Isocyanate-Free Polyurethane Technology for

Approaches to Reducing VOC

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Industrial wood surfaces, such as furniture and cabinetry, require coatings to help protect and extend their life. Polyurethane coatings provide enhanced appearance, stain and chemical resistance, as well as exterior durability. When formulated as ambient cure systems, traditional two-component polyurethanes typically must balance cure speed for pot life. This article describes clearcoat formulations using a novel nonisocyanate polyurethane technology based on the reaction of a polycarbamate with polyaldehydes. A major benefit of this system is the ability to decouple pot life and cure speed without adversely affecting fast hardness development and quick dry time. For the end user, this can lead to faster return to service and higher production rates. Additional coating benefits are high clarity, excellent durability and chemical resistance, and fast sandability. Reducing VOC is a major need for the applicator, and different approaches are presented aimed at reducing the VOC of a clear formulation for wood, which can maintain a useful pot life while retaining its fast cure and dry properties. An example is shown where a clear formulation is modified to meet the requirements of the Utah VOC Rule R307-343 Emission Standards for Wood Furniture

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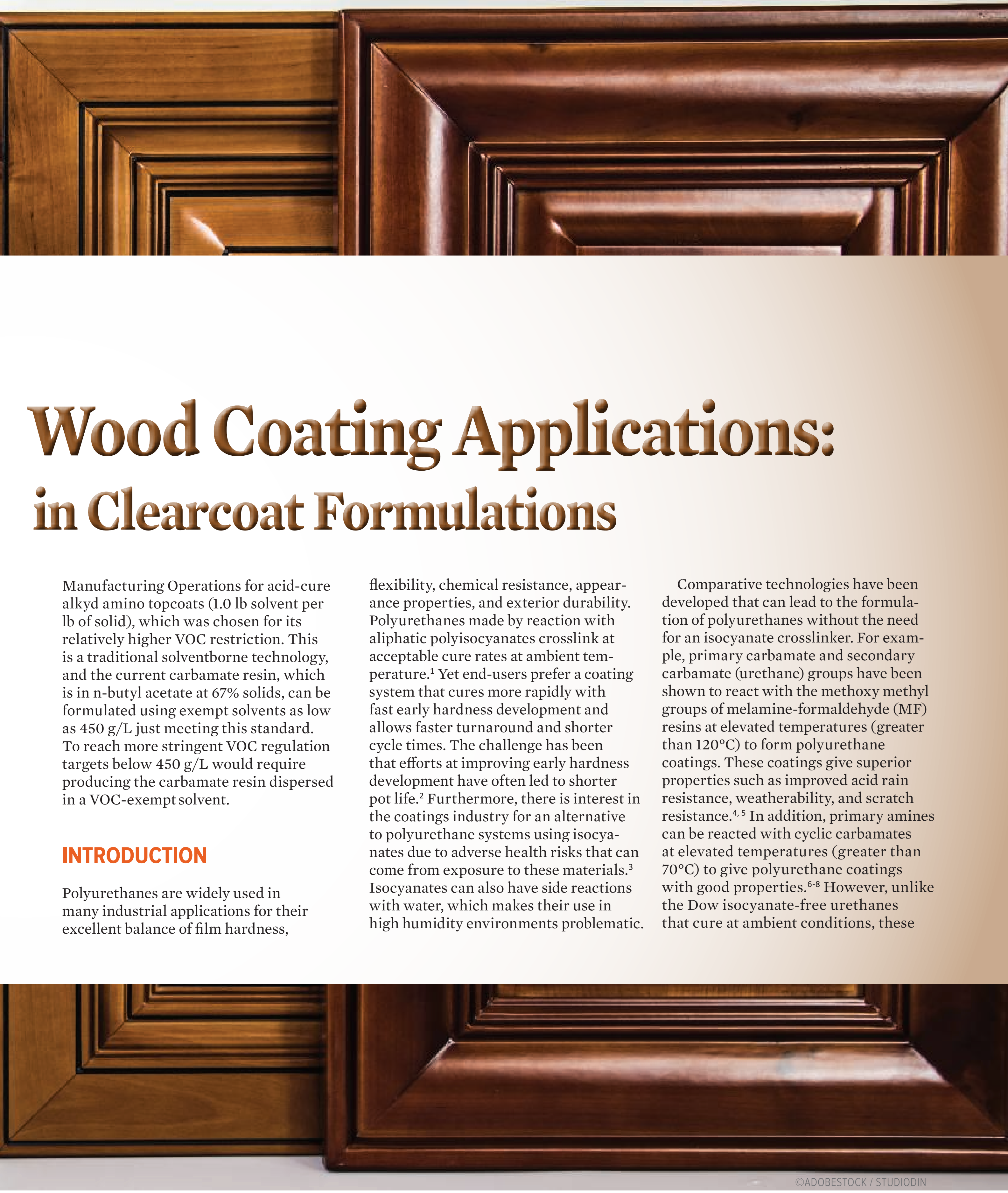

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Wood Coating Applications:

in Clearcoat Formulations

Manufacturing Operations for acid-cure alkyd amino topcoats (1.0 lb solvent per lb of solid), which was chosen for its relatively higher VOC restriction. This is a traditional solventborne technology, and the current carbamate resin, which is in n-butyl acetate at 67% solids, can be formulated using exempt solvents as low as 450 g/L just meeting this standard. To reach more stringent VOC regulation targets below 450 g/L would require producing the carbamate resin dispersed in a VOC-exempt solvent.

INTRODUCTION

Polyurethanes are widely used in many industrial applications for their excellent balance of film hardness, flexibility, chemical resistance, appearance properties, and exterior durability. Polyurethanes made by reaction with aliphatic polyisocyanates crosslink at acceptable cure rates at ambient temperature.[1] Yet end-users prefer a coating system that cures more rapidly with fast early hardness development and allows faster turnaround and shorter cycle times. The challenge has been that efforts at improving early hardness development have often led to shorter pot life.[2] Furthermore, there is interest in the coatings industry for an alternative to polyurethane systems using isocyanates due to adverse health risks that can come from exposure to these materials.[3] Isocyanates can also have side reactions with water, which makes their use in high humidity environments problematic.

Comparative technologies have been developed that can lead to the formulation of polyurethanes without the need for an isocyanate crosslinker. For example, primary carbamate and secondary carbamate (urethane) groups have been shown to react with the methoxy methyl groups of melamine-formaldehyde (MF) resins at elevated temperatures (greater than 120°C) to form polyurethane coatings. These coatings give superior properties such as improved acid rain resistance, weatherability, and scratch resistance.[4, 5] In addition, primary amines can be reacted with cyclic carbamates at elevated temperatures (greater than 70°C) to give polyurethane coatings with good properties.[6-8] However, unlike the Dow isocyanate-free urethanes that cure at ambient conditions, these coatings require heat to cure and are therefore limited to original equipment manufacturer (OEM) applications where the coating can be cured at elevated temperatures.

This article describes a novel isocyanate-free technology for making polyurethane coatings at ambient temperature from the reaction of polyaldehydes with carbamate functional polymers using an acid catalyst. A primary alcohol is used to enhance the pot life of the system. This novel crosslinking chemistry has the unique features of decoupling the pot life from the dry time and hardness development of the coating. An ever more important factor for using this technology is how to best formulate this coating technology to meet reduced VOC regulations in the various regions of the country, while not adversely affecting the coating performance and the pot life. In particular, this article reviews the different approaches for reducing VOC to meet the Utah regulations for acid-cured topcoats for wood coatings (R307-343). This regulation specifies that a coating meets the acid-cured pound for pound VOC requirement, which correlates to less than 450 g/L.

FIGURE 1—Formation of a polyurethane from the reaction of a polycarbamate and polyaldehyde.

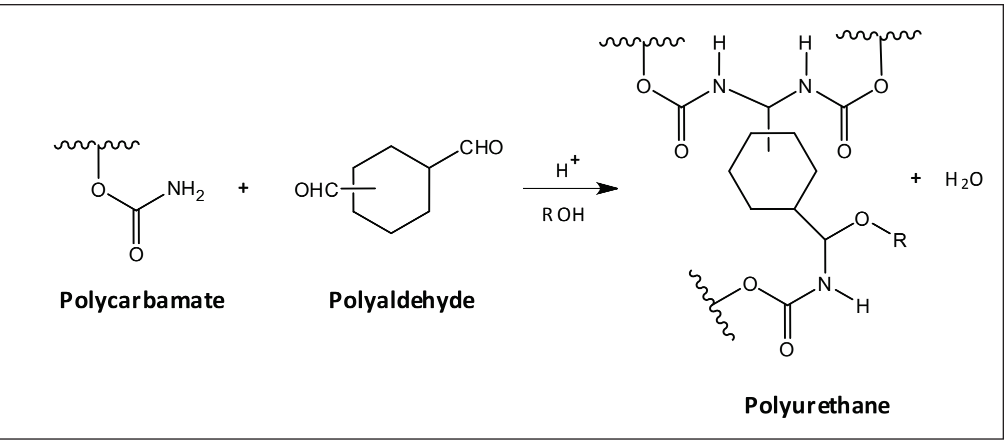


FIGURE 2—Preparation of polycarbamates from the reaction of polyols with urea.

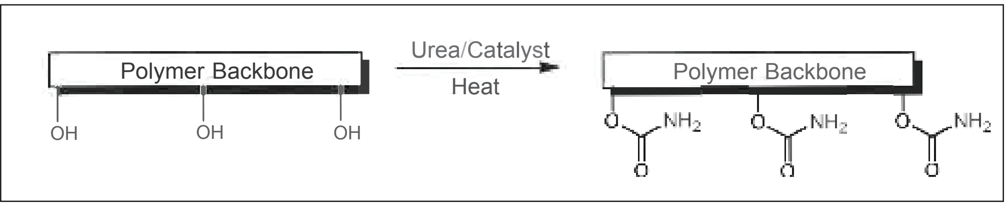
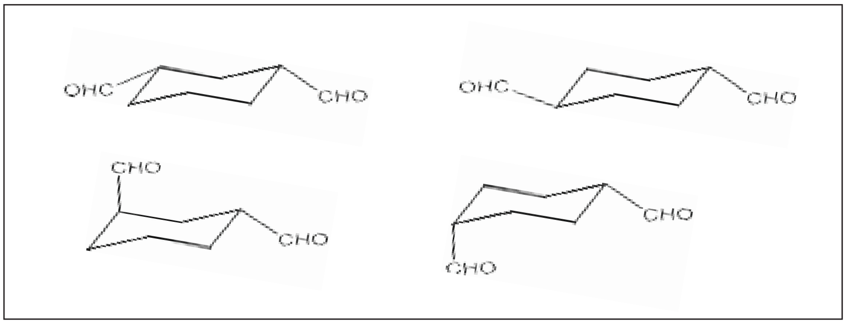


FIGURE 3—Chemical structure of the preferred polyaldehyde crosslinker CHDA.



BACKGROUND: CHEMISTRY OF THE ISOCYANATE-FREE POLYURETHANE TECHNOLOGY

An isocyanate-free system for the formation of a polyurethane coating at ambient temperatures from the reaction of a polycarbamate resin and a polyaldehyde crosslinker in the presence of an acid catalyst is presented in *Figure 1*.

The polycarbamate resin can be made from various polyol types such as acrylics or alkyds. The advantage of this approach is that polyols, a component in traditional polyurethane coatings, can be used in preparing the carbamylated resin. The polyols can be transformed into their corresponding polycarbamates through a transcarbamylation reaction of the polyol with urea at elevated temperatures using a catalyst (*Figure 2*). Final carbamate resin properties will be varied based on the properties of the parent polyol.

The crosslinker is a mixture of 1, 3-cyclohexanedicarboxaldehyde and 1, 4-cyclohexanedicarboxaldehyde (CHDA). The equivalent weight of the CHDA is 78.4. The structure of the crosslinker is shown in *Figure 3*.

MATERIALS AND METHODS

Strategy

The VOC of the standard isocyanate-free clear coating is approximately 560 g/L. To achieve reduced VOC with this 2K acid catalyzed system, the following approaches were studied.

First, various VOC-exempt solvent combinations that would allow lower VOC at approximately 450 g/L were studied to achieve less than 1.0 lb of solvent/1 lb acid-cured solid resin, and then a search for the optimum blend ratio of VOC-exempt solvents, based on the evaporation rate that will give excellent film build with fast air dry cure, was conducted. Solvent blends evaluated include t-butyl acetate (TBAC)/parachlorobenzotrifluoride (PCBTF), dimethyl carbonate (DMC)/PCBTF, and PCBTF/acetone. PCBTF was included in the blends to slow down the overall evaporation rate while the t-butyl acetate, dimethyl carbonate, and acetone are effective at reducing viscosity. The solids level of a coating can also be adjusted to reduce VOC, resulting in less free solvent in the formulation; although, in this study, the solids were adjusted to obtain a better initial viscosity. The solids range evaluated was from 39.9 to 43.1%.

In this crosslinking system, ethanol is present to block or hinder the reaction between the carbamylated resin and the CHDA, through the preformation of acetals. The addition of ethanol to the crosslinker is a crucial step for managing application. Without adequate ethanol the reaction of the CHDA and the carbamate resin would happen rapidly and not allow for an appropriate application window. However, ethanol also counts toward the overall VOC of the coating. To provide a greater latitude for reducing VOC, a decrease in the level of ethanol is necessary to reach 450 g/L. With less ethanol present, the pot life will become shorter. Consequently, other slower evaporating primary alcohols, such as propanol or butanol, were evaluated in a blend as a partial replacement for some of the remaining ethanol to help maintain and lengthen the pot life.

One other option to offset the shortened pot life involves using methanol in the formulation at the maximum allowable limit to help maintain the pot life. Methanol, at below a three percent level in a formulation, will not trigger a warning (health hazard statement) label on the Safety Data Sheet. Since methanol is the smallest primary alcohol, it will have the most efficient interaction with the CHDA and may be better at extending the pot life even at low levels.

The clear starting point formulation includes an alkyd polycarbamate resin at 67% solids in n-butyl acetate in the part A component, and the polyaldehyde crosslinker (CHDA) with ethanol and PTSA in the part B component. The polycarbamate resin has a polyol equivalent weight of 345 (based on solids), a glass transition temperature of 31°C, and a number average molecular weight (Mn) of 2500. The polyaldehyde crosslinker has an equivalent weight of 78.4.

The clearcoat formulations were applied by draw down over chromate treated 3003H14 aluminum panels (0.025 x 4 x 12 in.) with a 10 mil draw down bar for a 2 mil dry film thickness. Key properties of interest are solution viscosity, pot life, dry-to-touch time, dry through time, film hardness, and methyl ethyl ketone (MEK) double rubs.

Viscosity

Brookfield viscosity measurements were made with the Brookfield LVT Viscometer DV-III using spindle #2 at 12 RPM. Measurements were based on ASTM standards. The initial viscosity and the viscosity over time were recorded. Zahn cup readings (the time it takes for the cup to empty) were also measured using a Zahn cup #2. Because the initial Brookfield viscosity is quite low for the test formulations, we also measured the Zahn cup viscosity to track how the viscosity changes with time.

The pot life was determined as the amount of time for the Brookfield viscosity to double from the initial viscosity. Another way of monitoring the pot life is to record how long it takes to reach a Zahn cup reading of 26 sec. In general, it is best to prepare a formulation that gives a Zahn cup reading of 20 to 25 sec for optimum spraying. As the viscosity goes above 25 sec and approaches 30 sec, gels begin to form in the formulation and the mixture slowly becomes too thick for the best spray application. So, measuring the length of time to reach 26 sec is an effective way of understanding the workable pot life.

Film Hardness and Flexibility

A pendulum hardness tester (TQC Model SP0500) was used to track the Konig hardness over one, three, and seven days. The Konig hardness measurements were performed following ASTM D4366. The pencil hardness was also tracked based on ASTM D3363-05. Pencil hardness ranges from 6B (softest) through B, HB, F, and H through 8H (8H having the highest hardness). Mandrel flexibility involves bending 4 in. x 1.5 in. test specimens (2 mil dry films applied on treated aluminum) over 1/8, 1/4, and 1/2 in. diameter rods to determine the degree of flexibility of the coating. The panels that can be bent over the cylinder without film damage pass the mandrel flexibility at that particular diameter. While not a key property for wood coatings, it was included in the battery of tests.

Film Curing/Degree of Crosslinking

MEK rubs were measured to determine the extent of crosslinking that was occurring over time. The MEK rubs were determined by using a Crockmeter (Model CM-5, Atlas Electrical Device Co.) with a cheesecloth pad saturated

TABLE 1—Initial Starting Point Formulation based on the Polycarbamate Resin and CHDA at 561 g/L VOC (Control)

MATERIAL NAME	WEIGHT (LB)	VOLUME (GAL)
PART A		
POLYCARBAMATE RESIN A, 67%	375.05	42.62
TINUVIN 5100 (HALS)	0.88	0.10
BYK 378	0.28	0.03
N-BUTYL ACETATE	165.90	22.57
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SUBTOTAL - PART A	542.11	65.32
PART B		
CHDA CROSSLINKER	61.71	7.01
ETHANOL	183.76	27.93
K-CURE 1040 CATALYST	8.51	1.03
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SUBTOTAL PART B	253.98	35.97
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TOTAL – PARTS A + B	796.09	101.29
FORMULATION PROPERTIES:		
WEIGHT % SOLIDS	39.86	
DENSITY (LB/GAL)	7.86	
VOLUME SOLIDS (%)	32.33	
VOC (G/L)	561	
VOC (LB SOLVENT/LB ACID-CURED RESIN)	1.5	

TABLE 2—Survey of Various Combinations of VOC-exempt Solvents for Reducing the VOC of the Clear

FORMULATION	S-12	S-13	S-8	S-6	S-2	CONTROL
VOC-EXEMPT SOLVENT	PCBTF/ ACETONE	DMC/ PCBTF	PCBTF/ ACETONE	DMC/PCBTF	TBAC/PCBTF	NONE
SOLVENT USAGE IN RX	PARTS A + B	PARTS A + B	PART A	PART A	PART A	-----
SOLVENT RATIO	65/35	65/35	65/35	65/35	75/25	-----
WT % SOLIDS	39.86	39.86	39.86	39.86	39.86	39.86
DENSITY (LB/GAL)	8.31	8.43	8.19	8.29	7.99	7.86
VOL SOLIDS (%)	34.19	34.67	33.71	34.11	32.86	32.33
VOC (G/L)	456	456	469	477	477	561
VOC (LB SOLVENT/ LB ACID CURED RESIN)	0.90	0.90	1.0	1.0	1.0	1.5
BROOKFIELD VISC. (cP)	5	5	12	5	17	12
POT LIFE (H)	0.5	1	1	1.4	1.4	2
DRY-TO-TOUCH (MIN)	3	7	9	8	10	9
DRY THROUGH (MIN)	58	53	48	39	35	48
KONIG HARDNESS (SEC)						
1 DAY	115	95	111	110	119	139
7 DAY	174	168	175	171	167	173
MANDREL FLEXIBILITY						
1 DAY	P 1/4 IN.	P 1/2 IN.	P 1/8 IN.	P 1/8 IN.	P 1/8 IN.	P 1/8 IN.
7 DAY	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.

TABLE 3—Viscosity Adjustment of the Clear Formulation by Varying the Weight % Solids

FORMULATION	SOL-1	SOL-2	SOL-3	SOL-4	SOL-5 CONTROL
VOC-EXEMPT SOLVENT	PCBTF/ ACETONE	PCBTF/ ACETONE	PCBTF/ ACETONE	PCBTF/ ACETONE	NONE
SOLVENT USAGE IN RX	PARTS A + B	PARTS A + B	PARTS A + B	PARTS A + B	-----
SOLVENT RATIO	65/35	65/35	65/35	65/35	-----
WT % SOLIDS	39.86	40.87	41.95	43.08	39.86
DENSITY (LB/GAL)	8.31	8.30	8.28	8.26	7.86
VOL SOLIDS (%)	34.19	35.00	35.83	36.75	32.33
VOC (G/L)	456	456	456	456	561
VOC (LB SOLVENT/LB ACID-CURED RESIN)	0.90	0.90	0.90	0.90	1.5
BROOKFIELD VISCOSITY (cP)	15	17	20	27	10
ZAHN CUP#2 INITIAL (SEC)	18	18	19	20	18
POT LIFE (MIN)	60	50	55	65	65
ZAHN CUP TIME TO 26 SEC (MIN)	106	97	75	63	180
DRY-TO-TOUCH (MIN)	5	5	5	5	6
DRY THROUGH (MIN)	75	63	93	82	73
KONIG HARDNESS (SEC)					
1 DAY	87.5	112.1	95.7	92.4	105.2
2 DAY	116.1	129.6	114.1	114.6	130.1
7 DAY	147.2	148.6	137.8	140.6	146.4
MANDREL FLEXIBILITY					
1 DAY	P 1/4 IN.	P 1/4 IN.	P 1/4 IN.	P 1/2 IN.	P 1/4 IN.
2 DAY	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.	F 1/2 IN.	P 1/2 IN.
7 DAY	P 1/2 IN.	F 1/2 IN.	F 1/2 IN.	F 1/2 IN.	F 1/2 IN.
MEK RUBS – 1 DAY (NO RUBS)					
FIRST FAILURE	-----	54	64	62	58
REMOVED 100%	82	84	83	79	78
MEK RUBS – 7 DAYS					
FIRST FAILURE, NO.OF RUBS	80	82	69	90	80
% REMOVED AT 200 RUBS	10	10	10	10	10

with MEK attached to the unit in contact with the film. The pad moves back and forth across the film which is applied over treated aluminum panels. The test is run to a maximum of 200 cycles and the number of cycles is recorded for when there is the beginning of film failure (i.e., when the film thins to the point where the substrate is just becoming uncovered at spots in the test area), when 50% of the coating is removed, and when 100% of the coating is removed from the test area. The test was run with films that air cured for one and seven days.

RESULTS AND DISCUSSION

Survey of VOC-exempt Solvents

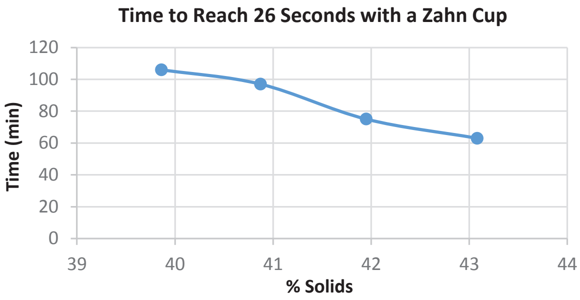
Various combinations of PCBTF/acetone, DMC/PCBTF, and TBAC/PCBTF were evaluated for reducing VOC while still providing a favorable balance of pot life, film hardness development, and flexibility. In the formulation, all the free n-butyl acetate in the control formulation component A was replaced with various VOC-exempt solvents. This reduces the VOC from 561 to about 477 g/L. To achieve a VOC of 450 g/L, some additional solvent must be removed from the part B component, and the only free solvent that can be reduced is the ethanol, which is used to hinder the crosslinker from reacting with the carbamylated resin. By removing 18% of the total ethanol and replacing it with VOC-exempt solvents, a VOC of approximately 450 g/L can be reached, but this results in a reduction of the pot life. *Table 2* shows the various combinations of VOC-exempt solvents evaluated in the clear formulation. The VOC can be achieved by using the different combinations of VOC-exempt solvents in both the part A and B components, but with a corresponding decrease in the pot life as measured by the Brookfield viscosity. Moreover, the dry through time tends to increase as more PCBTF is included in the formulation due to its high density (11.2 lb/gal). Based on the initial round of testing, the preferred solvent package is PCBTF/acetone, because both these solvents are accepted as VOC-exempt across the entire United States. The film hardness and flexibility are similar to the initial control formulation, but the initial viscosity is quite low. The next step in the development of a reduced VOC formulation was to increase the solids so that the initial viscosity was adjusted up to 30 to 40 cP by Brookfield viscosity (or 20 to 25 sec by Zahn cup #2).

Adjusting the % Solids

At this stage in the development, the formulation, now including PCBTF/acetone in the part A and B components, gives a VOC of about 450 g/L at 39.9% solids. To bring up the initial viscosity of the formulation, the mixture was further modified to evaluate the coating at various solids levels ranging from 39.9 through 43.1%. This was accomplished by removing some of the PCBTF/acetone solvent from both the part A and B components. *Table 3* shows that as the solids level increases, the initial viscosity and Zahn cup reading also tend to increase. For example, the clear formulation at 43.1% solids gives a Brookfield viscosity of 27 cP and a Zahn cup reading of 20 sec, which is very good for an initial viscosity. However, as the % solids content increases to 43.1%, the pot life decreases, requiring less time for the Zahn cup reading to reach 26 sec. The pot life of the 39.9% sample was 106 min, whereas the 43.1% sample had a pot life of only 63 min.

Plotting the time to reach 26 sec relative to the % solids shows that the time for optimum spraying decreases with higher solids and mirrors what would be expected from a shortened pot life (*Figure 4*).

FIGURE 4—Normal range on the Zahn cup #2 for conventional spray is 20 to 25 sec. Once the viscosity increase gives a Zahn cup greater than 26 to 30 sec, the spray quality will begin to decrease. The curve simulates the pot life behavior typically measured by the Brookfield viscosity.



Figures 5a through *5d* show the viscosity with respect to time for the clear formulations ranging from 39.9 to 43.1% at approximately 450 g/L relative to the initial starting point formulation at

FIGURE 5a—Formulation with PCBTF/acetone at a reduced VOC and at 39.86% solids (Sol-1 was set at 39.86% solids and approximately 450 g/L, and Sol-5 was the control at 39.86% solids at approximately 560 g/L).

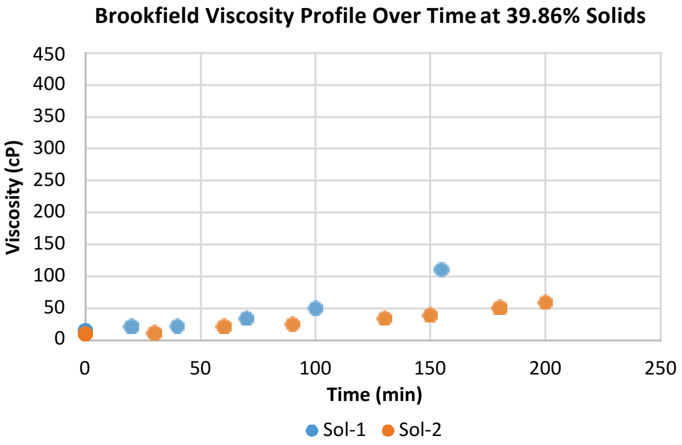


FIGURE 5b—Formulation with PCBTF/acetone at a reduced VOC and at 40.87% solids. (Sol-2 was set at 40.87% solids and approximately 450 g/L, and Sol-5 was the control at 39.86% solids at approximately 560 g/L).

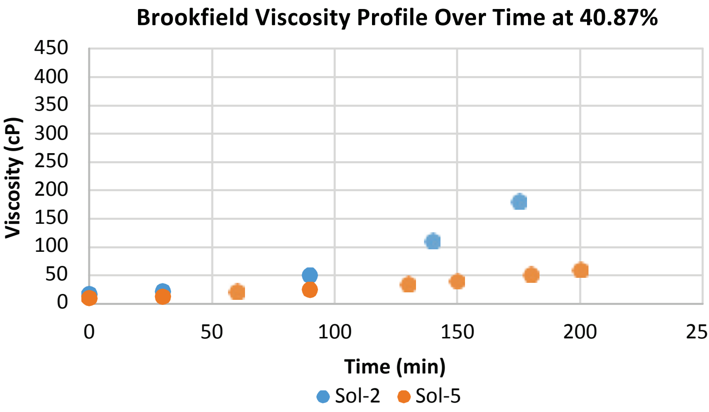


FIGURE 5c—Formulation with PCBTF/acetone at a reduced VOC and at 41.95% solids. (Sol-3 was set at 41.95% solids and approximately 450 g/L, and Sol-5 was the control at 39.86% solids at approximately 560 g/L).

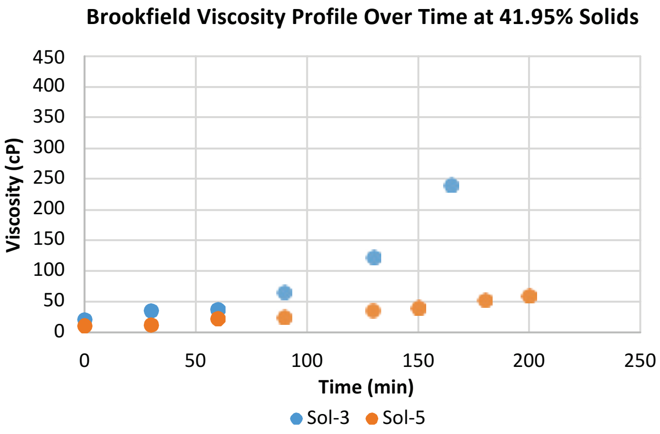
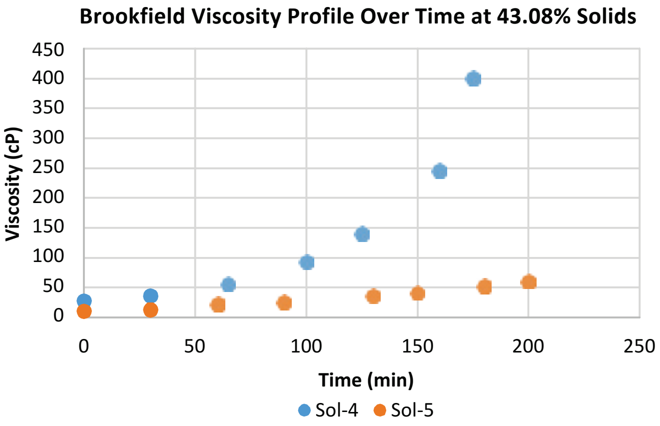


FIGURE 5d—Formulation with PCBTF/acetone at a reduced VOC and at 43.08% solids. (Sol-4 was set at 43.08% solids and approximately 450 g/L, and Sol-5 was the control at 39.86% solids at approximately 560 g/L).



39.9% and 561 g/L. As one reviews these four plots, it is evident that the viscosity profile rises more sharply as the solids of the formulation increases. So, just a 3% increase in solids has a significant impact on the change in viscosity with respect to time. However, in terms of coating properties, the films have similar film hardness and flexibility, as well as chemical resistance and MEK rubs, independent of the solids.

The modified formulation, changed to increase initial viscosity, had less ethanol, and was at a higher solids to achieve a better initial viscosity, but it has a shorter pot life. One possible option for extending the pot life was to replace some of the ethanol with a longer chain primary alcohol such as n-butanol.

Replacing Ethanol with Butanol

The next series explores the possibility of using butanol (a slower evaporating primary alcohol than ethanol) to help hinder the crosslinking between the CHDA and the carbamylated resin since the butanol will remain in solution longer than ethanol before evaporating. As a result, the butanol may continue to hinder the CHDA and thereby extend the pot life. A ladder was done based on replacing some of the ethanol with butanol ranging from 15 through 30%. The screening formulation was set at 43.1% solids and had a VOC of approximately 450 g/L. *Table 4* summarizes the results for this series. Although the pot life looks similar for all the clears based on Brookfield viscosity, the time to reach 26 sec on the Zahn cup indicates that the pot life decreases as higher levels of butanol are included in the formulation.

A plot of the Brookfield viscosity with time demonstrates that as the butanol level increases, the viscosity rise over time becomes greater and more rapid (*Figure 6*). Although butanol leaves the film more slowly than ethanol, it is less efficient at hindering the reaction of the CHDA and the resin. With less available ethanol in the formulation, the viscosity change with time becomes more pronounced. *Figure 6* shows that there is a step change in the viscosity profile when moving from the initial starting point formulation to the reduced VOC mixture where PCBTF/acetone replaces the n-butyl acetate,

TABLE 4—Addition of Butanol to Replace Some of the Ethanol in the Clear Formulation to Extend Pot Life

FORMULATION	B-1	B-2	B-3	B-4	B-5 CONTROL
% OF ETHANOL REPLACED W/BUTANOL	0	15	25	30	—
VOC-EXEMPT SOLVENT	PCBTF/ACETONE	PCBTF/ACETONE	PCBTF/ACETONE	PCBTF/ACETONE	NONE
SOLVENT USAGE IN RX	PARTS A + B	PARTS A + B	PARTS A + B	PARTS A + B	—
SOLVENT RATIO	65/35	65/35	65/35	65/35	—
WT% SOLIDS	43.08	43.08	43.08	43.08	39.86
DENSITY (LB/GAL)	8.26	8.27	8.28	8.28	7.86
VOL SOLIDS (%)	36.75	36.78	36.80	36.80	32.33
VOC (G/L)	456	456	456	456	561
VOC (LB SOLVENT/LB ACID-CURED RESIN)	0.9	0.9	0.9	0.9	1.5
BROOKFIELD VISCOSITY (cP)	25	28	28	35	10
ZAHN CUP#2 INITIAL (SEC)	20	21	21	21	17
POT LIFE (MIN)	60	60	55	50	65
ZAHN CUP TIME TO 26 SEC. (MIN)	75	55	45	40	180
DRY-TO-TOUCH (MIN)	6	7	8	9	9
DRY THROUGH (MIN)	64	75	108	94	62
KONIG HARDNESS (SEC) 1 DAY 2 DAY 7 DAY	 112.2 129.5 166.0	 95.7 114.5 158.0	 75.4 95.7 147.2	 65.2 87.9 142.8	 106.8 127.6 171.8
MANDREL FLEXIBILITY 1 DAY 2 DAY 7 DAY	 P 1/8 IN. P 1/2 IN. F 1/2 IN.	 P 1/8 IN. P 1/2 IN. F 1/2 IN.	 P 1/4 IN. P 1/4 IN. P 1/2 IN.	 P 1/8 IN. P 1/2 IN. P 1/2 IN.	 P 1/8 IN. P 1/2 IN. P 1/2 IN.
MEK RUBS—1 DAY (NO RUBS) FIRST FAILURE REMOVED 100%	 55 92	 41 84	 32 80	 32 72	 38 105
MEK RUBS—7 DAYS FIRST FAILURE, NO. OF RUBS % REMOVED AT 200 RUBS	 58 10	 75 65	 78 100	 82 100	 75 5

FIGURE 6—Effect on the Brookfield viscosity profile by replacing some ethanol with butanol.

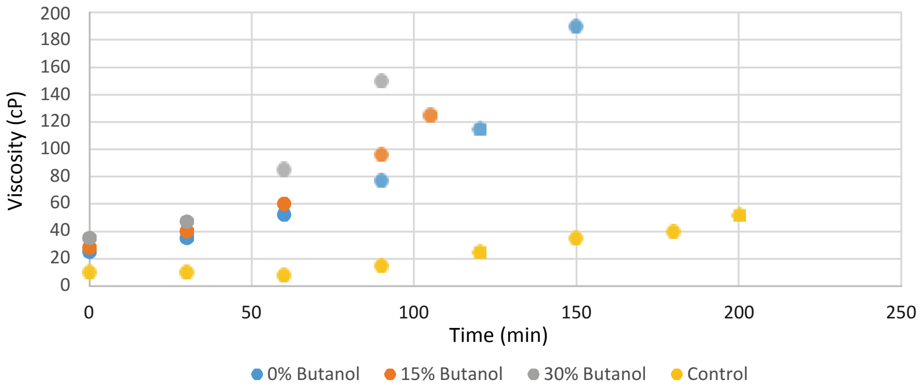
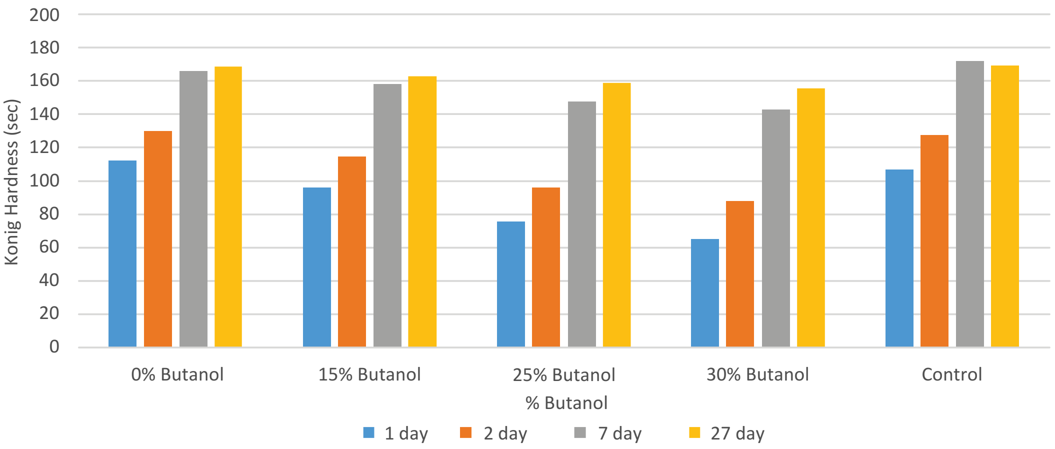


FIGURE 7—Effect of replacing some of the ethanol with butanol on film hardness development. (The % butanol is based on the total amount of ethanol in the formulation.)



and some of the ethanol is replaced with PCBTF/acetone in the component B portion. Additionally, the solids of the formulation is increased from 39.9 to 43.1%. So, the step change in the rate of viscosity increase is significant when comparing the control and the mixture at 43.1 % solids with no butanol added, lowering the pot life by 58%. As butanol is added into the formulation, the viscosity profile continues to become even steeper, decreasing the pot life by an additional 47%. The greatest effect on the rate of viscosity increase with time comes from increasing the solids of the formulation. The addition of butanol as a replacement for some of the ethanol impacts the viscosity profile over time, but seems less significant.

Butanol also affects the early film hardness and the MEK rubs. *Table 4* shows that the film hardness decreases with higher levels of butanol present because the butanol remains in the film and most likely plasticizes the film. For the very same reason, the higher level of butanol hurts the MEK rubs performance. However, after four weeks of drying, the coatings catch up in film hardness and MEK resistance compared with the formulations without butanol (*Figure 7*).

Since butanol did not give extended pot life and hurt the film hardness and MEK rubs performance, other primary alcohols were considered. Propanol is lighter than butanol in terms of carbon chain length, and may be more efficient at hindering the interaction of the CHDA with the carbamylated resin, yet it will evaporate slower than ethanol. Methanol is another alcohol included in this round of testing because, as the smallest primary alcohol, it is the most efficient at interacting with the CHDA.

Other Primary Alcohols (Propanol and Methanol)

In this series, clears were prepared at 43.1% solids with a VOC approximately 450 g/L. Butanol, propanol, and methanol were included in the screening formulation at 14.6% of the total amount of ethanol (which is at 3% of the total formulation weight). In addition, a formulation was included with butanol at 30% of the total amount of ethanol (which corresponds to 6% of the total formulation weight). *Table 5* summarizes the results from this round of experiments.

Propanol did not extend the pot life of the formulation and behaves similarly to butanol, especially when considering the time to reach 26 sec for the Zahn cup reading (60 min for 3% butanol and 68 min for 3% propanol). On the other hand, methanol gave improved pot life to the formulation at 43.1% solids, increasing it 51% compared with 3% butanol, although the pot life is not as long as the control. However, adding just 3% methanol, based on the total formulation weight, was quite effective at improving the pot life and bringing it to a more practical level. The Brookfield viscosity profile and the Zahn cup readings for the formulation with methanol gave a slower viscosity increase with time, which aligns with the observed improvement in pot life (*Figures* 8 and 9). In addition, this formulation had very good MEK rub resistance, similar to the control. However, this formulation gave films that have somewhat lower Konig hardness compared to the control. This may be due to the presence of PCBTF in the clear formulation. PCBTF is a very dense solvent at 11.2 lb/gal, which may not leave the film as easily as other typical solvents. In addition, it evaporates somewhat slower at an evaporation rate of about 0.9 (xylene has an evaporation rate around 0.6 and butyl acetate evaporation rate is 1.0).

The Zahn cup readings for the clear formulations with added propanol and methanol for extending the pot life compared with the initial starting point formulation at approximately 560 g/L is shown in *Figure 9*. As mentioned previously, it shows that the pot life can be extended to 91 min with 3% methanol added to the formulation before reaching 26 sec, whereas addition of 3% propanol resulted in a pot life of 68 min.

SUMMARY AND CONCLUSIONS

It has been demonstrated that a clear 2K polyurethane formulation based

TABLE 5—Effect of Propanol and Methanol on the Film Properties and Pot Life of the Clear Formulation

FORMULATION	PM-1	PM-2	PM-3	PM-4	PM-5 CONTROL
% ALCOHOL BASED ON TOTAL Rx WT	3% BUTANOL	3% PROPANOL	3% METHANOL	6.1 % BUTANOL	-----
% OF ETHANOL REPLACED W/ALTERNATIVE ALCOHOL	14.65% BUTANOL	14.65% PROPANOL	14.65% METHANOL	30% BUTANOL	-----
VOC-EXEMPT SOLVENT	PCBTF/ACETONE	PCBTF/ACETONE	PCBTF/ACETONE	PCBTF/ACETONE	NONE
SOLVENT USAGE IN Rx	PARTS A + B	PARTS A + B	PART A + B	PART A + B	-----
SOLVENT RATIO (PCBTF/ACETONE)	65/35	65/35	65/35	65/35	-----
WT% SOLIDS	43.08	43.08	43.08	43.08	39.86
DENSITY (LB/GAL)	8.27	8.26	8.26	8.28	7.86
VOL SOLIDS (%)	36.76	36.76	36.74	36.80	32.33
VOC (G/L)	456	456	456	456	561
VOC (LB SOLVENT/LB ACID-CURED RESIN)	0.9	0.9	0.9	0.9	1.5
BROOKFIELD VISCOSITY (CP)	3	23	3	25	10
ZAHN CUP#2 INITIAL (SEC)	20	20	19	22	17
POT LIFE (MIN)	57	60	63	42	97
ZAHN CUP TIME TO 26 SEC (MIN)	60	68	91	35	213
DR-TO-TOUCH (MIN)	9	7	9	10	8
DRY THROUGH (MIN)	127	99	92	150	81
KONIG HARDNESS (SEC)					
1 DAY	71.1	72.5	72.4	60.9	79.8
2 DAY	81.9	----	79.7	71.8	----
7 DAY	127.6	130.9	129.1	118.2	145.4
MANDREL FLEXIBILITY					
1 DAY	P 1/4 IN.	P 1/8 IN.	P 1/8 IN.	P 1/8 IN.	P 1/8 IN.
2 DAY	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.	P 1/4 IN.	P 1/2 IN.
7 DAY	F 1/4 IN.	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.	P 1/2 IN.
MEK RUBS- 1 DAY (NO RUBS)					
FIRST FAILURE	46	60	49	47	50
REMOVED 100%	95	75	100	70	75
MEK RUBS – 7 DAYS					
FIRST FAILURE, NO. OF RUBS	95	95	110	78	70
% REMOVED AT 200 RUBS	10	65	15	100	10

FIGURE 8—Brookfield viscosity profile over time—effect of methanol and propanol on extending the pot life of a reduced VOC clear formulation.

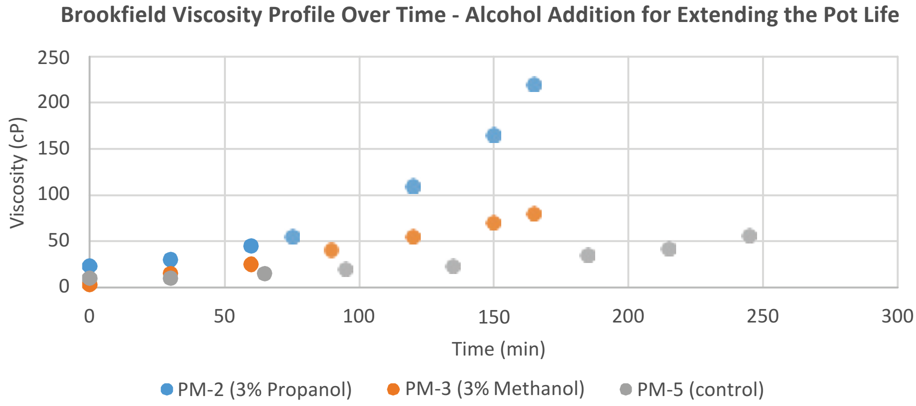
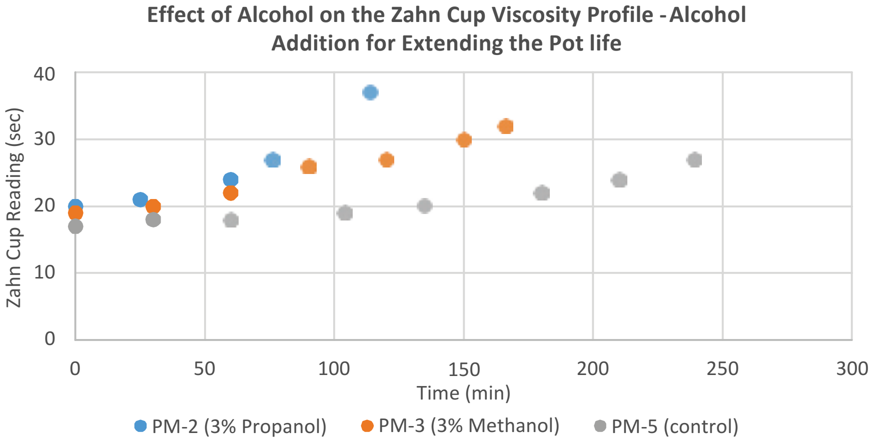


FIGURE 9—Zahn cup viscosity profile over time—effect of methanol and propanol on extending the pot life of a reduced VOC clear formulation.



on a nonisocyanate approach can be modified with VOC-exempt solvents to achieve a lower VOC meeting R307-343 Utah's VOC regulation for acid-cured topcoats. By using an optimized combination of VOC-exempt solvents, weight % solids, and balancing of the primary alcohol(s), a 2K systems can be developed. The modified formulation that is at 43.1% solids and approximately 450 g/L VOC is shown in *Table* 6.

Different solvent packages were evaluated including t-butyl acetate/PCBTF, dimethyl carbonate/PCBTF, and PCBTF/acetone. Although various combinations of these solvents gave workable formulations, the preferred combination consists of PCBTF/acetone, since it is considered VOC-exempt throughout the United States.

The formulation % solids can be used to decrease the amount of free solvent and can be an effective way to reduce VOC, especially when all the free solvent counts toward the VOC. In this case, increasing the weight % solids of the formulation was used to adjust the initial viscosity. In one experiment, we varied the % solids from 39.9 through 43.1%. Ideally, it would be best to achieve a solids of about 42% to balance out the initial viscosity and its effect on the viscosity profile over time. Since removing some of the ethanol from the part B component was necessary to bring down the VOC to approximately 450 g/L, a combination of primary alcohols was needed to maintain a workable pot life.

Butanol, propanol, and methanol were evaluated as possible options to extend the pot life and bring it back closer to the initial standard VOC starting point formulation. Butanol tended to remain in the film longer than ethanol because it is a longer chain primary alcohol,

TABLE 6—Modified Starting Point Formulation Based on a Polycarbamate Resin and CHDA Crosslinker at 43.1% Solids and Approximately 450 g/L VOC

MATERIAL NAME	WEIGHT (LB)	VOLUME (GAL)
PART A		
POLYCARBAMATE RESIN A, 67%	375.05	42.62
TINUVIN 5100 (HALS)	0.86	0.10
BYK 378	0.26	0.03
PCBTF	75.48	6.74
ACETONE	40.66	6.16
	----------	----------
SUBTOTAL PART A	492.31	55.65
PART B		
CHDA CROSSLINKER	61.71	7.01
ETHANOL	128.62	19.55
METHANOL	22.07	3.33
PCBTF	15.06	1.34
ACETONE	8.09	1.23
K-CURE 1040 CATALYST	8.52	1.03
	----------	----------
SUBTOTAL PART B	244.07	33.49
	----------	----------
TOTAL – PARTS A + B	736.38	89.14
FORMULATION PROPERTIES:		
WEIGHT % SOLIDS	43.1	
DENSITY (LB/GAL)	8.26	
VOLUME SOLIDS (%)	36.74	
VOC (G/L)	456	
VOC (LB SOLVENT/LB ACID-CURED RESIN)	0.90	

but it did not hinder the crosslinker as effectively as ethanol leading to a reduced pot life, and the butanol plasticized the film, slowing down the hardness development and chemical resistance. However, by using methanol (3% of the total formulation weight for the maximum allowable limit) along with the ethanol, the pot life could be extended back to a level closer to the original standard VOC starting point formulation. ❊

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