Macromol. Symp. ***187****, 187–198 (2002)*

New Generation Decorative Paint Technology

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Summary: The growth of waterborne paints in the higher performance decorative paint segments (like in high gloss paints, trim paints and also in stains and varnishes) has been slowed down due to a lack of open time, rheology, film build and scratch resistance.

Over the years the improvement of the open time has been an intense area of research, but to date the typical paint rheology and brushing performance of a solvent based paint could not be achieved in a waterborne system. In this paper very low viscosity oligomers are presented as a solution for the open time problem. These oligomers remain liquid even after the evaporation of water and are self-crosslinking to achieve good final properties. The oligomers are combined with a dispersed polymer to reduce tack free times of the resulting coatings and to increase the rate of development of the properties. A model system is described where this effect is demonstrated.

1. Introduction

1.1 Definition of open time and wet edge time

Figure 1 schematically represents a drying paint on a substrate. In the literature (1), the open time of the paint has been defined as the period of time, during which a painter can make corrections to the freshly applied wet paint film without leaving brush marks. Wet edge time (also referred to as lapping time) has been defined as the period of time during which no edge marks are produced when a freshly applied paint film is lapped over a previously painted area. The edges of the paint film are thinner and therefore will dry more rapidly. If the edge of the paint is dry and is subsequently repainted with a new layer of paint, the dried edge will telegraph through the freshly applied paint layer and cause an irregularity at the paint surface. This is undesirable. Since the edges dry faster than the bulk of the paint the wet edge time is the most critical parameter determining how long the paint remains "open".

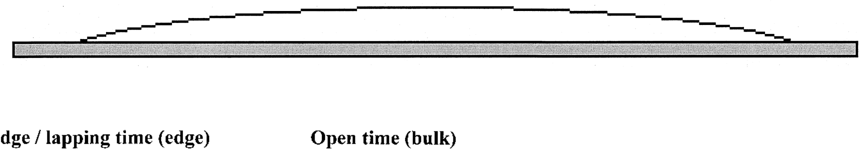

Figure 1. *Wet edge time / lapping and open time.*

CCC 1022-1360/00/$ 17.50+.50/0

1.2 Open time, through drying and viscosity of paints and coatings

In Figure 2, three important viscosity based events are related to the speed of drying. Firstly, the paint requires a certain open time as discussed above (low viscosity). The next stage is inevitably a tacky paint film (medium viscosity), which can no longer be corrected but will easily be damaged. Preferably this stage is very short. Then a certain hardness and abrasion resistance will be achieved (high viscosity), and the paint film should become sandable if a second coat needs to be applied. At this stage, the paint film is not easily damaged any more. This final stage should preferably be reached as quickly as possible.

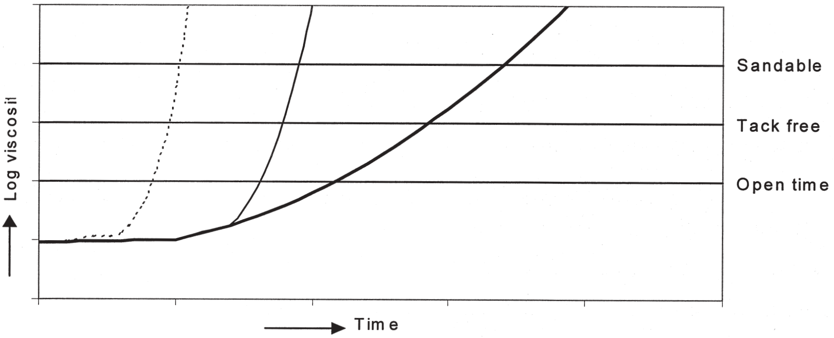

Figure 2. Drying profiles of different paints.

Conventional acrylic dispersions typically have a drying profile represented by the dotted line in Figure 2. They have a short open time, but are also rapidly achieving final properties, and become tack free in a short period of time. The bold straight line in Figure 2 represents conventional solvent based alkyd paints. Whereas they have a long open time, solvent based alkyds in many cases probably dry too slowly; tack free times are most usually many hours. Therefore, in a perfect system the open time would be much longer than for the current waterborne systems, but once this time has elapsed the final stage should be reached rapidly, like is depicted by the thin line in Figure 2. In other words, in the initial stages the drying behaviour of a solvent based alkyd is desired, while at the later stages the drying behaviour of a waterborne dispersion becomes more preferred.

1.3 Novel low viscosity oligomers

To achieve the desired improvement in open time and wet edge time the viscosity of the drying film needs to be low beyond the point after which most water has evaporated. The evaporation of water is too fast, even if techniques are used to delay this evaporation, or if very hydrophilic polymers are used. The desired very low viscosity after evaporation of water can only be achieved if low molecular weight oligomers, with preferably limited chain interactions (such as hydrogen bridging) are used. Of course small amounts of slowly evaporating solvents can be added to achieve even more control over the viscosity and rheology.

2. Results and Discussion

2.1 Experimental Section

2.1.1 Synthesis model system for a waterborne paint with good open time.

For the development of waterborne paint with a good open time and to illustrate the concept, we used a model binder system consisting of an oligomer dispersion and an acrylic dispersed polymer latex. The oligomer dispersion is prepared by dispersion of a carboxylic acid containing fatty acid functional urethane oligomer in water with the aid of a neutralising agent and a small amount of organic solvents. The urethane oligomer PU-1 is the product of the addition reaction between a diisocyanate and a polyol mixture consisting of a fatty acid polyol, dimethylol propionic acid, methoxy polyethylene glycol 750 and cyclohexane dimethanol (2). A drier salt is used for autoxidative crosslinking of the fatty acid functionality of the urethane oligomer. The acrylic dispersed polymer latex P-1 is a BA/MMA/AA copolymer prepared by a standard emulsion polymerisation technique (3). The oligomer polymer paint system is prepared by blending of the oligomer dispersion with the acrylic dispersed polymer latex and subsequent formulation of the binder to a paint system.

2.1.2 Test methods for wet edge open time, dust free and tack free time

To test the wet edge open time, the aqueous pigmented paint was applied to a test chart (18x24cm, form 8B - display, available from Leneta Company) using a wire rod, at a wet film thickness of 120μm. Wet edge open time tests were performed at fairly regular time intervals, the intervals between measurements decreasing towards the end of the run. The measurements were carried out at relative humidity levels of 50 +/- 5%, temperatures of 23 +/- 2°C and an airflow ≤ 0.1m/s.

The *wet edge open time* (4) was determined by brushing a virgin 25cm^2 edge area of the coated chart with a brush (Monoblock no 12, pure bristles/polyester 5408-12) carrying some more of the composition with a brush pressure of 100-150g during 30 seconds. In this time the brush was moved in one set of 5 times in the direction of the width of the substrate and 5 times in the direction of length of the substrate before visually assessing the coating.

Once the composition carried on the brush no longer formed a homogeneous layer with the coating on the substrate and/or a visible lap line could be seen the wet edge time was considered to be over. To test the wet edge time, the binders were evaluated in a pigmented paint formulation; see table 1:

Table 1. *A typical pigmented paint formulation*

	Ingredients		Part by weight
1.	Binder (based on PU-1 and P-1)		118.4
2.	Water		11.8
3.	Dehydran 1293	(defoamer trademark from Cognis)	0.8
4.	Disperbyk 181	(wetting agent trademark from Byk Chemie)	1.6
5.	TiO_2 RDIS	(Trademark from Finntitan)	45.8
6.	Dehydran 1293	(defoamer trademark from Cognis)	2.0
7.	NLS-210	(low shear thickener trademark from Hercules)	1.0
8.	Nuvis FX-1070	(high shear thickener trademark from Sasol Servo)	4.0
9.	Dapro 5005	(Drier salt trademark from Elementis Specialties)	0.15
		Total:	185.6

2.2 Phase inversion

The oligomers used for these new decorative coating systems are initially present as dispersed particles in the water phase. However, upon drying these particles will coalesce and eventually form the continuous phase after "phase inversion" has taken place. Since this newly formed continuous phase has a low viscosity and has the required rheological behaviour as also found in solvent based paints, the open time of the paint has been decoupled from the evaporation of water. As will be explained in more detail, the phase inversion point is a critical point in such a system. Certain aqueous binders, like for instance alkyd emulsions, are going from an oil in water to a water in oil dispersion during drying. Generally, a very high viscosity peak is observed during this phase inversion process, which is very undesirable when good open time and lapping are required. This can be observed in Figure 3, in which two solids-viscosity curves are presented.

In this graph a conventional oligomer is compared with the low viscosity oligomer PU-1. The latter has a significantly lower and more narrow phase inversion peak. As a consequence, it will require less force to brush through a paint film based on this novel oligomer at the phase inversion solids than it would be for a paint based on the conventional oligomer. With the conventional oligomer system a painter would experience severe tugging and a lack of flow of the paint.

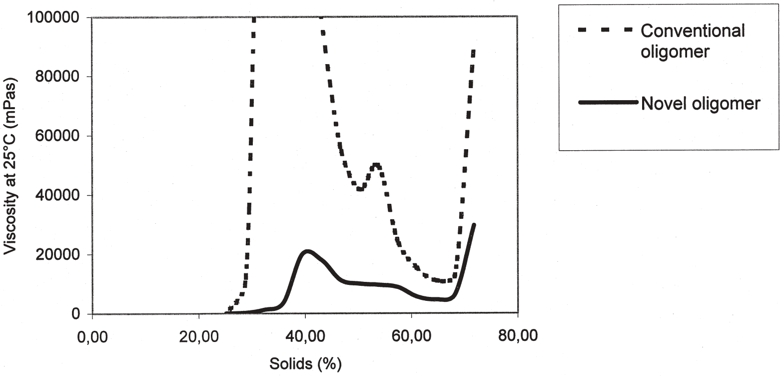

Figure 3. *Phase inversion peak of the low viscosity urethane oligomer PU-1 and of a conventional oligomer, in which the solids is decreased by diluting the oligomers with water.*

In Figure 4, the viscosity and conductivity of the urethane oligomer during phase inversion is measured, starting at low solids and increasing the solids level by blowing N_2 over the surface of the sample. If the conductivity is measured during drying a decrease in conductivity is found during the phase inversion, which is expected since water will no longer be the continuous phase, but will become a dispersed phase inside a continuous oligomer phase. A small increase in conductivity is found at around 50% solids, which is most likely caused by disappearance of the dispersed water droplets. The remaining water, and salts dissolved in this water, will now dissolve in the continuous phase causing the increased conductivity. From here on the conductivity will gradually decrease further since the dissolved water will continue to evaporate.

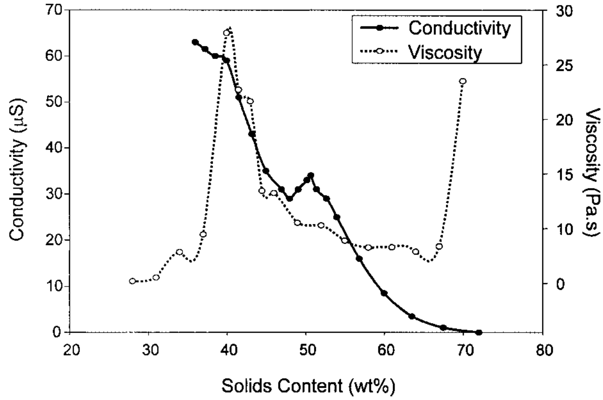

Figure 4. *Phase inversion of the urethane oligomer PU-1, starting at low solids; increase in solids is obtained by blowing N_2 over the sample surface.*

It is important to observe that the viscosity recovers to a very low value after the phase inversion, where in conventional waterborne systems the viscosity would remain infinitely high after the particles have come in contact with each other. This demonstrates that the concept of using low viscosity oligomers to control the rheology after evaporation of most of the water will indeed result in a significantly extended time during which the coating film will remain low in viscosity and hence "open". One of the reasons why the low and narrow phase inversion peak for PU-1 will not result in brush drag is that the solids increase due to water evaporation, as discussed earlier, will be dependent on the distance from a certain location in the coating to the coating surface. Therefore, the degree of phase inversion during drying will not be equal at all depths in the coating (See Figure 5) and especially for narrow phase inversion peaks this will result in a "smoothing" of the viscosity peak of the paint film. The painter will only experience the total force needed for brushing, so very thin layers with a solids close to phase inversion solids and with the concomitant high phase inversion viscosity, will not ruin the brushability, since the painter will only experience the average force needed to brush through the whole paint film. By strictly controlling the design of the oligomers, the undesired (high and broad) phase inversion peak viscosity could be further reduced and almost eliminated.

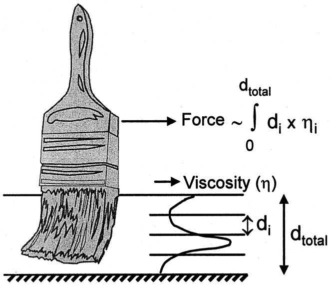

Figure 5. Viscosity profile through the drying paint film.

The phase inversion is also visualised in Figure 6 showing the appearance of the urethane oligomer PU-1 at different solids. It can clearly be seen from this Figure that the "phase inversion" followed by the dissolution of the water droplets, is completed at ca. 52% solids.

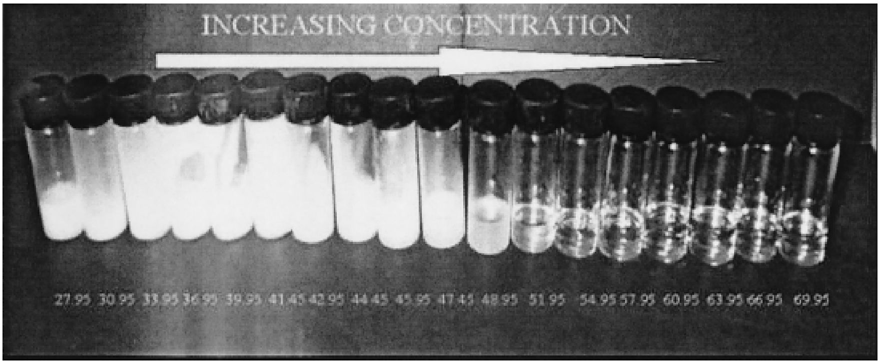

Figure 6. *Appearance of the oligomers at increasing solids level.*

During the drying process, the ratio of solvent to water will continue to increase (see Figure 7) since the evaporation rate of the solvents used is lower than that of water. Due to this increased solvent to water ratio the oligomer particle will "dissolve" in a solvent/water mixture after a critical solvent/water ratio is reached. If a less water miscible solvent is used,the "dissolution" of oligomer particles in the continuous phase will be delayed and a more conventional phase inversion from "oil in water" to "water in oil" will occur.

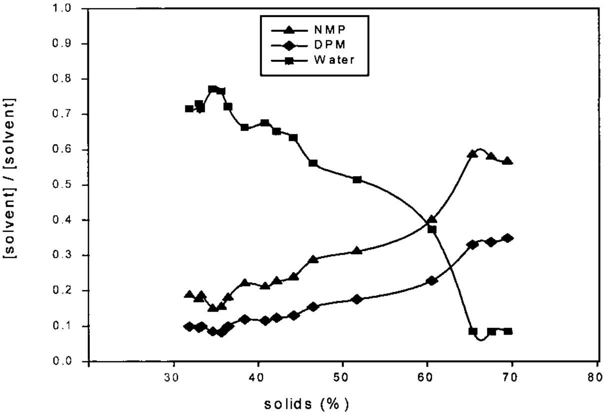

Figure 7. *Fractional solvent content during drying of the urethane oligomer dispersion PU-1.*

The rheology of the oligomer dispersion (see Figure 8) before phase inversion is (slightly) shear thinning like most waterborne dispersions. This can be expected since at this stage the oligomers are present as dispersed particles. The shear thinning behaviour progressively increases with increasing solids. At phase inversion and the associated viscosity maximum, the system is strongly shear thinning. After the phase inversion the system behaves Newtonian (5).

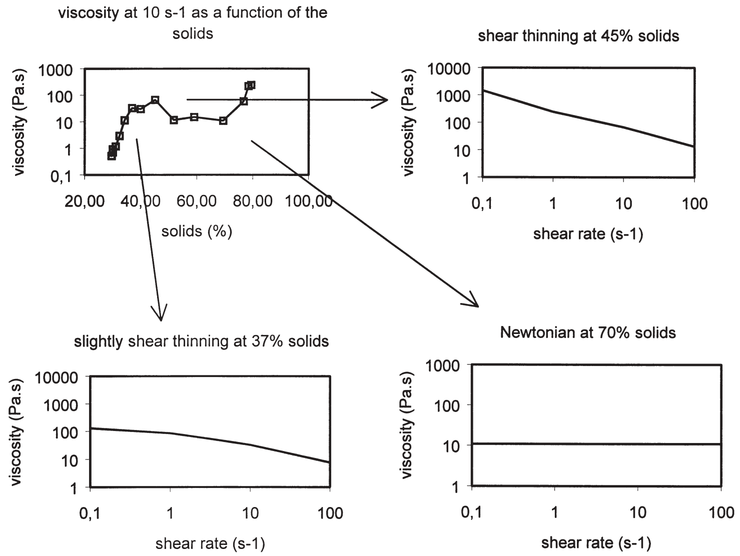

Figure 8. *Rheology profiles of the urethane oligomer dispersion PU-1 at various points on the solids/viscosity curve.*

2.3 Closing the paint

Obviously, if oligomers of low viscosity are used as the sole binder component, the resulting paint layer will remain open forever, which is clearly not desired. The final paint should have a reasonable dust and tack free time as well and should become sandable within a specific timeframe so that it can be repainted if required. Conventional solvent based alkyd paints close because:

1. the solvents are evaporating (alkyds are not that low in viscosity that they still flow at 100% solids).
2. alkyds are self-crosslinking by autoxidation (the crosslinking will build the molecular weight, and thereby the properties of the coating will improve).

Similarly, the closing of waterborne paints containing oligomers can be controlled by:

1. evaporation of water (and the solvent(s) that are optionally present).
2. self-crosslinking of the oligomers (to build the molecular weight and final properties).
3. combination with a dispersed polymer, of which it is known that good final properties can be achieved very rapidly.

The advantage of using small amounts of slow evaporating solvent(s) is that the viscosity is reduced even at relatively high oligomer molecular weights. When the oligomers have a higher initial molecular weight, less crosslinking will be required to achieve the desired properties, which will also occur faster.

The addition of a dispersed polymer of high molecular weight will certainly help to reach the desired end properties more rapidly (see Figure 9). If the dispersed polymer is designed to be stable as a dispersion in water and also stable as a dispersion in the oligomer phase after phase inversion, the final film will consist of a matrix of self-crosslinking oligomers with high molecular weight polymeric particles dispersed herein. Depending on the loading of the dispersed polymer in this system the polymer particles can even touch each other to form a bi-continuous film.

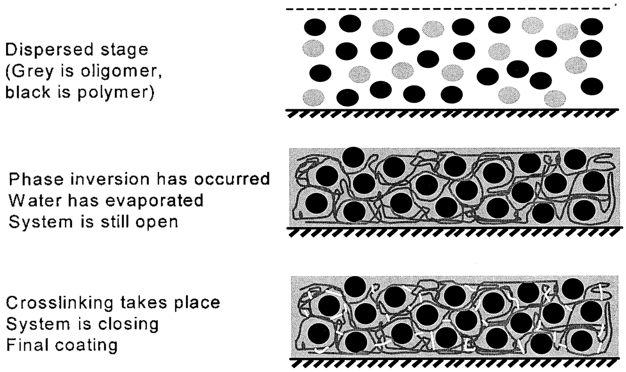

Figure 9. Film formation of the waterborne open time system.

But even if they do not touch the entanglement of the crosslinking oligomers with chains of the polymer inside the particles will cause a very rapid property development. The film formation process, as depicted in Figure 9, starts with the initial dispersion with dispersed particles of oligomer as well as dispersed polymer particles. Upon evaporation of water, phase inversion will occur and the continuous phase will now be the oligomer with polymeric particles being dispersed therein. At this stage the film is still "open". Due to the combined effect of molecular weight build up by self-crosslinking(20, 21). and the continued evaporation of water and cosolvent, the wet paint will start to close and the final properties are building up rapidly. Using this approach the combination of the excellent final properties of acrylic dispersions can be combined with the strongly desired rheological behaviour of conventional solvent based paints.

2.4 Drying at different blend ratios of oligomer and polymer

A set of oligomer/polymer blend ratios were prepared to study the optimal ratio for a good wet edge open time with good through drying times. These blend systems were formulated into a paint (see Section 2.1) and checked for their drying characteristics. For reference purposes, a set of blend ratios of a conventional oligomer (alkyd emulsion) with the same acrylic dispersion was compared in the same paint formulation. The results are summarised in Figures 10 and 11.

As can be seen from Figure 10, good (wet edge) open times can be achieved by using PU-1 oligomer levels as low as 30% on binder solids, whereas the (wet edge) open time of alkyd emulsion based paints are short throughout the range of oligomer polymer ratios. From Figure 11 can be seen that acceptable dust and tack free times can be achieved by selection of the appropriate level of dispersed polymer in the paint. In conclusion, especially at oligomer levels between 20 and 60% an interesting combination of drying properties can be obtained. Below 20 % oligomer wet edge times become very short and above 60 %, tack free times get unacceptably long.

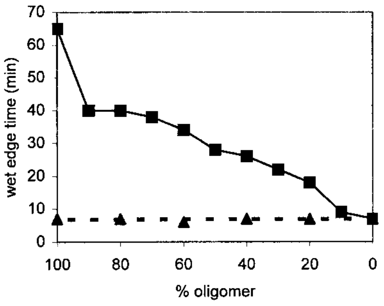

Figure 10. Wet edge open times of paint systems on Leneta test chart based on different ratios of the blend of the urethane oligomer PU-1 and the acrylic dispersed polymer P-1 (straight line), compared to similar blends of a commercial alkyd emulsion and P-1 (dashed line).

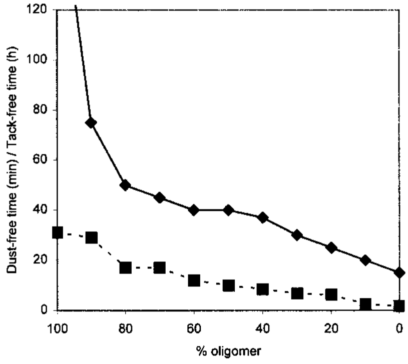

Figure 11. Dust free times (straight line) and tack free times (dashed line) of paint systems based on different ratios of the urethane oligomer PU-1and the acrylic dispersed polymer P-1.

2.5 Comparison of the new technology with commercial paints.

As illustrated already in some detail, there is a clear difference between paint systems based on solvent borne technology, waterborne latex technology, alkyd emulsion technology and this new oligomer polymer paint technology.

Benchmarking commercial products which are available in the decorative market resulted in the following overview in figure 12. For reference purposes, the results for open time of the new oligomer/polymer concept are compared to the formulated acrylic dispersion TX200, a formulated alkyd emulsion, four commercial products as well as a solvent based alkyd.

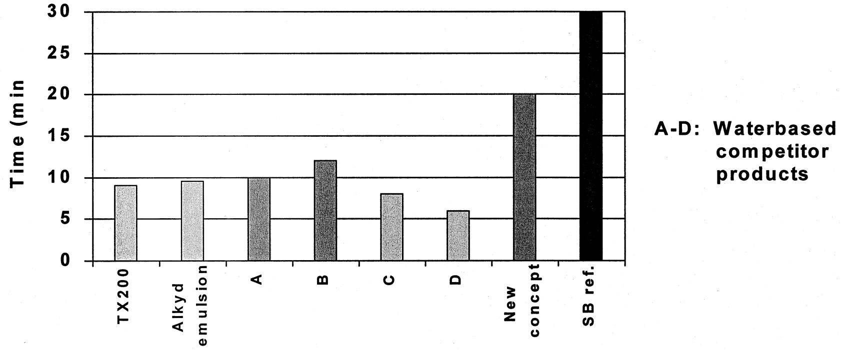

Figure 12. *An overview of the open time of waterbased paints compared to the new concept and a solvent based alkyd; all paints evaluated on Leneta test chart (non-absorbing).*

This figure clearly shows that still a big gap exists between open time of the current -state of the art- waterbased products and a solvent based alkyd. The new oligomer/polymer system is clearly outperforming all current waterbased paints available on the market with respect to open time.

3. Conclusion

A waterborne paint with an improved wet edge open time and a relatively short tack free time can now be obtained by the combination of a dispersion of a very low viscosity oligomer and a high Mw dispersed polymer. The lack of this piece of technology has retarded the changeover from solvent based to waterborne decorative coatings for the last twenty years. The expectation is warranted that we will see significant activity in the coatings industry in the coming years to explore the potential of this new technology for further improvement of the safety, health and environmental profile of decorative coatings.

4. Acknowledgements

We would like to thank Emilio Martin, Pablo Steenwinkel, Tom Annable John Padget, Jurgen Scheerder, Ludy van Hilst, Ad Ernst, Ankie van Gorkum, John Gerrard, Rob le Febre, Sjoerd Buil, Frank Nettenbreijers, Mourad Aabich, and Lex Donders for their contribution to the theoretical and practical work described in this paper.

Part of this article has been presented during the 2002 Athens Conference on Coatings Science & Technology.

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