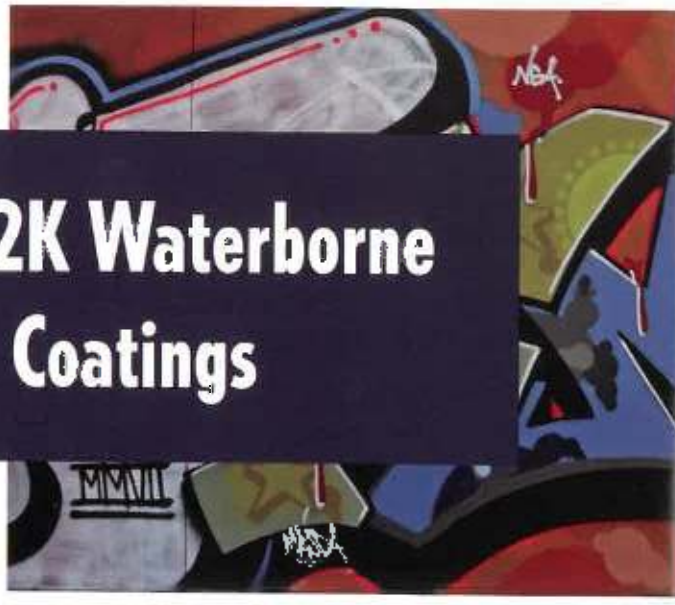


Development of Low-VOC 2K Waterborne Polyurethane Anti-Graffiti Coatings

by Xiaodong Wu and Richard P. Rosen
Rhodia, Inc.*

A low-VOC 2K waterborne polyurethane anti graffiti coating has been developed to address the industrial need for low-odor formulations using less solvent. The formulation platform methodology has effectively been applied to explore and optimize the film properties with a number of formulation parameters. The effect of isocyanate composition, NCO/OH ratio, and percentage of fluorine content on anti-graffiti performance has been studied. The surface and bulk film properties have been correlated with the anti-graffiti performance. It is found that the fluorine content at or near the coating surface and incorporating chain-stiffening IPDT to improve barrier properties are the most important factors for excellent anti-graffiti performance. In addition, these waterborne coatings demonstrate excellent recoatability and chemical resistance.

INTRODUCTION

Whether it is viewed as art or awful, graffiti has been targeted by the growing arsenal of technology. It is estimated that the cost of graffiti abatement programs runs in excess of $12 billion annually in the U.S. alone.[1,2] It has been reported that fluorinated polymers are the best candidates to give a coating surface with low surface free energy, to render hydrophobic and oleophobic characteristics. In addition, fluorinated polymers excel in durability and weatherability in comparison with other materials.[3,4]

The development of coatings having anti-graffiti performance has been ongoing for many years in the coatings industry. Coatings based on urethane chemistry remain the preferred technology for permanent anti-graffiti coatings due to the overall film properties, including mechanical properties, durability, and light stability. The most common approach is to make a coating with a very low surface free energy by incorporating fluoro-, perfluoro, or silicone component in the formulation. However, the resulting non-stick sur-

Presented at the 35th Annual International Waterborne, High-Solids, and Powder Coatings Symposium, Jan. 30-Feb. 1, 2008, in New Orleans, LA.

*350 George Patterson Blvd., Bristol, PA 19007.

face would lead to the problem of recoatability. After its service life, the coating has to be stripped before a new coating is applied.

The graffiti paint contains at least one composition of dye and solvent. After the graffiti paint is sprayed or applied onto the coating surface, the dye and solvent molecules will tend to diffuse or penetrate into the coating. The deeper the penetration, the more difficult the removal process will be. Therefore, an important design concept of a good anti-graffiti coating is the barrier property. For waterborne polyurethane coatings, the coating should have high enough crosslinking density to resist or guard against the swelling and diffusion of the graffiti paints, especially at the surface or near the surface. In addition, since anti-graffiti performance is more of a surface property, a coating surface must have low surface energy to minimize the contact of the graffiti paint. A key to the formulation is to find the right composition of the fluorinated polyol used in order to balance the lower surface energy, crosslinking density, recoatability, as well as the cost effectiveness. It should also be noted that the chain stiffness of the polymer network structure plays a very important role in the barrier properties. Therefore, incorporating the chain stiffening structure of IPDT in the polyurethane network will be a new design concept to achieve improved barrier properties for the anti-graffiti performance.

Currently, the trend in the coatings market is moving towards waterborne and low-emission "green" products. In this article, the emphasis on understanding the film properties that contribute to the anti-graffiti performance in two-component (2K) waterborne polyurethane coatings and finding the best method to characterize these coating systems has been addressed. In addition, the formulation platform methodology has been applied to analyze and optimize the anti-graffiti performance by using a statistical design of experiment (DOE) approach to deliver a cost-effective coating system.

EXPERIMENTAL

Materials

In 2K waterborne polyurethane coatings, a blend of a water dispersible acrylic polyol (Polyol A) and fluorinated acrylic polyol (Polyol F) is used in the polyol part, or Part A. Both polyols are commercial products and used as received. The fluorine content in the coating formulation can be adjusted by the blend ratio of the acrylic and fluorinated polyol.

In the isocyanate part, or Part B, hydrophilically modified polyisocyanates are used. Hardener M is based on HDT technology, trimer of hexamethylene diisocyanate (HDI), and Hardener D is based on both HDT and IPDT, trimer of isophorone diisocyanate (IPDI) technology. HDI has a linear structure, which gives a soft and flexible nature to the molecules, thus the T_g of its homopolymer is around –56°C. The introduction of the cyclohexyl group into the structure of IPDI significantly increases the chain stiffness or rigidity. The T_g of its homopolymer of IPDI is about 73°C.[5] In the formulations, either Hardener M with 10 wt% solvent is used as Hardener 1 or a blend of Hardener M and Hardener D at 1:1 weight ratio is used as Hardener 2. A formulation example is presented in Appendix A.

Regarding the graffiti removal, the representative testing paints and markers as well as the removal systems are listed in *Table* 1 in order to evaluate the anti-graffiti performance of these waterborne coatings. The removal systems are typical brands available at big box home improvement retail stores and used with tools such as cotton pad, sponge, or brush to clean the coating surface.

It should be noted that good anti-graffiti performance is more complicated due to the large variety of choices in paints and permanent markers with different

Table 1—List of Testing Graffiti Paints and Markers as well as Removal Systems

- Permanent Sharpie Marker
  - Blue, red, black, silver metallic
- Dry erase marker
  - Green, blue, brown
- Blue spray paint
- Green enamel paint
- Graffiti removal agent
  - Motsenbocker's Liftoff #3
  - Motsenbocker's Liftoff #4
  - Motsenbocker's Liftoff #5
  - KleanStrip brand of graffiti remover

Table 2—DOE Design for 2K Waterborne Polyurethane Anti-Graffiti Coatings

Sample #	Polyol A	Polyol F	Isocyanate Type	NCO/OH
161	60	40	Hardener 1	1.50
162	80	20	Hardener 1	1.50
163	100	0	Hardener 1	1.50
164	60	40	Hardener 1	2.50
165	80	20	Hardener 1	2.50
166	100	0	Hardener 1	2.50
170	60	40	Hardener 2	1.50
171	80	20	Hardener 2	1.50
172	100	0	Hardener 2	1.50
173	60	40	Hardener 2	2.50
174	80	20	Hardener 2	2.50
175	100	0	Hardener 2	2.50

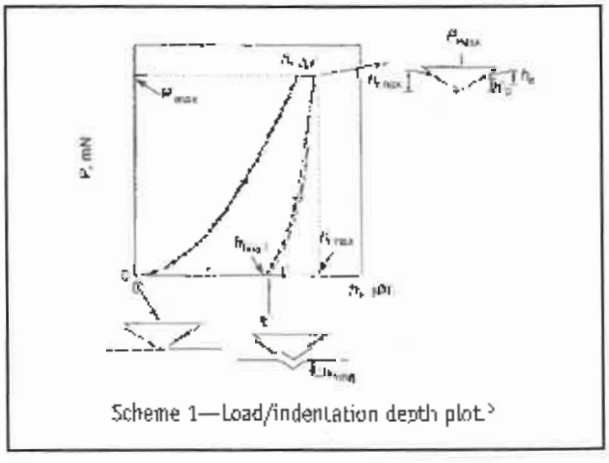
chemical compositions. In addition, selecting the proper graffiti removal agent is crucial to reach a good result (e.g., Liftoff #3 for latex paints; Liftoff #4 for spray paints; Liftoff #5 for markers; KleanStrip Brand of graffiti remover by W. M. Barr & Co., Inc. is a more aggressive removal agent). In some cases, a combination of two removal systems is found necessary to be able to reach total surface cleaning.

Dynamic Mechanical Analysis

Dynamic mechanical analysis of the waterborne coatings was performed on a TA Instruments DMA Q-800. The film samples were analyzed in tension at 1.0 Hz and 0.2% strain over a temperature range of 30°C and 160°C at a ramp rate of 3°C/min.

Instrumented Indentation Method

The mechanical properties of the coatings were also studied by the micro-indentation method. The hardness of the waterborne coatings, or Martens hardness HM, was measured on a Fischerscope HM2000 by Fischer Technology, Inc.[6,7] The indenter is a square diamond pyramid indenter with an opening angle of 136°. The waterborne coating was applied on an iron-phosphated steel panel and cured in a Controlled Temperature and Controlled Humidity (CTCH) room (75°F and 50% RH). All indentation measurements were conducted at the coating surface where the film thickness is 2.5 mils.



Scheme 1—Load/indentation depth plot.[7]

The test condition in this study is performed as follows: the normal test load increases at constant speed to reach 50 mN over a 20 sec period of time, and holds thereafter at 50 mN for 5 sec to allow the coating to creep. Subsequently, the load is released at the same rate as in the loading cycle. The result generates a load and indentation depth plot as shown in *Scheme* 1. It is illustrated that during the loading stage the indentation depth reaches h_1 at the maximum load. At the creep stage, the indentation depth increases Δ_h to h_{max}. After unloading the force, the residual indentation depth is at h_{final}. Martens hardness HM of the coating is determined from the plot during the loading stage.

Coating Formulation Design

Based on the previous studies, it was found that using acrylic polyols with hydrophilic polyisocyanates resulted in film with excellent hardness and crosslinking.[7] It was also found that the fluorinated acrylic polyol has lower reactivity towards hydrophilic polyisocyanates, especially Hardener D that contains IPDT. In addition, using above 50 wt% blend ratio of Polyol F in Polyol A results in poor film formation and phase separation occurs.[8] Therefore, the blend ratio between 0 and 40 wt% of Polyol F in Polyol A has been selected in the design at three levels including the midpoint at 0, 20, 40 wt%. Obviously, the enrichment of fluorinated moieties at the surface or near the surface can be adjusted by the amount of Polyol F used for the needs of anti-graffiti performance.

In the polyisocyanate side, two types of hydrophilic polyisocyanates are used: Hardener 1, which is HDT-based polyisocyanate, and Hardener 2, which incorporates both HDT and IPDT. The third factor in the coating design, the NCO/OH index ratio in the formulation, is studied at two levels, 1.5 and 2.5.

Therefore, using the full factorial design, the design of a total of 12 experiments is listed in *Table* 2. JMP 7.0 software from SAS Institute Inc. was used to analyze the anti-graffiti performance of the coatings.

RESULTS AND DISCUSSION

First, the film properties of these waterborne coatings were evaluated after curing at CTCH room. It was found that the coatings studied in this formulation range result in films having:

(1) High gloss: > 85 @ 60°

(2) Excellent MEK double rub test (1day): 200+ without fluorinated polyol; 300+ after incorporating fluorinated polyol.

(3) Good film hardness: > 200 sec (7 day Persoz)

(4) Good dry time: Tack-free ~ 3 hr; Dry-through 8 ~ 14 hr

(5) Pot life: ~ 6 hr

The anti-graffiti performance of these waterborne coatings after seven-day cure is then evaluated by applying the graffiti and leaving for one day before the removal system is used. The ratings for the total seven paints or markers are recorded and listed in *Table 3* with 1 equaling no removal and 5 representing total removal. Plus, an average rating is calculated.

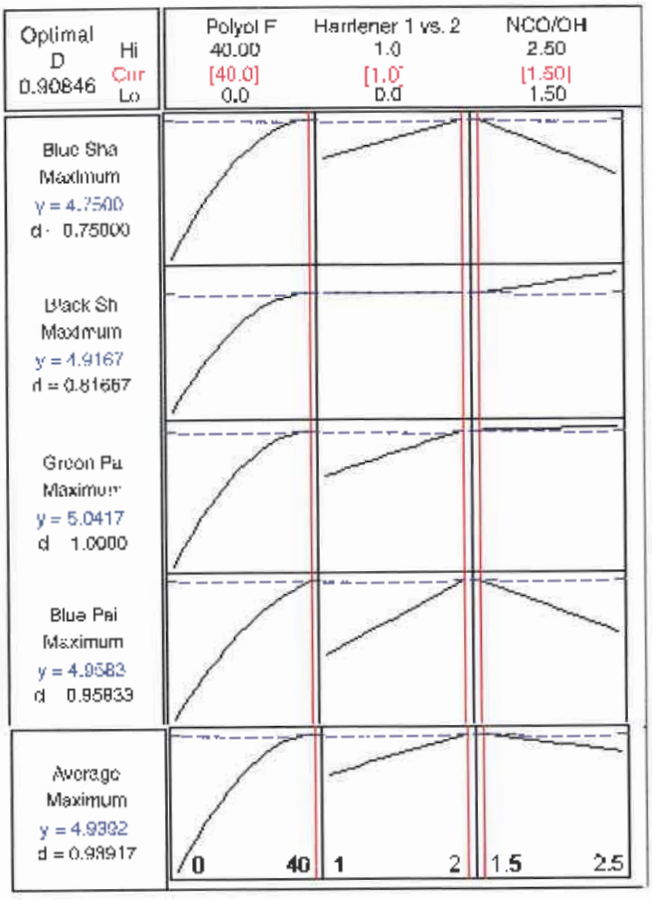
Using JMP 7.0 software and its Prediction Profiler, an understanding of how changes in the three factors affect the anti-graffiti performance is shown in *Figure 1*. The analysis suggests that:

(1) Fluorine content in the coating formulation has the greatest impact on the anti-graffiti performance towards all graffiti paints with increasing fluorine concentration, resulting in improved anti-graffiti performance.

(2) Incorporating IPDI in the HDT-based polyisocyanate (Hardener 2) will improve anti-graffiti performance towards every testing graffiti except the black Sharpie.

(3) For the case of the blue Sharpie and blue spray paint, increasing the NCO/OH ratio does not improve the anti graffiti performance; while for black Sharpie and green spray paint, higher NCO/OH ratio slightly favors the anti-graffiti performance. Overall, however, higher index does not improve anti-graffiti performance as indicated by the average ratings for all seven testing graffiti.

Figure 1—DOE statistical analysis on anti-graffiti performance.



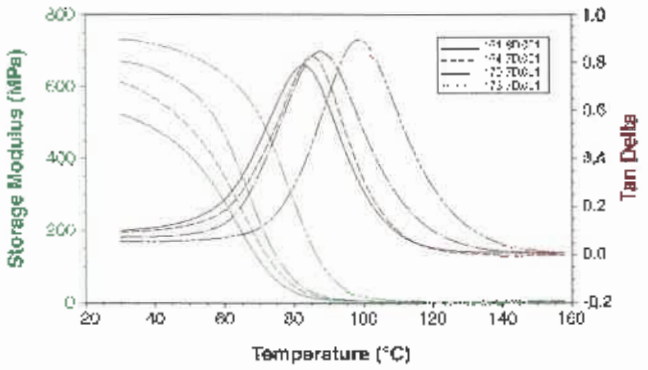
Regarding the fluorinated component in the formulation, due to the very low surface free energy, fluorinated polyols tend to migrate to the surface during film formation. An XPS study reveals that the distribution of fluorine atoms at the coating surface or near the surface is linear with the weight fraction of the fluorine in the formulation.[4] Therefore, the model indicates that the higher fluorine content at the surface or near the surface, the better the anti-graffiti performance of the formulation.

The seemingly surprising analysis on the factor of NCO/OH ratio suggests that a large excess amount of polyisocyanate does not favor anti-graffiti performance.

Table 3—Evaluations of Waterborne Coatings on Anti-Graffiti Performance

Sample #	Blue Sharpie	Red Sharpie	Black Sharpie	Silver Metallic Sharpie	Green Eraser	Green Paint	Blue Paint	Average
161	4	5	5	5	5	4	4	4.57
162	4	5	4.5	5	5	4	3	4.36
163	3	4	4	5	5	2	2	3.57
164	4.5	5	5	5	5	5	4.5	4.86
165	4	5	5	5	5	4.5	4	4.64
166	3	4	4	5	5	4	3	4.00
170	5	5	5	5	5	5	5	5.00
171	4.5	5	4.5	5	5	4	4	4.57
172	3	4.5	4	5	5	2	3	3.79
173	4	5	5	5	5	5	4	4.71
174	4	5	5	5	5	5	4	4.71
175	4	5	4	5	5	2	2	3.86

Figure 2—DMA studies on the waterborne coatings after seven-day cure.



One possible explanation is that a large excess amount of polyisocyanate does not participate in the initial crosslinking network formation due to the low reactivity between fluorinated Polyol F and hydrophilic polyisocyanates. As a result, these polyisocyanate colloidal particles stay in the crosslinking morphology during the film formation and are eventually partly consumed by moisture to form urea. Therefore, a large excess amount of polyisocyanate is not favored for early anti-graffiti performance.

Besides these two factors, the studies on the bulk and surface properties of these waterborne coatings by DMA and instrumented indentation methods provide further structural and morphological evidence on the crosslinking and viscoelastic properties of these waterborne coatings.

The bulk properties of film crosslinking density are studied by DMA. The representative results that include all four samples containing 10 wt% Polyol F after seven-day cure are shown in *Figure* 2. The storage modulus E' and glass transition temperature as well as the crosslinking density of the coatings are calculated and listed in *Table* 4.

The crosslinking density is calculated from the storage modulus E' at temperature $T = T_g + 50°C$ where the material is in the rubbery plateau region using the following equation based on the classical rubber elasticity theory:

Table 4—DMA Results on Waterborne Coatings After Seven-Day Cure

Sample #	Storage Amount E' @ 30°C (MPa)	T_g (°C)	Crosslinking Density ν_e (mol/cm³)
161	523	83.8	5.42 E-4
164	612	85.4	5.56 E-4
170	669	87.6	4.13 E-4
173	730	98.6	5.20 E-4

$$\nu_e = E'/3RT$$

where ν_e is the moles of elastically effective crosslink chains per cm³ of the coating.[9]

The results in *Table* 4 show that using HDT-based Hardener 1 (Sample #161 and #164) gives a coating with higher crosslinking density but a lower storage modulus and glass transition temperature, while using the IPDT-containing Hardener 2 (Sample #170 and #173) results in coatings having higher storage modulus and glass transition temperature, but lower crosslinking density and a relatively broader molecular weight distribution in the network structure, indicated by the half peak width of the tan δ results. The lower crosslinking density of the coatings incorporating IPDT does not give a definite explanation to the DOE analysis as Hardener 2 delivers better anti-graffiti performance.

The film properties are further studied by the micro-indentation method, and the Martens hardness results are listed in *Table* 5 and compared with Persoz hardness of the coatings after one-day and seven-day cure. Both hardness values show similar trends as film hardness develops. However, Persoz hardness measures the damping time of an oscillating pendulum on the coating surface; while the micro-indentation method uses an indenter to probe both elastic and plastic deformation behaviors of the coatings.

More importantly, the load/indentation depth plot shows distinctive advantage to interpret the mechanical properties of the coatings. The results of four representative samples (Samples #163, #164, #170, #173) after one-day and seven-day cure are shown in *Figures* 3 and 4. Each of these two samples (#163 and #164 versus #170 and #173) is selected to demonstrate the range of indentation depth for Hardener 1 and Hardener 2, respectively.

Table 5—Martens Hardness HM and Persoz Hardness of Waterborne Coatings After One-Day and Seven Day Cure

Sample #	1D Persoz (sec)	1D HM (N/mm²)	7D Persoz (sec)	7D HM (N/mm²)
161	156	28.4	248	113.6
162	171	45.7	245	115.2
163	158	47.4	211	100.5
164	89	7.6	283	111.4
165	146	14.0	289	117.1
166	187	42.4	268	121.6
170	230	68.9	276	133.6
171	226	80.2	266	130.9
172	177	66.8	238	125.2
173	217	30.9	296	132.6
174	237	53.2	303	142.3
175	227	80.4	281	134.8

Figure 3—Load/indentation depth plot for coatings after one-day cure (sequence from left to right, #170, #163, #173, #164).

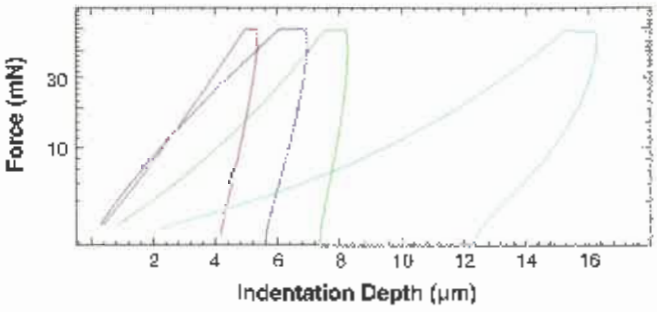
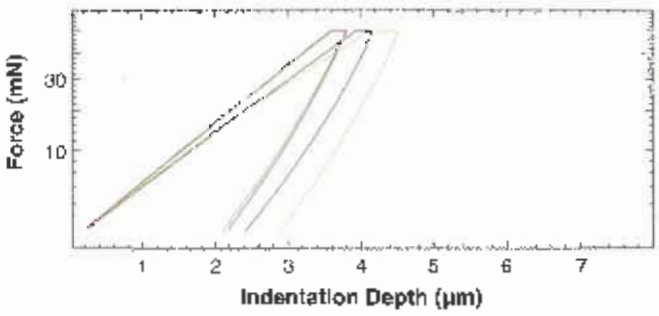


Figure 4—Load/indentation depth plot for coatings after seven-day cure (sequence from left to right, #173, #170, #164, #163).



The plots of the square root of the test load versus indentation depth during the loading stage (*Figures* 3 and 4) have shown an advantage for studying the solidification of the waterborne coatings as we consider the relationship

$$HM = \frac{F}{A_s(h)} = \frac{F}{26.43 \times h^2} \quad (1)$$

We can rewrite this as

$$h^2 = \frac{F}{26.43 \times HM} \quad (2)$$

For homogeneous materials, the hardness will be a constant and not dependent on the applied test load. The above formula can then be expressed in terms of a constant slope factor m_f:

$$m_f = \frac{1}{26.43 \times HM} \quad (3)$$

We can then rewrite

$$h = \sqrt{m_f} \cdot \sqrt{F} \quad (4)$$

Therefore, any changes in the slope of the indentation depth versus square root of load plot during the loading stage indicate an inhomogeneity in the material under test.[20] For coatings using HDT-based Hardener 1 (#163 and #164), the curves of one-day cure as shown in *Figure* 3 are far from linear, indicating that the film is still soft and curing is not complete at the surface and throughout the film. Using the IPDT containing Hardener 2 (#170 and #173), on the other hand, the curves of one-day cure are relatively more linear, indicating the nature of physical drying by incorporating the higher T_g component of IPDT.

After seven-day cure shown in *Figure* 4, as the crosslinking density increases and modulus builds up, the coatings become more resistant to penetration. The indentation depth h_f decreases significantly. In addition, all the curves show better linearity, suggesting that the coatings reach sufficient cure and result in homogeneous solid films.

If we look into the indentation depth of the coatings after seven-day cure at each stage of the indentation test as listed in *Table* 6, we can find systematically that incorporating IPDT lowers the indentation depth after the coating reaches sufficient crosslinking. The reason for that is IPDT increases the stiffness of the network chains and thus increases the glass transition temperature of the coatings, giving rise to a higher degree of resistance and elastic response for the coatings.

The micro-indentation method clearly demonstrates the difference between the two hardener systems, which helps interpret why Hardener 2 has better anti-graffiti performance than that of Hardener 1. Once the coatings reach a certain degree of crosslinking density, the stiff chain network structure becomes more important than the molecular weight distribution in the crosslinking morphology, as it significantly slows down the diffusion of the dye and solvent molecules. As a result, incorporating IPDT in HDT-based polyisocyanate enhances the barrier properties of these waterborne coatings for anti-graffiti performance.

Using the blending approach on both polyols and hydrophilic polyisocyanates, the resulting coatings have the advantage of meeting the anti-graffiti performance with excellent barrier properties at lower fluorine content, thus sufficient for recoatability. It is found that all the formulations in the design have a wide recoatability

Table 6—Indentation Depth at Each Stage of the Micro-Indentation Test for Coatings After Seven-Day Cure

Sample #	h_f	Δ_h	h_{max}
163	4.13	0.37	2.89
164	3.93	0.25	2.40
170	3.59	0.21	2.17
173	3.59	0.21	2.10

window, confirmed by the excellent results in the adhesion test.

Based upon the above studies, it is determined that a formulation using 40 wt% Polyol F in Polyol A with Hardener 2 containing IPDT at NCO/OH ratio at 1.50 delivers the best anti-graffiti performance. The anti-graffiti performance of this formulation is validated and demonstrated in Appendix B. In the first Sharpie marker test, a white primer was applied onto a steel panel before three layers of anti-graffiti polyurethane coatings were draw down at a wet film thickness of 8 mils. The time span between each layer is one day. The coating was let cure at ambient conditions for two weeks. Then the Sharpie marker and dry erasers were applied and left for one day. After using the removal systems, total removal is seen to be achieved.

In the second test, on an epoxy primed concrete board, two layers of anti-graffiti coatings have been brushed in a time span of around 6 hr. The coating was let cure at ambient conditions for one week. Then spray paints were applied and left for one day. Sponge or brush was used with the removal system to achieve easy cleaning.

CONCLUSIONS

Using the instrumented indentation method, the evaluation of elastic and plastic deformation behaviors of the coatings help interpret the barrier properties. It is found that incorporating proper amounts of IPDT in HDT based hydrophilic polyisocyanate increases the stiffness of the network structure, thus improving the barrier properties of the coatings once the coating reaches sufficient crosslinking. Since the micro-indentation test is also regarded as a nondestructive method and automation capable, it could be an ideal choice for the work flow in the formulation development.

The formulation platform methodology has been effectively used in the development of a 2K waterborne polyurethane anti-graffiti coating to achieve excellent anti-graffiti performance below 100 g/L. It is found that the fluorine content in the formulation and the barrier properties are the key factors for anti-graffiti performance. Using DOE design, an optimized formulation is obtained to achieve the film properties necessary for the anti-graffiti performance at low VOC. In addition, these waterborne coatings demonstrate excellent recoatability.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Paul Hung, Dr. Philippe Barbeau, Dr. Philippe Olier, Dr. Amit Sehgal, and Dr. Lichang Zhou for many insightful discussions on waterborne polyurethane coatings. The authors would also like to thank Fischer Technology, Inc. for the support of this study.

References

(1) Maty, J., *J. Arch. Coat.*, p. 18-26 (2007).
(2) Zielnik, A., *J. Arch. Coat.*, p. 29-34 (2007).
(3) Stadler, R., Maier, A., and Steidl, N., *Jur. Coat. J.*, 7-8, 63 (2003).
(4) Schuerder, J., Visscher, N., Kabumra, T., and Overbeek, A., "Novel, Water-Based Fluorinated Polymers with Excellent Antigraffiti Properties," *J. Coat. Technol. Res.*, 2, No. 8, 617-625 (2005).
(5) Wu, X., Sehgal, A., Trivedi, S., and Rosen, R.P., *Proc. 34th Annual International Waterborne, High Solids, and Powder Coatings Symposium*, p. 39, 2007.
(6) (1) Balta Calleja, F.J., in *Encyclopedia of Polymer Science and Technology*, Mark, H.F. (Ed.), 3rd Ed., Vol. 2, John Wiley & Sons, Inc., Hoboken, NJ, 688-689, 2003; (2) ISO 14577-1:2002(E).
(7) Bell, J.J., Bendeli, A., Field, J.S., Swain, M.W., and Thwaite, E.G., *Metrologia*, Vol. 28, 463-469 (1991).
(8) Internal lab results.
(9) Rawlins, J.W. and Davis, K., *Proc. 33rd Annual International Waterborne, High-Solids, and Powder Coatings Symposium*, p. 171, 2006.
(10) Weiler, W., *British Journal of Non-Destructive Testing*, Vol. 31, No. 5, 253-258 (1989).

APPENDIX A

Formulations for 2K Waterborne Polyurethane Anti-Graffiti Coatings

Ingredients	Wt%	Formulation A	Formulation B
Polyol A		17.38	24.43
Polyol F		17.96	25.24
Eastman EEP		0.34	3.75
Water		29.05	17.99
Defoamer		0.22	0.22
Surface Additive A		0.55	0.55
Surface Additive B		0.21	0.21
Hardener D			13.80
Hardener M		30.85	13.80
Eastman EEP		3.43	—
	Total	100.00	100.00

APPENDIX B

Graffiti Removal