Low VOC Topcoats Using

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Ultra High Solids Resins

By Dr. Gautam Haldankar and Niel Pfendt, allnex

In the North American coatings market, traditional solventborne resins are still used to a large extent, enabled by regulations that allow for the use of certain solvents exempt from restrictions placed on most volatile organic compounds (VOCs) in the United States. The future of the exempt status of parachlorobenzotrifluoride (PCBTF) and tertiary butyl acetate (TBAc) is a concern in certain districts of California, and other regions may follow suit.

Coating companies are ramping up their research efforts in formulating paint without exempt solvents. Researchers are opting to formulate with high solids resins.

High-performance acrylic polyols were studied to understand the effect of various resin parameters on coatings performance. A set of resins with 80-90% solids was tested in pigmented topcoat formulations.

These topcoats contained VOCs ranging from 200 to 250 g/L, without the use of exempt solvents. Various conventional and advanced film properties were evaluated, including weathering performance by xenon arc exposure, cure kinetics using infrared (IR) spectroscopy, and crosslink density by dynamic mechanical thermal analysis (DMTA).

Correlation was obtained between coatings performance properties and resin characteristics such as equivalent weight, glass transition temperature, etc. The understanding of structure property correlation offers tremendous value not only for North American coatings researchers but also to the global community.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has regulated the VOC limit to 450 g/L in the United States, and Canada has a restriction of 340 g/L for industrial metal (IM) topcoats. The California Air Resource Board (CARB) has a limit of 250 g/L and many other states, such as Utah, are following suit.

In North America, formulators can use exempt solvents (e.g. PCBTF, TBAc, acetone, etc.) to achieve a lower VOC of 250 g/L. Among these, PCBTF has more favorable characteristics than other exempt solvents, as it evaporates slowly, has a higher flash point, and is therefore less flammable than many other exempt solvents such as acetone.

However, effective June 28, 2019, the Office of Environmental Health Hazard Assessment (OEHHA) added PCBTF to the list of chemicals known to the state of California to cause cancer for purposes of Proposition 65. In addition, the South Coast Air Quality Management District (SCAQMD) is considering delisting PCBTF from the list of exempt solvents.

As the future of PCBTF as an exempt solvent is a concern, it is beneficial if new coatings are formulated without the use of it. If coatings are formulated without any exempt solvent, paint formulators don't have to reformulate when the exempt status of any solvent is changed. Formulating without the use of exempt solvent has one more advantage, especially for global companies, which is that one formula can be used throughout the global market.

It is a challenge to achieve performance of low-solids solventborne coatings with high-solids coatings. Among all the coatings components, resin plays most important role in lowering the VOC. This requires higher-performing, lower-molecular-weight resins.

Two component (2K) polyurethane chemistry provides excellent durability, chemical resistance, appearance, and speed of cure, which makes the urethane technology a valuable tool for the coatings industry[1-2] (*Figure 1*). In both protective and industrial maintenance (IM) coatings, solventborne 2K systems are predominantly used. For the same reason, this study focuses on two component (2K) polyurethane chemistry[3-4].

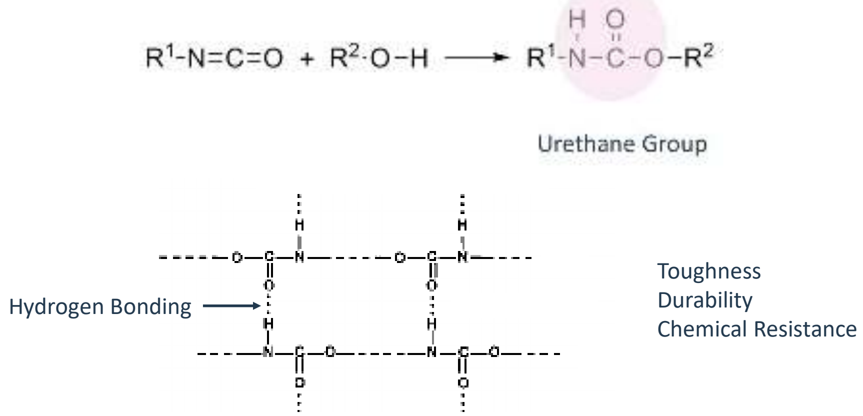
There are various synthesis techniques, such as group transfer polymerization (GTP), atom transfer radical polymerization (ATRP), and reverse addition fragmentation chain transfer (RAFT), that give excellent control over acrylic polymer architecture to produce high-performing resins[5-7].

These techniques pose some challenge in manufacturing and are not competitive from a commercial aspect. A commercially competitive polymerization process, controlled molecular structure polymerization (CMSP), has been developed that gives excellent control over molecular weight and polydispersity[8].

If oligomeric polyols are synthesized by conventional route, a few oligomers will not contain hydroxyl functionality, and those oligomers will act as a plasticizer, degrading the film performance. The CMSP process gives guaranteed functionality to oligomeric polyols maintaining high performance of the resin.

To achieve good film performance, a balance of solids (which is indirectly

FIGURE 1—Urethane Formation



related to molecular weight), equivalent weight, and glass transition temperature (T_g) is necessary. Exterior durability is dependent on the crosslink density (XLD) of the film as well as the monomer composition of the resin.

This paper is a presentation of results from coatings evaluation using resins with solids ranging from 80-90% by weight, hydroxyl equivalent weights (HEW) from 230 to 400, and glass transition temperatures (T_g) from 2 to 15 °C.

EXPERIMENTAL FINDINGS

Resin Characteristics

Resins were synthesized using several approaches. A large set of resins were screened to obtain a coating VOC of ≤ 250 g/L. Upon screening, four resins were selected for further evaluation in a protective topcoat formula.

To achieve low VOC and desired properties, the upper limit for the T_g was determined to be approximately 20 °C and the upper limit for HEW was approximately 450. All four selected resins had a percentage of nonvolatile compounds by weight of 80% or higher. Characteristics of these resins are shown in *Table 1*.

Resins A, C, and D contain acrylic backbones, whereas Resin B is a hybrid resin with an acrylic as well as a polyester backbone. As the solids of resins were increased, with the exception of Resin B, the HEW of the resin was decreased to maintain adequate functionality for good film properties.

Formulation and Evaluation of Clear Films

A clear paint was formulated using the following generic formula (*Table 2*) and the clearcoat was drawn down on a thermoplastic elastomeric olefin (TEO) panel. The panels were air-dried for four weeks at 23 °C and between 40% and 60% relative humidity. Clear films were peeled from the TEO and were evaluated by DMTA to obtain T_g and XLD[12].

TABLE 1—Characteristics of Polyol Resins

RESIN	RESIN A	RESIN B	RESIN C	RESIN D
% NV by Wt	80%	82%	85%	90%
Viscosity (Poise)	4.1	5.5	19.6	7.4
Hydroxy Eq. Wt. (on NV)	400	255	320	230
Glass Transition Temp., T_g (°C)	8	2	15	5
Solvent	BuAcetate	BuAcetate	BuAcetate	BuAcetate

TABLE 2—Formulation Guide to Prepare Clear Film for DMTA Analysis

PARAMETER	VALUE
Resin	A, B, C & D
Flow & Leveling Agent	0.20%
Catalyst (DBTDL)	0.02% on Resin Solids
Solvent	nBuAc:MAK = 1:1
Hardener	Isocyanurate Trimer (Low Visc.)
NCO:OH Stoichiometry	1.1:1.0
Application Solids	75.00%

Among various film characteristics, T_g and crosslink density play major roles. The higher the T_g of the clear film, the higher the hardness of the coating. In general, for better chemical resistance and film properties, higher crosslink density is desired.

Figure 2 shows the T_g of the clear films. Films made from Resins C and D produced T_g ≥ 50 °C and Resins A and B produced T_g around 40 °C. *Figure 3* shows crosslink density of the films. Based on experience, films with XLD of less than 0.7 mmole/cc exhibit poor

FIGURE 2—Glass Transition Temperature of Clear Films by DMTA

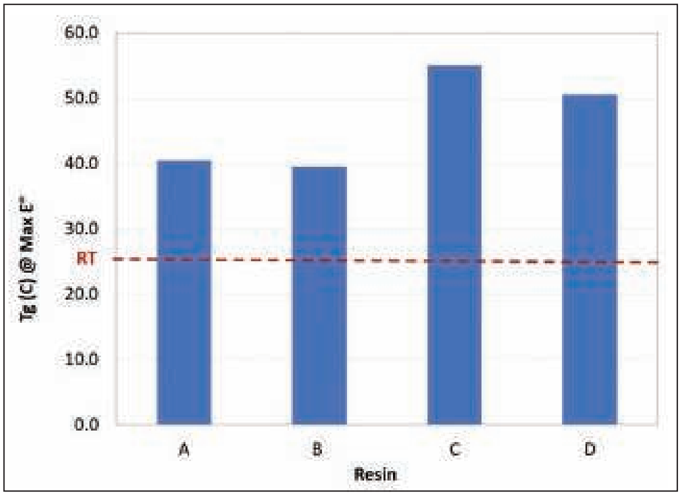


FIGURE 3—Crosslink Density of Clear Films by DMTA

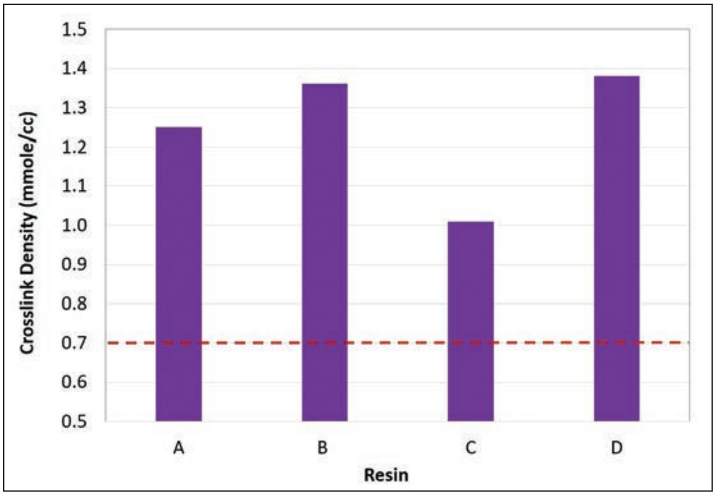


TABLE 3—Formulation of White 2K Topcoat with VOC ≤ 250 g/L

PARAMETER	VALUE
Resin	A, B, C & D
TiO_2	P:B =1.0
Dispersing Agent	2% on TiO_2
Flow & Leveling agent	0.24%
Anti-settling Agent	1.0%
UVA + HALS	0.6%
Catalyst (DBTDL)	0.02% on Resin Solids
Pot-life Extender	0.7%
Solvent	nBuAc:MAK = 1:1
Hardener	Isocyanurate Trimer (Low Visc.)
NCO:OH Stoichiometry	1.1:1.0
VOC	250 g/L or lower
Viscosity	~ 400 cPs

film properties. All the films gave much higher crosslink densities than 0.7 mmole/cc and Resin D gave the highest XLD of 1.38 mmole/cc.

Formulation of White Topcoat

White paint was formulated using the above guidelines (*Table 3*) and with the use of a speed mixer. The viscosity of the paint was adjusted using a solvent mixture of n-butyl acetate and methyl amyl ketone (1:1).

The final viscosity of the paints was between 350 to 500 cP. Among four resins, Resin D produced the lowest VOC of 205 g/L, much lower than other resins studied (*Table 4*). For comparison, a commercial white topcoat (VOC of 245 g/L) manufactured by an international coatings company was used as a reference.

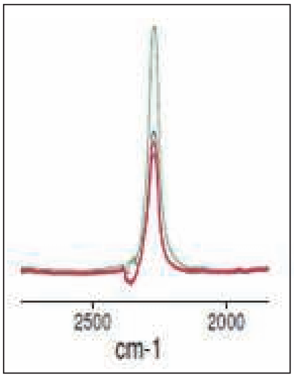
The volume solids of the paint formulated with resins under investigation were higher than the commercial reference paint. Specifically, paint made from Resin D was remarkably higher in volume solids. Nonvolatiles by volume, VOC and viscosity are tabulated in *Table 4*.

Evaluation of White Topcoat

White topcoats were applied at a thickness of 2.3-2.6 mils and were tested for the following:

a. Isocyanate (-NCO) disappearance by IR spectroscopy: Ratio of areas at 2270 cm^{-1} (N=C=O stretching) and 765 cm^{-1} (C-H bending) were calculated at various intervals of time (*Figure 4*).

FIGURE 4—Disappearance of -NCO peak with time



b. Film drying characteristics using circular drying time recorder (ASTM D5895).

c. Hardness development over time using König Hardness measurements (ASTM D4366).

d. Flexibility using conical mandrel after 4 weeks of cure at 23 °C (ASTM D522).

e. Chemical resistance after 4 weeks of cure, with various chemicals exposed for 24 hours.

f. Xenon Weatherometer Exposure (ASTM D7869)

RESULTS AND DISCUSSION

Disappearance of Isocyanate by FTIR

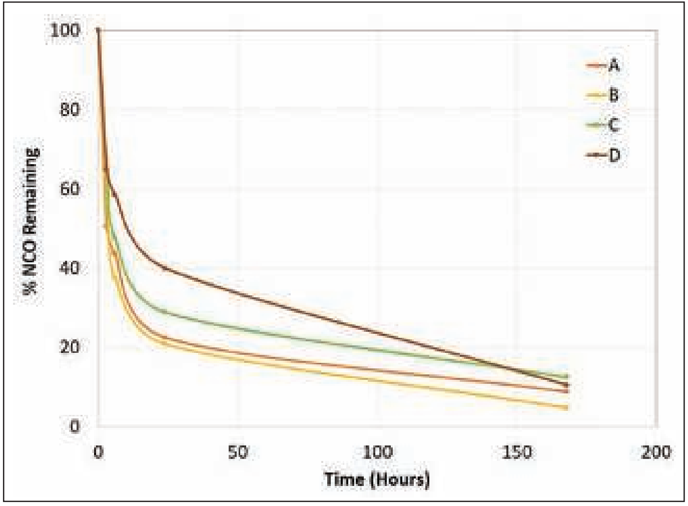
The curing reaction progress was monitored by the disappearance of -NCO group. *Figure 5* shows the plot of disappearance of -NCO as a function of time. Based on the plot, the initial rate of reaction of Resins A and B was much faster and almost 80% of the -NCO was reacted within 24 hours. The reaction rate of Resin D was much slower and only 60% of the -NCO was consumed within 24 hours.

After one week of cure, the percentage of NCO remaining for all the films was between 5% and 12%. It is noteworthy that the lowest percentage of NCO left was in Film B, which also had the lowest T_g of the

TABLE 4—Characteristics of Formulated White Topcoat

PAINT	A	B	C	D	COMMERCIAL
Application VOC [g/L]	250	250	250	205	245
Initial Viscosity at 25 s^{-1} [cP]	493	367	421	344	481
Application %Non volatiles by Vol.	72.6%	74.0%	72.4%	77.6%	71.5%

FIGURE 5—Disappearance of NCO by FTIR and its correlation to T_g of the Resin & Clear Film



RESIN	RESIN T_g (° C)	CLEAR FILM T_g
A	8	41
B	2	39
C	15	55
D	5	51

clear films at 39.5 °C. Conversely, the highest percentage of NCO left was in the film 'C', which had the highest T_g at 55.0 °C.

This indicates that due to the higher T_g of Resin C, the film vitrified sooner, the crosslinking reaction was relatively hindered, and the amount of unreacted NCO after one week was higher as a result. Resin D exhibited a relatively low T_g but yielded a film with relatively high T_g. This is a good example of how reactivity, equivalent weight, and T_g each play a balanced role in the curing reaction.

Comparative Film Properties of White Topcoat

Figure 6 shows drying characteristics of white topcoats in comparison to a commercial control. The dry-hard stage is important as at this stage the object can be handled without damaging the coating. When the film reaches the dry-through stage, objects are ready to be transported and are free of water spotting. Comparing all the topcoats, Resin A produced a much faster dry-through time, Resins B and C were comparable, and Resin D took much longer time than the commercial control.

FIGURE 6—Drying characteristics of 250 g/L white topcoats

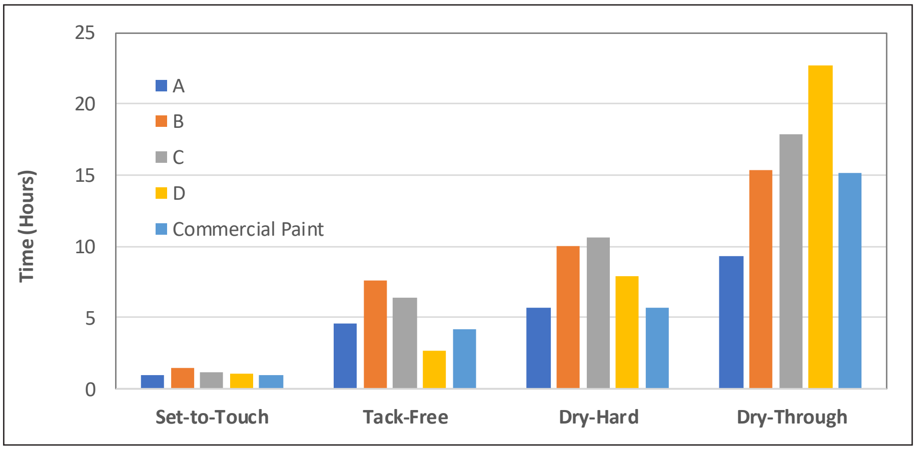


FIGURE 7—Hardness Development of 250 g/L white topcoats

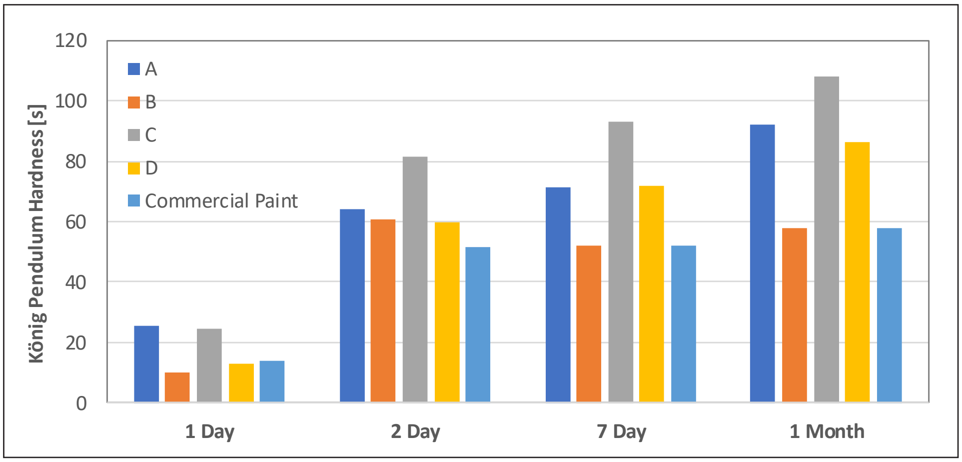


TABLE 5—Flexibility of the film after one month of cure

PAINT	A	B	C	D	COMMERCIAL
Conical Mandrel Bend	pass 1/8"	pass 1/8"	pass 1/8"	pass 1/8"	pass 1/8"
Scotch 898 tape, 180° pull	no loss	no loss	no loss	no loss	no loss

Figure 7 shows the development of hardness of the coatings made from the resin studied. All the coatings gave similar or higher hardness as compared to the commercial control. Paint made with Resin C produced a much higher hardness versus the other paints. Recall that Resin C, as well as its clear film, exhibited the highest T_g among all samples (*Table 1, Figure 2*).

Table 5 shows flexibility results by conical mandrel bend. All the paints passed the flexibility test without any cracks or loss of adhesion.

Taber Abrasion results (*Figure 8*) indicate that all the resins studied gave better abrasion resistance than the commercial control. In comparison, Resins B and C gave distinctly improved abrasion resistance.

Chemical resistance was tested by exposing a coated panel with the chemicals listed in *Table 6* for 24 hours. Overall, all the paint films gave good chemical resistance with ratings of 4 and 5. Among all films, Resin B showed slightly superior performance with only slight softening with xylene. All the coatings tested showed some softening with exposure to xylene.

Xenon Weatherometer Testing

All the coatings were tested in the xenon weatherometer (WOM) chamber for accelerated weathering. Among UV-A, UV-B, and xenon exposure cabinets, the xenon WOM provides result that correlate more closely with actual Florida exposure. For glossy topcoats, when the gloss drops below 70 gloss units (GU), it can be considered failing. All the coatings performed well until

FIGURE 8—Taber Abrasion using C-17 wheel and 1 kg weight

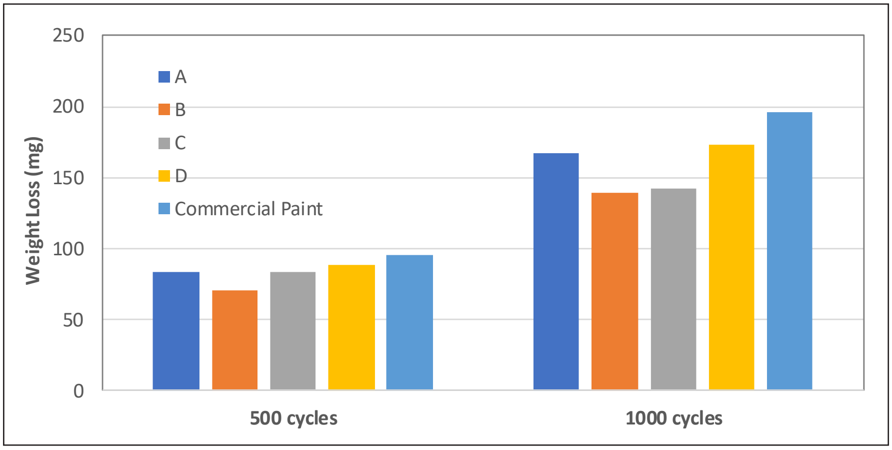


TABLE 6—Chemical Resistance of ≤ 250 g/L white topcoats

PAINT	A	B	C	D	COMMERCIAL
MEK Double Rubs	> 500	> 500	> 500	> 500	> 500
10% Sufuric Acid	5	5	5	5	5
25% NaOH	5	5	5	4	5
10% Ammonia	5	5	4	5	5
Unleaded Gas	4	5	4	4	4
Bleach	5	5	5	5	5
Motor Oil 5W-20	5	5	5	5	5
Xylene	4	4	4	4	4
Detergent (Tide)	5	5	5	5	5
Average	4.8	4.9	4.6	4.6	4.8

5 = no damage
4 = sl.staining and/or softening
3 = staining, adhesion loss (with BBSM*), and/or softening
2 = severe staining, lifting, and/or softening
1 = dissolving of coating

FIGURE 9—Xenon Weatherometer - 60° Gloss Retention of White Topcoats (with UVA and HALS)

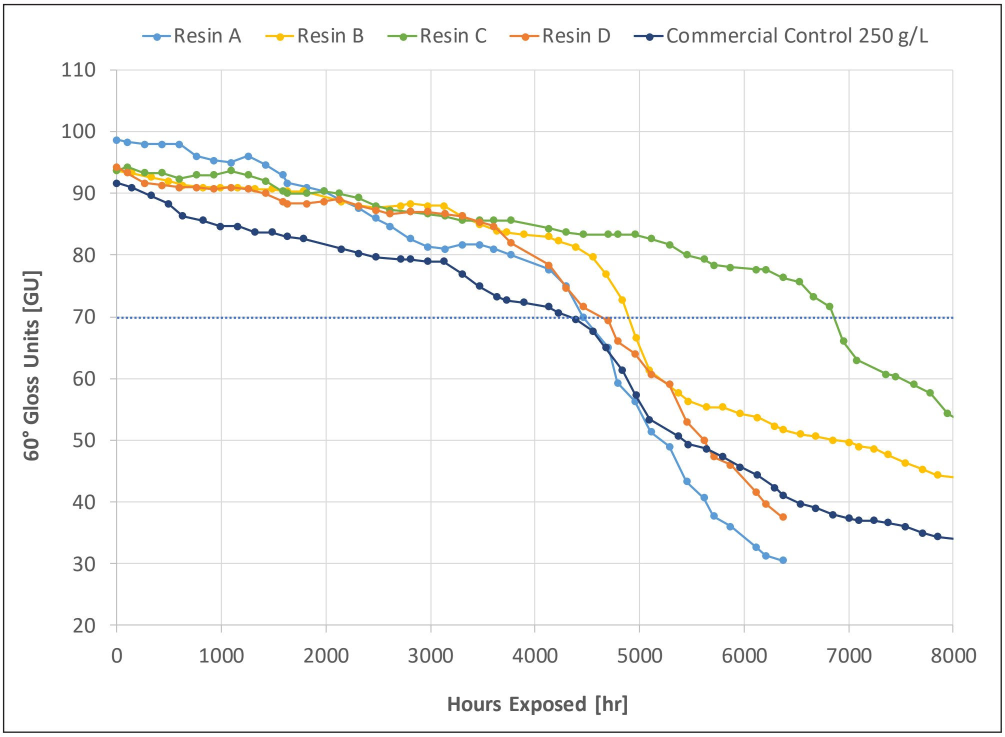
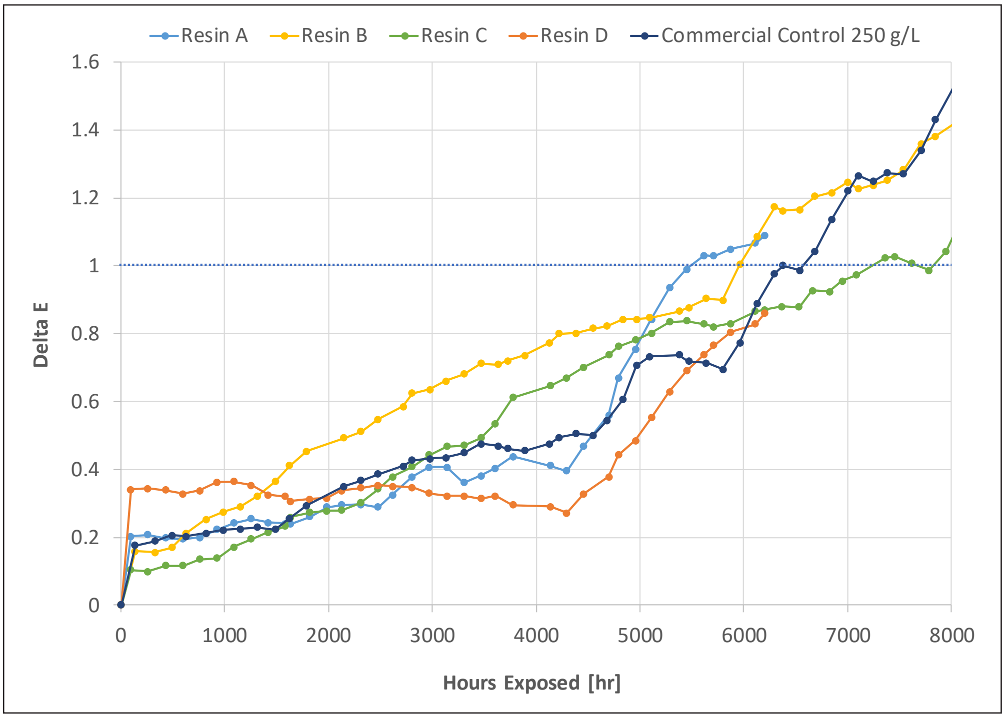


FIGURE 10—Xenon WOM - DE of White Topcoats (with UVA & HALS)



4,500 hours exposure (*Figure 9*). Among the coatings, Resin C retained its gloss of ≥ 70 GU for almost 7,000 hours and showed significantly higher weathering resistance than all other coatings.

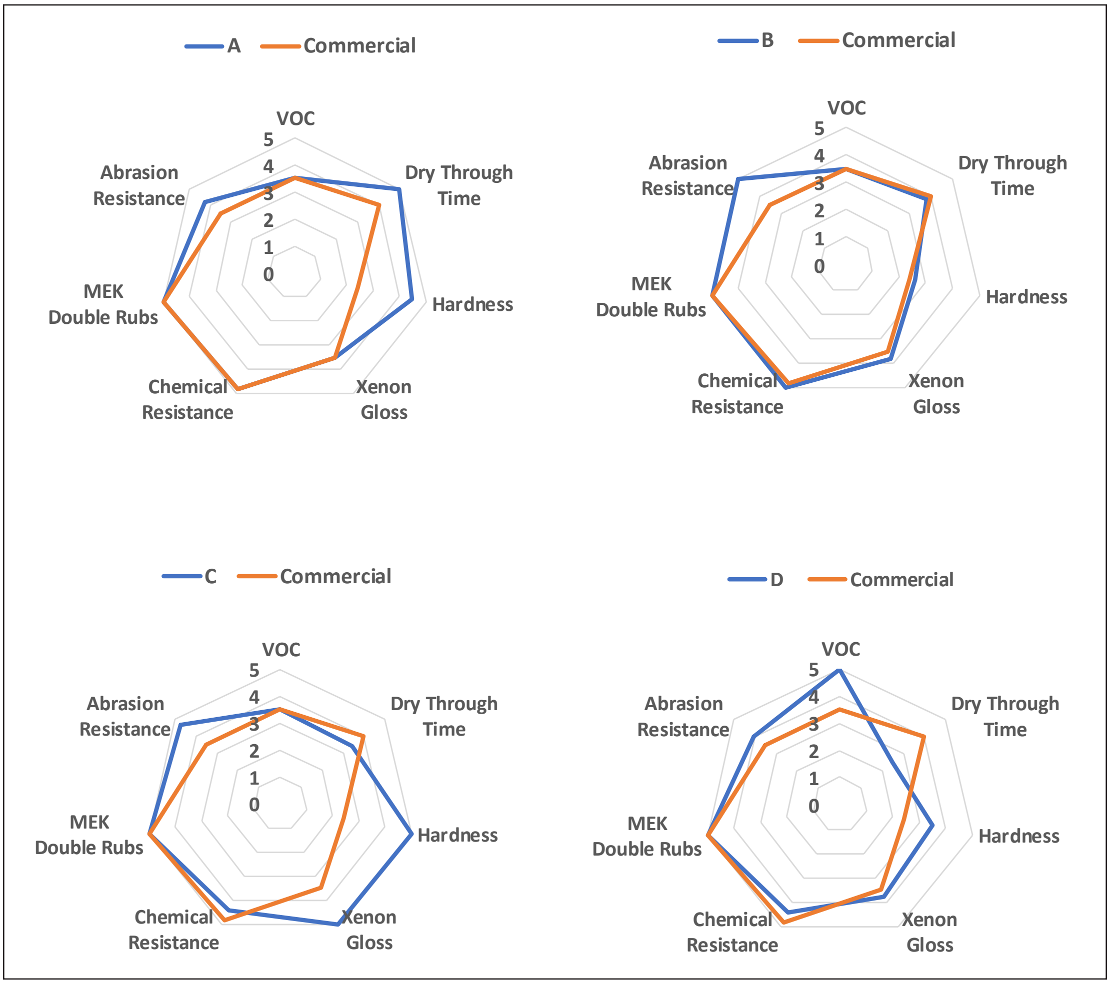
For a high-quality paint, a color difference of ΔE ≤ 1 is desirable. For high-quality topcoats, the expectation is ΔE < 1 for about 5,000 hours. All the coatings tested showed ΔE of < 1 for up to 5,000 hours and passed the desired performance (*Figure 10*). Among these, Resin C again showed the highest performance with ΔE reaching a value of 1 after only 7,000 hours of exposure.

SUMMARY OF RESULTS

The summary of test results is shown in the *Figure 11*. It shows that each resin studied offers unique advantages over the reference commercial paint. This study gives formulators tools to improve performance based on the importance of any desired property.

Resin A has the lowest demand for isocyanate hardener and shows better performance overall than the commercial reference, making it a suitable candidate for coatings with an excellent

FIGURE 11—Spider plots comparing coating properties of A, B, C, and D with commercial control



price-performance balance. A major advantage of Resin B is improvement in abrasion resistance. Resin C gives superior durability, hardness, and abrasion resistance, making it suitable for high-performance coatings. With Resin D, a much lower VOC coating (≤ 200 g/L) can be formulated with some sacrifice of dry-through time.

CONCLUSIONS

Using all the resins studied, protective or industrial maintenance coatings can be formulated at ≤ 250 g/L without the use of any exempt solvent and can be used in global or universal formulations.

Each resin gives unique advantages over the commercial reference paint.

- Resin A: Hardness, dry-through time, and abrasion resistance
- Resin B: Abrasion resistance
- Resin C: Superior weathering, hardness, and abrasion resistance
- Resin D: Very low VOC of ≤ 200 g/L

Using a proper blend of these resins, coatings can be formulated to tailor to the specific needs of the end customer. ❊

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DR. GAUTAM HALDANKAR and **NIEL PFENDT**, allnex, 4730 Crittenden Drive, Louisville, KY 40209; Gautam.Haldankar@allnex.com.