO_2 pigment[13,14] can improve the paint film integrity[15–19] that effectively eliminates tannin migration.

To investigate the interaction of tannin with the specified surface-coated pigments, a tannin retention test was conducted on both Si–Al–TiO_2/Al–TiO_2 pigments. The aqueous tannin acid solution was mixed with a specified pigment slurry. The mixture was sonicated for 5 min and then centrifuged. The upper clear solution was removed and fresh water was used to flush the pigment. These steps were repeated three times, and after the third flushing, the solution was collected and subjected to transmittance measurement. The tannin% in solution was calculated at a wavelength of 400 nm by UV-visible spectroscopy. The low concentration of tannin acid in the flushed solution suggested that more tannin acid was adsorbed by the pigment. The Al–TiO_2 pigment imparted a stronger capability than the Si–Al TiO_2 pigment for tannin interaction, as shown in Fig. 4.

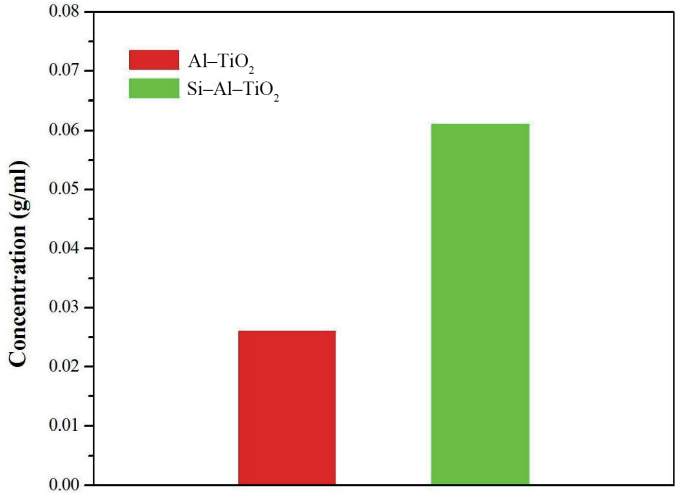

Fig. 4. (Color online) Tannin acid retention on Al–TiO_2 and Si–Al–TiO_2.

The design concept for the entire paint system was applied to the commercial wood paint formulation in collaboration with a wood paint producer and a dispersant supplier. Currently, the work is still under way.

4. Conclusion

Tannin stain can cause paint discoloration, which serves as a sensor for the malfunction of the paint system. The described waterborne wood paint that is formulated with alumina surface-coated TiO_2 in combination with an anionic acrylate resin system demonstrates exceptional tannin stain resistance in comparison with that formulated with silica/alumina surface-coated TiO_2. A good compatibility with an acrylate resin system and a strong affinity toward tannin for alumina on a pigment surface are instrumental in mitigating waterborne wood paint discoloration.

Acknowledgments

I am grateful to Nana Chiang, Sarah Ko, and Herman Lim for their excellent experimental work.

References

1 E. Burke, N. Slavik, T. Bonura, D. Connelly, T. Faris, A. Nebelsick, B. Stuart, R. S. Williams, and A. C Wiedenhoeft: CoatingsTech **7** (2010) 48. https://www.paint.org/wp-content/uploads/2021/09/Extractive-Bleed_Mar-2010.pdf
2 J. Jankolovits, A. Kusoglu, A. Z. Weber, A. Van Dyk, J. Bohling, J. A. Roper III, C. J. Radke, and A. Katz: Langmuir **32** (2016) 1929. https://doi.org/10.1021/acs.langmuir.5b03718
3 M. J. Cran, G. E. Morris, and L. Britcher: Colloids Surf., A **684** (2024) 133027. https://doi.org/10.1016/j.colsurfa.2023.133027
4 J. P. Boisvert, J. Persello, J. C. Castaing, and B. Cabane: Colloids Surf., A **178** (2001) 187. https://doi.org/10.1016/S0927-7757(00)00705-6
5 S. Farrokhpay: Adv. Colloid Interface Sci. **151** (2009) 24. https://doi.org/10.1016/j.cis.2009.07.004
6 G. E. Morris, W. A. Skinner, P. G. Self, and R. St. C. Smart: Colloids Surf., A **155** (1999) 27. https://doi.org/10.1016/S0927-7757(98)00631-1
7 T. E. McNeel and J. A. Harrell: EP0482961A2 (1991). https://patents.google.com/patent/EP0482961A2/en
8 G. Monaghan and A. Pinnix: CoatingsTech **16** (2019) 26. https://www.paint.org/coatingstech-magazine/articles/cationic-stain-blocking-primer-technology/
9 R. Feola and M. Gobec: Paint Coat. Ind. **9** (2005) 86. https://www.researchgate.net/publication/290009871_New_waterborne_cationic_binders_for_primer_applications
10 A. A. Zaman, R. Tsuchiya, and B. M. Moudgil: J. Colloid Interface Sci. **256** (2002) 73. https://doi.org/10.1006/jcis.2001.7941
11 K Vermöhlen, H. Lewandowski, H. D. Narres, and E. Koglin: Colloids Surf., A **170** (2000) 181. https://doi.org/10.1016/S0927-7757(00)00408-8
12 D. H. Lee, R. A. Condrate Sr., and J. S. Reed: J. Mater. Sci. **31** (1996) 471. https://doi.org/10.1007/BF01139166
13 B. Wang, Y. P. Wang, P. Zhou, Z. Q. Liu, S. Z. Luo, W. Chu, and Z. Guo: Colloids Surf., A **514** (2017) 168. https://doi.org/10.1016/j.colsurfa.2016.11.051
14 L. Liu, S. Z. Luo, B. Wang, and Z. H. Guo: Appl. Surf. Sci. **345** (2015) 116. https://doi.org/10.1016/j.apsusc.2015.03.145
15 D. Löf, G. Hamieau, M. Zalich, P. Ducher, S. Kynde, S. R. Midtgaard, C. F. Parasida, L. Arleth, and G. V. Jense: Prog. Org. Coat. **142** (2020) 105590. https://doi.org/10.1016/j.porgcoat.2020.105590
16 F. Karakaş and M.S. Çelik: Colloids Surf., A **434** (2013) 185. https://doi.org/10.1016/j.colsurfa.2013.05.051

17 F. Li, J. Jiang, L. Niu, J. Chen, Y. Zhang, Y. S. Wang, X. H. Li, and Z. J. Zhang: Prog. Org. Coat. **189** (2024) 108321. https://doi.org/10.1016/j.porgcoat.2024.108321
18 T. C. Rezende, J. C. M. Silvestre, P. V. Mendonça, J. Moniz, A. C. Serra, and J. F. J. Coelho: Prog. Org. Coat. **165** (2022) 106734. https://doi.org/10.1016/j.porgcoat.2022.106734
19 S. M. Fufa, B. P. Jelle, and P. J. Hovde: Prog. Org. Coat. **76** (2013) 1543. https://doi.org/10.1016/j.porgcoat.2013.06.008

About the Authors

Wen-Cheng (Agingu) Shih received his Ph.D. degree from Taiwan University, Taiwan, in 2007. After that, he has played multiple roles in R&D, technical marketing, and operation in the titanium dioxide industry. His research interests are in heterogeneous catalysis and surface modifications of inorganic oxide on pigment. (agingu.shih@gmail.com)