

EFFECT OF UNTREATED SILICA ON MATT FINISHED OF  
POLYACRYLIC/POLYURETHANE WATERBORNE TOPCOAT

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## ABSTRACT

Matt-finished coating is one of trendy aesthetics characters that regarded to a reduction in the amount of a specular reflected light as a result of the surface roughness. Transparency is a challenge to produce a clear matt-finished topcoat. Incorporating matting agent into the system will affect the transparency of the coating. Waterborne polyacrylic/polyurethane (PA/PU) topcoats at three different PA/PU ratios (100:0, 80:20, 60:40) were blended with untreated silica as a matting agent at different weight percentages, namely, 0.5 wt%, 1.0 wt% and 1.5 wt%. Liquid paint properties and dried film were analysed and characterized. From a Fourier transform infrared analysis, the absorption peaks of PU were detected at  $1720 - 1730 \text{ cm}^{-1}$  for  $\text{-C=O}$  vibration and  $3360 - 3380 \text{ cm}^{-1}$  for  $\text{-NH}$  vibration. Meanwhile, the characteristic groups of PA were observed at  $1440 - 1450 \text{ cm}^{-1}$ ,  $1720 - 1730 \text{ cm}^{-1}$  and  $1150 - 1160 \text{ cm}^{-1}$  corresponding to C-H bonding,  $\text{-C=O}$  vibration and  $\text{-C-O-C}$  vibration, respectively. For fumed silica, the absorption peaks were detected at 801, 975 and  $1066 \text{ cm}^{-1}$ , corresponded to the silanol group. All these peaks confirmed the successful of incorporation of silica into PA/PU blend. For the liquid paint properties, non-volatile content of the waterborne paints showed increment when adding the untreated silica and PU as both contribute 100% and 40% respectively of solid content. Meanwhile, the gloss values of dried PA/PU film decreased with increasing silica amount due to the increase of surface roughness. Silica particles that embedded on the surface of film reflected the incident light at a certain specular angle ( $60^\circ$ ). As more silica was added into the formulations, more specular lights were scattered, hence imparted more matt-finished look (dull and flat). This was supported by the images from scanning electron microscopy that showed the formation of rough surface with the addition of silica. However, a sample that had PU in the formulation showed a bit smoother surface compared with the sample with 100% PA. This was thought due to the elastomeric part of PU had buried the silica particles deep into the PU matrix. Hence, less scattered specular lights were projected to the surface. The arguments were supported by the opacity analysis where sample with 20 wt% PU at 1wt% silica had a lower contrast ratio of 6.26 (less matte) compared to the sample with 100% PA at 1 wt% silica which had 6.32 (more matte). This implied that PA/PU ratio had also influenced the opacity of the sample. Based on the study, incorporation of untreated silica will affect the transparency and will reduce down the gloss of the film coating. The higher the dosage is, the less transparent the film coating will be, thus more matt the finishing will be. On the other hand, it was failed to prove that the untreated silica can be the associative thickener in the system due to the incorporation of the PU thickener.

## ABSTRAK

Salutan kusam adalah salah satu nilai estetika terkini yang merujuk kepada pengurangan jumlah cahaya spekulat yang dipantulkan oleh cahaya insiden yang disebabkan oleh kekasaran permukaan. Penghasilan filem yang lutsinar adalah satu cabaran untuk membuat salutan kusam. Ini disebabkan ejen pengkusaman yang dimasukkan ke dalam sistem akan memberi kesan kepada salutan filem yang lutsinar. Lapisan atas poliakrilik / poliuriten (PA / PU) berasaskan air dihasilkan pada tiga nisbah berbeza; PA / PU (100: 0, 80:20, 60:40) telah dicampur dengan silika tidak dirawat sebagai ejen pengkusaman pada peratusan berat yang berbeza, iaitu, 0.5% berat, 1.0% dan 1.5%. Sifat cat air dan filem telah dianalisis dan dicirikan melalui kaedah Fourier transformasi inframerah (FTIR). Puncak penyerapan PU dikesan pada  $1720 - 1730 \text{ cm}^{-1}$  untuk  $\text{-C = O}$  getaran dan  $3360-3380 \text{ cm}^{-1}$  untuk getaran  $\text{-NH}$ . Sementara itu, kumpulan ciri PA diperhatikan pada  $1440 - 1450 \text{ cm}^{-1}$ ,  $1720-1730 \text{ cm}^{-1}$  dan  $1150-1160 \text{ cm}^{-1}$  yang sepadan dengan ikatan C-H,  $\text{-C = O}$  getaran dan  $\text{-C-O-C}$  getaran, masing-masing. Untuk silika marah akibat, puncak penyerapan dikesan pada  $801 \text{ cm}^{-1}$ ,  $975 \text{ cm}^{-1}$  dan  $1066 \text{ cm}^{-1}$ , merujuk kepada kumpulan silanol. Semua puncak ini mengesahkan bahawa silika berjaya disatukan dalam sistem campuran PA / PU. Bagi ciri-ciri cat cecair, kandungan tidak meruap daripada cat air menunjukkan peningkatan apabila silika yang tidak dirawat dan PU ditambah kerana masing-masing menyumbang 100% dan 40% kandungan pepejal. Sementara itu, nilai kekilatan filem PA / PU menurun dengan peningkatan jumlah silika kerana peningkatan kekasaran permukaan. Zarah silika yang tertanam di permukaan filem memantulkan cahaya insiden pada sudut spekulat tertentu ( $60^\circ$ ). Oleh sebab lebih silika telah ditambah ke dalam formulasi, kurang pemantulan cahaya spekulat dan menghasilkan filem kusam (kusam dan rata). Ini disokong oleh imej dari imbasan mikroskop elektron (SEM) yang menunjukkan pembentukan permukaan kasar dengan penambahan silika. Walau bagaimanapun, sampel yang mempunyai PU menunjukkan permukaan yang lebih licin berbanding dengan sampel dengan 100% PA. Ini barangkali disebabkan oleh bahagian elastomer daripada PU telah menyebabkan zarah silika tertanam jauh ke dalam matriks PU ini. Oleh itu, cahaya spekulat kurang dipantulkan ke permukaan. Hujah-hujah yang disokong oleh analisis kelegapan di mana sampel dengan 20% PU di 1% silika mempunyai nisbah kontras yang lebih rendah sebanyak 6.26 (kurang kusam) berbanding sampel dengan 100% PA pada 1% silika yang mempunyai 6.32 (lebih kusam). Ini bermaksud bahawa nisbah PA / PU juga telah mempengaruhi kelegapan sampel. Berdasarkan kajian, penambahan silika yang tidak dirawat akan menjejaskan lutsinar dan akan mengurangkan kekilatan salutan filem. Semakin tinggi dos silika yang ditambah, filem semakin kurang lutsinar, maka filem akan lebih kusam. Selain itu, kajian ini telah gagal membuktikan bahawa silika yang tidak dirawat boleh menjadi pemekat bersekutu dalam sistem kerana kehadiran pemekat PU.

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**LIST OF ABBREVIATION**

ASTM	-	American Society for Testing and Material
FTIR	-	Fourier Transform Infrared
MFFT	-	Minimum Film-Formation Temperature
PA	-	Polyacrylic
PU	-	Polyurethane
PVAC	-	Polyvinyl acetate
VOC	-	Volatile Organic Compound

**LIST OF SYMBOLS**

%	-	Percent
°C	-	Degree Celsius
wt%	-	Weight percentage
T <sub>g</sub>	-	Glass transition temperature
hr	-	Hour
kg	-	Kilogram
g	-	Gram
rpm	-	Rotation per minute
μm	-	Micro meter

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Study

Coatings are usually applied as multi-layered systems that are composed of primer and topcoat. Each coating layer is applied to perform certain specific functions, though its activities are influenced by the other layers in the system (Fletcher, 2001). Primer coating imparts the adhesion of the coating with the substrate, while topcoat is used for protection and durability of the final coating. Apart from retaining the aesthetic appearance and protecting the underlying substrates, topcoats are susceptible to damage caused by many elements such as scratch and abrasion. For woodwork such as wooden furniture, scratch resistance can be obtained by formulating the highly cross-linked films but they have poor impact resistance (Mathiazhagan and Joseph, 2011). On the contrary, soft films with less cross-linked show better anti-fingerprint and impact resistance but have poor scratch and abrasion resistances (Li *et. al*, 2014). Thus, in order to obtain optimal characters between impact and scratch resistance, the correct combination of hardness and flexibility is crucial.

For wood surface, waterborne polyurethane (PU) is one of the popular choices of topcoat binder. It has excellent flexibility, toughness good pigment-wetting properties and good scratch resistance (Vilas *et. al.*, 2009). After all, the hydroxyl group (OH) that attached to its molecular structure could contribute to the formation of hydrogen bonding with cellulose of wood surface, thus giving good

interfacial adhesion. Like other waterborne systems such as polyacrylic (PA) and polyvinyl acetate (pVAc), waterborne PU uses water as a dispersion medium, thus making it with low volatile organic compound (VOC) and eco-friendly (Overbeek, 2010). It has high solid content (80%) and easy to apply onto the substrate (Karl, 1997). However, PU has poor durability, transparency, rigidity, chemical and weather resistance. Normally PU will be blended with other amorphous resin such as PA to obtain such a balance properties (Lambourne and Strivens, 1999). In return, this also can cut the production cost due to the expensive price of PU over PA. Hence, in this study, PA/PU blend was used as a binder of the topcoat in which the combination between PA/PU blend exhibits the right balance between hardness and flexibility. Furthermore, both binders can be formulated as clear coats or pigmented topcoats with a high gloss finish (Gunde *et. al.*, 2007).

In the modern era, matt-finished topcoats are becoming the new trend due to its 'dull-aesthetic appearance'. The most important aspect of matt-finished surface is its excellent ability to hide surface imperfections compared with a higher gloss surface (Marta, 2006). The glossiness of paint films can be classified according to the degree of specular reflection where elements such as intensity of specular reflection, distinctness of images and grazing incidence sheen affect the gloss (Bullett, 1999). These elements are correlated with substrates, film thickness, the film smoothness and the appearance of the film. However, the matt-finished film shows no specular reflection even at grazing incidence. To produce matt-finished topcoats, matting agents such as silica, wax and fillers are normally added into binders. Among the agents, untreated silica offers advantages such as very high matting efficiency, high transparency and suitable for the coating system that difficult to be matted (Evonik Industries, 2014). Furthermore, with higher concentration, it can act as an associative thickener for the coating system and can be used in many clear waterborne coatings (Butler *et. al.*, 2005).

In this study, waterborne topcoat was prepared. PA and PU was blended at different PA:PU ratios which were 100:0, 80:20 and 60:40, respectively. Various amounts of untreated silica powder at 0.5wt%, 1.0wt% and 1.5wt% were added into

each binder accordingly. The paints were casted on black and white card as films and dried prior to characterizations.

## **1.2 Problem Statement**

Transparency is an important criterion for topcoat application. However, for a matte-finished topcoat, the addition of matting agent i.e. untreated silica into the binder affects a degree of clarity, thus transparency of the film. As reported by previous research, the clarity of film is affected by the amount of matting agent, type of binder and thickness of the film (Evonik Industries, 2014). Apart from that, the compatibility of binder with matting agent also influences the dispersity of matting particles across the binder. Therefore, in this research, the amount untreated silica and the ratio of PA/PU binder were varied. Properties such as glossiness and surface morphology were investigated. Meanwhile, because untreated silica is able to play second role as an associative thickener, the viscosity of the binder and total solid content were also verified. Viscosity is important to ensure that the topcoat can be applied or sprayed on the substrates. To date, no comprehensive study has been made on the effects of untreated silica on the matting degree and surface morphology of the waterborne PA/PU topcoat for wood substrate.

## **1.3 Objective**

The main objective of this research is to study the effect of untreated silica as matting agent on the matt-finished topcoat waterborne PA/PU. This objective can be divided into two subtopics as follows:

1. To analyze the effect of various contents of untreated silica towards the properties of PA/PU binder in terms of glossiness, surface morphology, viscosity and total solid content.

2. To investigate the effect of various blending ratio of PA:PU in terms of glossiness, surface morphology, viscosity and total solid content.

#### **1.4 Scope of Study**

Following are scopes of study in order to achieve the objectives:

1. Preparation of paint at various PA:PU ratios (100:0, 80:20 and 60:40)
2. Addition of untreated silica at 0.0wt%, 0.5wt%, 1.0wt% and 1.5wt% into PA/PU binders.
3. The formulated topcoats were drawn-down to form films using bar coater with wet film thickness of 90 micron and 120 micron on white and black card.
4. Testing and characterizations.
  - i. The samples were prepared in film and latex form. They had undergone few characterizations as follows;
  - ii. Fourier transform infrared spectroscopy (FTIR)
  - iii. Scanning electron microscopy (SEM)
  - iv. Gloss measurement
  - v. Viscosity measurement with flow cup DIN 6 (ASTM D1200)
  - vi. Non-volatile content of paint (total solid content) according to ASTM D2832.
  - vii. pH measurement
  - viii. Analysis of transparency using Datacolor 650 series based on contrast reading.

## REFERENCES

- Barthel, H., Heinemann, M., Stintz, M. and Wessely, B. (1998). Particle Sizes of Fumed Silica. *Chemical Engineering Technology*. 21, 9.
- Butler, L. N., Fellows, C. M., Gilbert, R. G. (2005). Effect of Surfactants Used for Binder Synthesis on The Properties of Latex Paints. *Progress in Organic Coatings*. 53(2), 112-118.
- Christ, U., Bittner, A. (1994). Rheology Control of Organic Coatings with New Hydrophobic Silicas. *Progress in Organic Coatings*. 24(9), 29-41.
- Christopher, P. R. (2000). The Behaviour of Silica in Matt Water-based Lacquers. Doctor of Philosophy. St. Catherine's College, Cambridge.
- Doren, K., Freitag, W., Stoye, D. (1994). Water-Borne Coatings: The Environmentally-friendly Alternative, Hanser Publishers, Munich Vienna New York, US. 49-50.
- Evonik Industries (2013). Novel matting agents for low VOC coatings. [Brochure]. Germany: Author.
- Fletcher, T.E. (2001). A Simple Model to Describe Relationships Between Gloss Behaviour, Matting Agent Concentration and The Rheology of Matted Paints and Coatings. *Progress in Organics Coatings*. 44(5), 25-36.
- Faouzi, N., Naceur, A. and Chevalier, Y. (2008). Matting Agent Concentration and Its Effect on the Colour and the Rheology of Matted Coatings. *Journal of Applied Sciences*. 8(8), 1527-1533.
- Gunde, M.K., Kunaver, M., Cekada, M. (2006). Surface Analysis of Matt Powder Coatings. *Dyes and Pigments*. 74(1), 202-207.
- Hellgren, A.C., Weissenborn, P., Holmberg, K. (1999). Surfactants in Water-borne Paints. *Progress in Organic Coatings*. 35(2), 79-87.

- Hinder, S.J., Lowe, C., Maxted, J. T., Perruchot, C., Watts, J. F. (2005). Intercoat Adhesion Failure in A Multilayer Coating System: An X-ray Photoelectron Spectroscopy Study. *Progress in Organic Coatings*. 54(3), 20-27.
- Hinder, S.J., Lowe, C., Maxted, J. T., Watts, J. F. (2005). Migration and Segregation Phenomena of A Silicone Additive in A Multilayer Organic Coating. *Progress in Organic Coatings*. 54(4), 104-112.
- Karl, L. N. (1997). Waterborne polyurethanes. *Progress in Organic Coatings*. 32(4), 131–136.
- Kukanja, D., Golob, J., Valant, A. Z. and Kranja, M. (1999). The Structure and Properties of Acrylic/Polyurethane Hybrid Emulsions and Comparison with Physical Blends. *Journal of Applied Polymer Science*. 78, 67-80.
- Lambourne, R and Strivens T.A. (1999). Paint and Surface Coatings: Theory and Practice, William Andrew Publishing, Cambridge, England. 44, 642-643.
- Li, J., Zheng, W., Zhang, D., Peng, X. (2014). Structure, Properties and Application of A Novel Low-glossed Waterborne Polyurethane. *Applied Surface Science*. 307(4), 255-262.
- Mathiazhagan, A. and Joseph, R. (2011) Nanotechnology-A New Prospective in Organic Coating –Review. *International Journal of Chemical Engineering and Applications*. 2(4), 225-237.
- Overbeek, A. D. (2010). Polymer Heterogeneity in Waterborne Coatings. *Journal of Coating Technology Resources*. 7(1), 1–21.
- Ou, J., Zhang, M., Liu, H., Zhang, L. and Pang, H. (2014). Matting Film Prepared from Waterborne Acrylic / Micro-SiO<sub>2</sub> Blends. *Journal of Applied polymer Science*.10(1002), 41707.
- Pardini, O. R. and Amalvy, J. I. (2007). FTIR, <sup>1</sup>H-NMR Spectra and Thermal Characterization of Water-based Polyurethane/Acrylic Hybrids. *Journal of Applied Polymer Science*. 107, 1207-1214.
- Rabea, A.M., Mohseni, M., Mirabedini, S. M., Tabatabaei, M. H. (2011). Surface Analysis and Anti-Graffiti Behaviour of A Weathered Polyurethane-based Coating Embedded with Hydrophobic Nano Silica. *Applied Surface Science*. 258, 4391-4396.

- Rajput, S.D., Hundiwale, D.G., Mahulikar, P.P., Gite, V. V. (2014). Fatty Acids Based Transparent Polyurethane Films and Coatings. *Progress in Organic Coatings*. 77, 1360-1368.
- Reza Eslami, Rouhollah Bagheri, Yasser Hashemzadeh, Mehdi Salehi. (2014). Optical and Mechanical Properties of Transparent Acrylic Based Polyurethane Nano Silica Composites Coatings. *Progress in Organic Coatings*. 77, 1184-1190.
- Scrinzi, E., Rossi, S., Deflorian, F. and Zanella, C. (2011). Evaluation of Aesthetic Durability of Waterborne Polyurethane Coatings Applied on Wood for Interior Applications. *Progress in Organic Coatings*. 72, 81-87.
- Son, S.J., Kim, K. B., Lee, Y.H., Lee, D.J. and Kim, H.D. (2011). Effect of Acrylic Monomer Content on The Properties of Waterborne Poly(urethane-urea)/Acrylic Hybrid Materials. *Journal of Applied Polymer Science*. 124, 5113-5121.
- Talbert, R. (2008). Paint Technology Handbook, CRC Press Taylor & Francis Group, United States of America. 87, 176.
- Vilas, D., Athawale, M. and Kulkarni A. (2009) Preparation and Properties of Urethane/Acrylate Composite by Emulsion Polymerization Technique. *Progress in Organic Coatings*. 65(3), 392–400.
- Wang, N., Xiong, D. (2014) Comparison of Micro-/Nano-Hierarchical and Nano-Scale Roughness of Silica Membranes in Terms of Wetting Behaviour and Transparency. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 446, 8–14.
- Weldon, D. G. (2009). Failure Analysis of Paints and Coatings, John Wiley and Sons, Ltd, West Sussex. United Kingdom. 92, 152, 238.
- Wu, L., Yu, H., Yan, J. and You, B. (2001). Structure and Composition of The Surface of Urethane/Acrylic Composite Latex Films. *Polymer International*. 50, 1288-1293.