New Polyurethane Prepolymers for Ultra-Low VOC Plural Component Coatings

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SUMMARY

The drive toward lower and lower VOC coatings has led to a resurgent interest in plural component spray application technology. With this equipment, the reactive components are mixed just before or at the spray gun. Separating the components in this way before spraying allows the use of elevated temperatures to reduce formulation viscosity without concerns over the working life of the formulation, reducing or eliminating the need for solvent. The development of a new technology for producing very narrow molecular weight distribution isocyanate-terminated prepolymers with very low residual diisocyanate monomer has improved the viability of this process. These prepolymers decrease rapidly in viscosity with increasing temperature, and the low monomer content reduces worker exposure potential. This paper will introduce this prepolymer technology and illustrate the use of these prepolymers in formulating very low or near zero VOC polyurethane topcoats for high performance applications.

INTRODUCTION

Two part solvent-based coatings systems utilizing aliphatic isocyanates and polyester or acrylic polyols have become the industry standard for weatherable topcoats. These coatings systems combine exceptional resistance to chemical and physical damage with high gloss levels and long term retention of gloss, color and mechanical properties. Traditionally, these coatings systems have been formulated with a liquid polyisocyanate as one component and a high molecular weight, high functionality polyol and associated pigments and additives as the second component.[1]

A major driving force in the reformulation of coatings the world over is the need to reduce solvent emissions on application. One disadvantage of these traditional polyurethane formulations is the high solvent demand of the polyol component. This factor has limited the volatile organic content (VOC) reduction available with traditional polyol systems. One route to lowering VOC is to employ lower molecular weight polyols. As formulators incorporate more and more lower molecular weight (lower viscosity) polyols or reactive diluents into their systems, there has been an inevitable trade-off in physical properties of the resulting coatings and/or handling of the reactive mixture. Many low VOC polyurethane coatings today suffer from poor solvent resistance, poor flexibility, and an extreme sensitivity to catalyst level as it affects cure profile. In addition, with less solvent in the formulation and fewer ingredients to manipulate, maintaining convenient mixing ratios has also been a struggle.

Isocyanate producers have done an excellent job in educating their customers on the safe use of isocyanates in coatings and are constantly working to lessen any potential problems associated with these materials. One approach toward further improving isocyanate handling, described here, is to utilize higher molecular weight, isocyanate-terminated prepolymers as a source of isocyanate.

Concurrent with the drive toward lower and lower VOC for conventionally applied coatings, formulators and applicators have also increased the use of more specialized application equipment. Plural component application equipment has been used for many years to apply 100% reactive, fast reacting polyurethane coatings for thick film linings and for adhesives and sealants. With this equipment, the reactive components are metered into a chamber designed to rapidly mix the components. The reactive mixture is then pumped to a traditional airless or air-assisted airless spray gun.

This process has a number of advantages over conventional application equipment. Since material is used only on demand, little product is wasted, and start-up and shut-down times are reduced. In fact, for reasons of the productivity enhancement alone seen with this equipment, product finishers have sharply increased their use of plural component polyurethane coatings on industrial finishing lines. Often traditional solvent-borne, lower VOC coatings are used with increased catalyst levels to speed cure times and lower oven temperatures. Since the reactive components are mixed only seconds before application, short potlives can easily be tolerated. In fact, for extremely fast systems, equipment exists which mixes the components in the spray gun itself a fraction of a second before application.

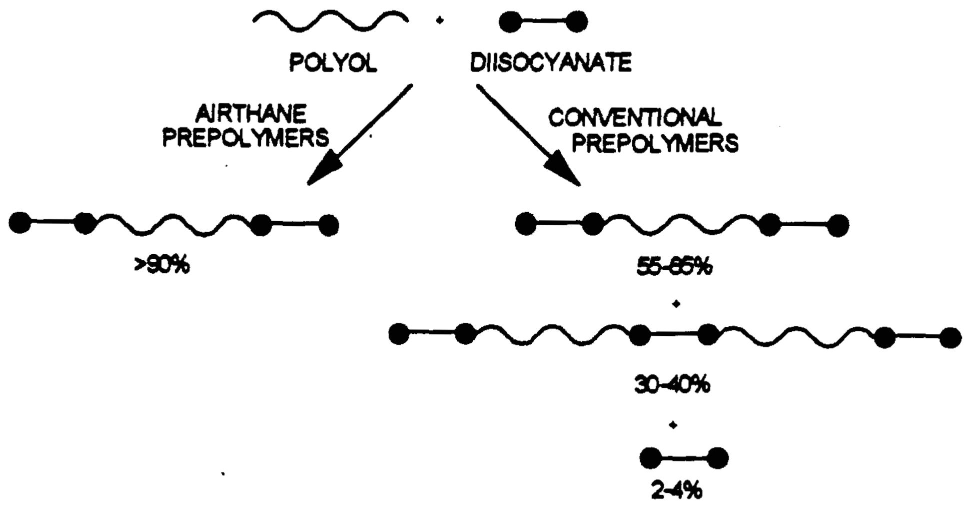
Perhaps more important for low VOC formulations, since short potlives can be tolerated, elevated temperatures can be used to lower the viscosity of the components instead of solvent. Using this approach, extremely high non-volatile material (NVM) coatings--approaching 100% NVM--may be possible using raw materials currently employed in conventional higher NVM formulations. Protective coating applicators and formulators are beginning to take advantage of these attributes to apply high quality primers and weatherable topcoats. This type of system works well in a controlled environment with stationery equipment, such as shop-applied rail car coatings or shop-coated structural steel. As equipment and formulations are refined, the potential also exists to take this type of equipment into the field.

This paper presents the use of newly developed isocyanate prepolymers--defined here as isocyanate/polyol adducts--as one alternative to formulating two component polyurethane topcoats. These prepolymers offer the advantages of a narrow molecular weight distribution, rapid viscosity reduction with increasing temperature or solvent level, very low diisocyanate monomer content, equivalent or improved film properties and weatherability characteristics compared to conventional coatings of this type, less sensitivity to catalyst level variability, and the ability to be formulated at a 1:1 volume ratio. While these prepolymers also are being used to formulate conventionally applied primers and topcoats[2], this paper will focus on the development of formulations specifically for plural component applied coatings where the unique characteristics of these prepolymers are used to overcome a number of formulating difficulties.

New Polyurethane Prepolymer Technology

Polyurethane prepolymers have been employed in certain segments of the coatings, adhesives, sealants, and elastomer industries for many years.[3] By forming a "pre"-polymer (see **Fig. 1**), diisocyanate monomer content is reduced and the reactivity of this partially reacted system is simpler to control. These prepolymers, however, have seen limited use in higher NVM coatings formulations. An examination of the synthesis process sheds some light on why this is so.

Figure 1: Comparison of Prepolymer Synthesis Technologies



The traditional synthesis process, depicted on the right side of Figure 1, typically involves the exothermic reaction of one equivalent of polyol with two equivalents of diisocyanate monomer. The desired end product, the isocyanate-capped polyol, makes up only around half of the weight of the final product mixture. Using this process, many of the diisocyanate monomer molecules react through both isocyanate groups, creating high molecular weight oligomers. These oligomeric species, which can be much larger than the simple 3:2 diisocyanate:polyol adduct shown in Figure 1, lead to the high solvent demand, relatively short pot lives, and poor sprayability of many prepolymer-based coatings formulations.

New technology, described in detail elsewhere,[4,5,6] has made available polyurethane prepolymers, tradenamed AIRTHANE® prepolymers, with half the viscosity of their conventional counterparts and extremely low diisocyanate monomer levels (<0.1% for aromatic isocyanates, <1.0% for aliphatic isocyanates). These materials, made by a process that keeps oligomer content very low, have the lower solvent demand and favorable pot life/dry time balance needed for high NVM formulating (see **Figures 2 and 3** and **Table 1**).

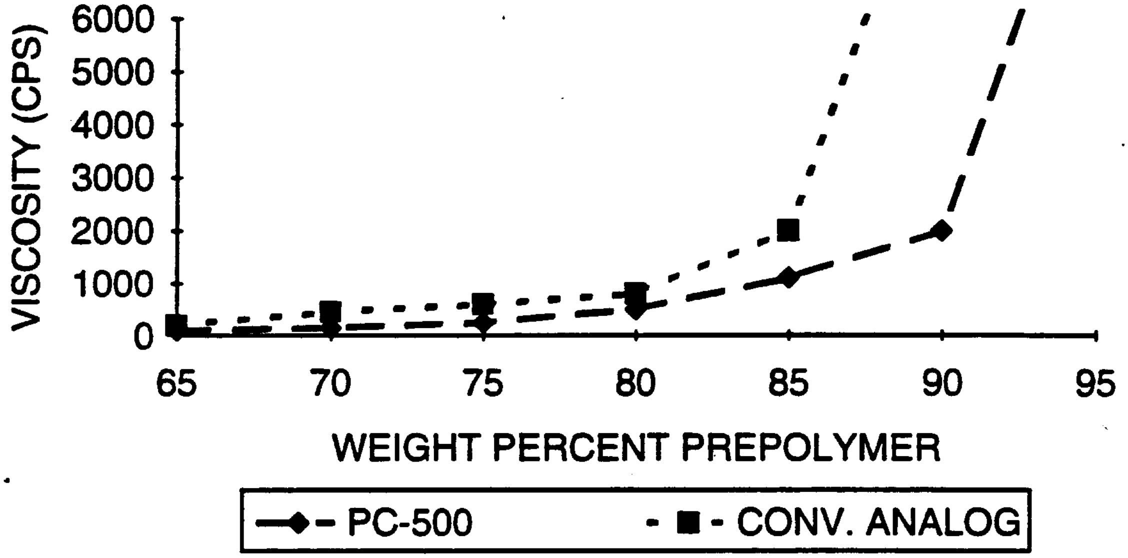


Figure 2: Comparison of Prepolymer Viscosities in Xylene

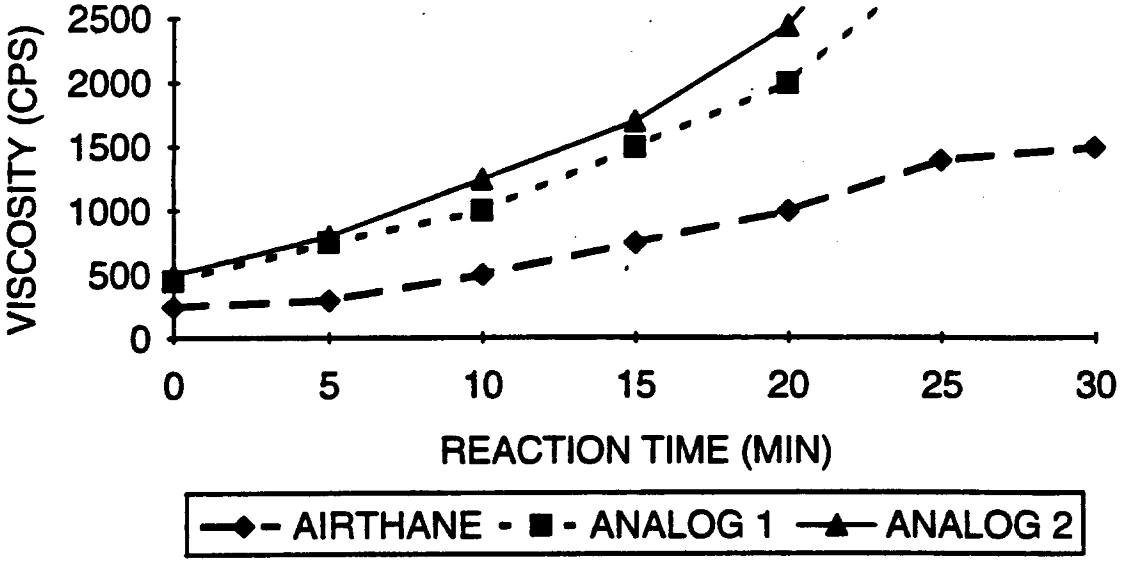


Figure 3: Comparison of Viscosity Build of Typical Prepolymer-based 2K Formulations

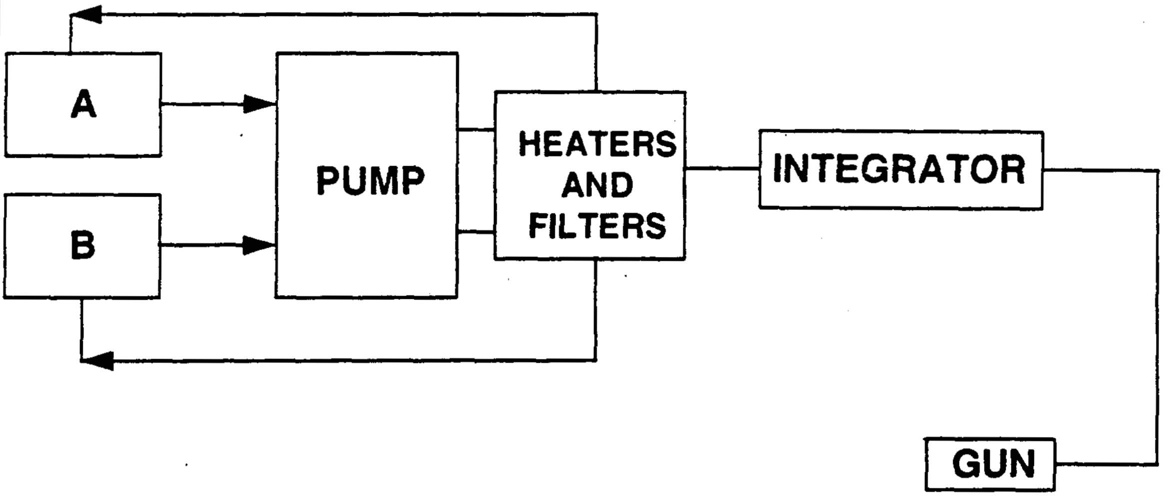
Table 1: Comparison of pot life (doubling of initial viscosity) and thin film cure times for a conventional prepolymer and its analog prepared by the Airthane prepolymer process.

Prepolymer	Wt. Solids (%)	Pot life	Cure time
Conventional Prepolymer	80	40 min	4.5 h
Airthane Prepolymer	85	2 h	6 h

Formulating for Plural Component Equipment

A typical plural component spray system contains the units described below in **Figure 4**. The reacting components are either pumped directly from their drums or from heated pots. The pumping mechanisms are typically reciprocating piston pumps that can deliver the two fluids at a set or variable volume ratio. The more common equipment will deliver a set ratio of 1:1, 2:1, or 4:1. Many set ups include in-line heaters and filters and may include a recirculation capability prior to the integrator. The integrator is a static mixer, often a proprietary design of the manufacturer. Following the integrator, the material is pumped through a "whip" section of hose to a standard airless or air-assisted airless spray gun.

Figure 4: Typical Plural Component Spray Equipment



The most critical event in the application of a successful system is the mixing of the components in the integrator. While different integrator designs affect how well the components mix, there are certain characteristics of the liquids that will lead to good mixing. It is generally believed[7] that in situations of laminar flow, it is easier to mix materials of more equal viscosity. If viscosities are unequal, it is easier to mix a small amount of a low viscosity material into a higher viscosity material than vice versa. Most plural component polyurethane formulations fall into the latter catagory, where a relatively small low viscosity isocyanate component is mixed into a larger pigmented polyol component. However, it would be better yet if nearly equal amounts of materials with matching viscosities could be used.

Problems also arise when, as frequently happens, the delivered ratio of the proportioning equipment varies slightly from the nominal. While equipment technology is improving at a rapid rate, mechanical proportioners such as those described above can often vary by up to 5%. Equipment that is not very carefully maintained can vary even further. For consistent application of high quality coatings, the formulation needs to be somewhat forgiving of ratio variations. These fluctuations are much more detrimental to a high ratio formulation (4:1 and up) than to a 1:1 ratio formulation since changes in the volume of the small volume component will have a more significant effect on the stoichiometry of the reacting system. Our goal, then, in formulating two part polyurethane coatings for plural component application was to develop systems at a 1:1 volume mix ratio wherein in the two components would have similar viscosities at application temperature.

Formulation Details and Coating Performance

Two types of formulations were developed. The first, for more weatherable applications, is based on acrylic polyols and is considered a high NVM system. A typical formulation is detailed in **Table 2**. The isocyanate component of this formulation is a prepolymer based isophorone diisocyanate (IPDI) and a mixture of neopentyl glycol adipates. It has a nominal equivalent weight of 540 g/eq (on solids) and an average functionality of about 2.5. It is used in this formulation as an 85% NVM solution in methyl amyl ketone (MAK). This formulation is delivered at a 1:1 volume mix ratio with an NCO/OH of 1.1. The viscosity profiles versus temperature for the isocyanate and polyol components are shown in **Figures 5** and **6**, respectively. Note that the two components have very similar viscosities at the application temperature of 50°C.

Table 2: Typical formulation for high NVM weatherable topcoat.

Material	Weight (lb)	Volume (gal)	Supplier	Comments
Component I				
Chempol 17-3855	242.19	27.84	CCP	acrylic polyol
Zoldine RD4	21.53	2.84	Angus	reactive diluent
Ti-Pure R960	384.49	11.58	DuPont	pigment
Disperbyk 110	18.20	2.14	Byk-Chemie	dispersant
Dislon NS-30	1.58	0.21	King Industries	thixotrope
Tinuvin 292	8.87	1.06	Ciba-Geigy	HALS
Tinuvin 400	10.44	1.26	Ciba-Geigy	UVA
Tego 980	4.14	0.52	Tego Chemie	air release
DABCO 120	0.59	0.07	Air Products	catalyst
18% Zn-Oct	3.52	0.40	OMG	catalyst
MAK	13.96	2.05		solvent
Subtotal	709.51	**49.97**		

Table 2: (continued)

Material	Weight (lb)	Volume (gal)	Supplier	Comments
Component II				
Airthane ASN-540M	442.64	50.03	Air Products	isocyanate prepolymer
Totals	**1152.15**	**100.00**		

Weight percent NVM = 87.76%; Volume percent NVM = 79.94%; PVC = 15.27%; VOC = 1.41 lb/gal (169 g/L); Mix Ratio: 1:1

Figure 5: Thermal Profile for ASN-540M

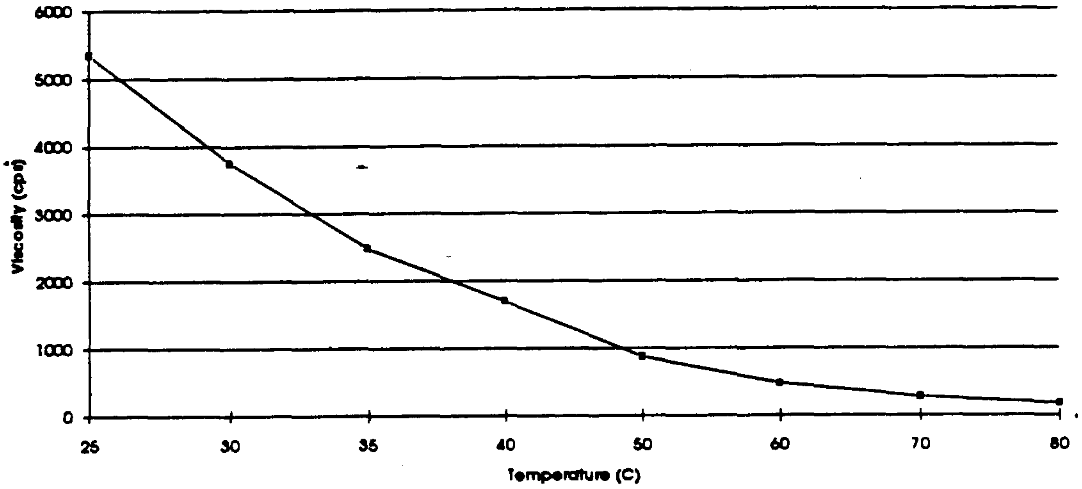
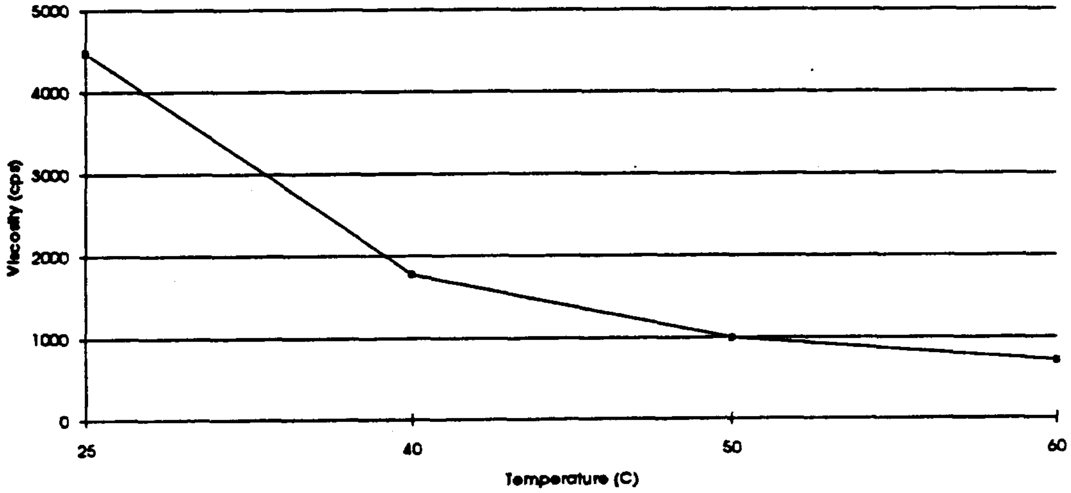


Figure 6: Thermal Profile for Pigment Grind of High NVM Formulation



The second type of formulation developed is based on polyester polyols and can be formulated at less than 0.20 lb/gal (24 g/L). A typical formulation is detailed in **Table 3**. The isocyanate component of this formulation is a mixture of the prepolymer used above with polyisocyanates based on hexamethylene diisocyanate (HDI). This unique combination of isocyanates provides low viscosity, high crosslink density, and sufficient molecular weight to formulate at a 1:1 mix ratio with an NCO/OH of 1.1. The use of the low oligomer prepolymer is critical to the success of this mixture. A conventional prepolymer would have too high a viscosity and most likely impart poor sprayability to the formulation. The viscosity profiles versus temperature for the isocyanate and polyol components are shown in **Figures 7** and **8**, respectively. Note, again, that the two components have very similar viscosities at the application temperature of 50°C.

Table 3: Typical formulation for very low VOC topcoat.

Material	Weight (lb)	Volume (gal)	Supplier	Comments
Component I				
Chempol 18-2244	192.10	20.11	CCP	polyester polyol
Tone 0301	82.33	9.10	Union Carbide	poly-caprolactone
Ti-Pure R960	483.85	14.57	DuPont	pigment
Disperbyk 110	21.47	2.52	Byk-Chemie	dispersant
Dislon NS-30	1.99	0.27	King Industries	thixotrope
Tinuvin 292	7.44	0.89	Ciba-Geigy	HALS
Tinuvin 400	8.76	1.06	Ciba-Geigy	UVA
Tego 980	3.72	0.47	Tego Chemie	air release
Byk 320	4.29	0.61	Byk-Chemie	flow aid
DABCO 120	0.37	0.04	Air Products	catalyst
18% Zn-Oct	4.43	0.51	OMG	catalyst
Subtotal	810.75	**50.15**		
Component II				
Airthane ASN-540M	234.98	25.38	Air Products	isocyanate prepolymer
Desmodur N3300	117.49	12.12	Miles/Bayer	HDI isocyanurate
Luxate HD-100	117.49	12.35	Olin	HDI uretdione
Subtotal	469.96	**49.85**		
Totals	1280.71	**100.00**		

Weight percent NVM = 98.74%; Volume percent NVM = 97.94%; PVC = 15.57%; VOC = 0.16 lb/gal (19 g/L); Mix Ratio: 1:1

Figure 7: Thermal Profile for 100% NVM Isocyanate Blend

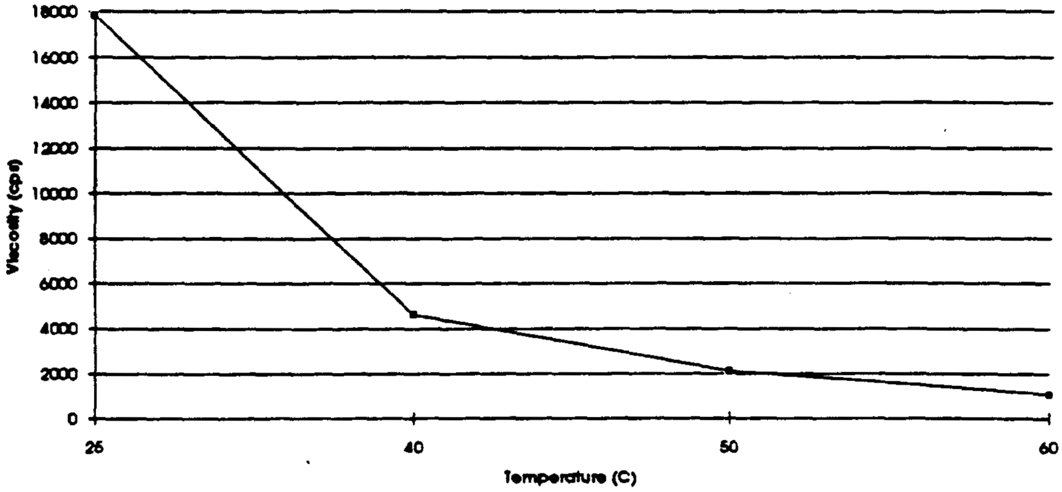
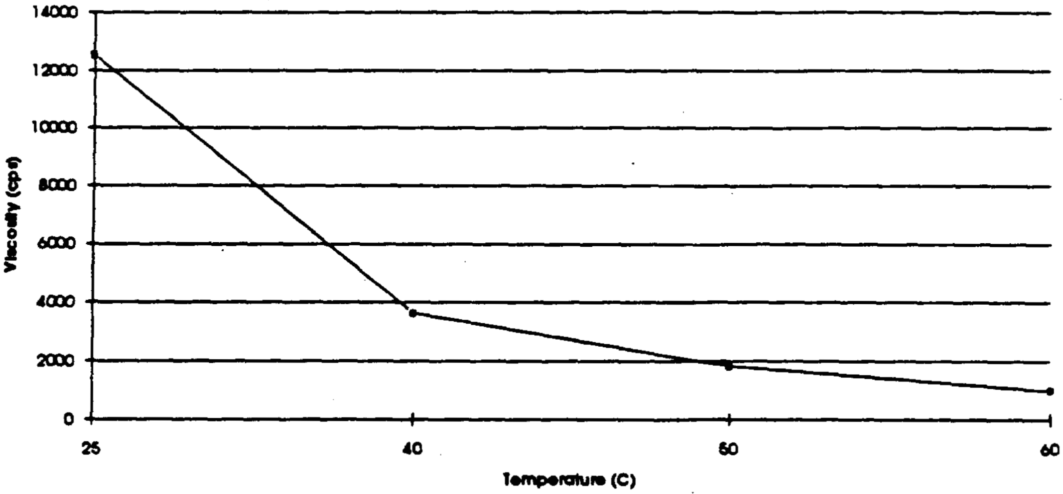


Figure 8: Thermal Profile for Very Low VOC Pigment Grind



The properties of these coatings are representative of traditional solvent borne urethanes and compare well with those of an HDI isocyanurate control. Physical and mechanical property comparisons are shown in **Table 4**. It is important to note that handling the isocyanurate control was much more difficult than the prepolymer based formulations. The control formulation required a 4:1 mix ratio (non-integer mix ratios were needed with other control formulations tried) and showed an extreme sensitivity to catalyst level. This was demonstrated by measuring the pot life of each of the formulations. The prepolymer formulations described above did not gel for several hours when mixed at ambient temperatures. The control formulations with no catalyst also had a pot life of several hours. The control formulations with the same modest catalyst levels used with the prepolymers, however, gelled in less than 15 minutes. Current work is aimed at better quantifying the relative catalysis lattitude of the prepolymer and control formulations, but it is apparent that the prepolymer approach is much less sensitive to variations in catalyst level.

Table 4: Representative Coating Film Property Comparison

Property	Prepolymer Acrylic	Isocyanurate Acrylic Control	Prepolymer Polyester
Set time (hours)	3	3	2
Dry hard (hours)	16	15.5	3
Pencil Hardness	HB	HB	HB
Dry Adhesion (ASTM D3359)	5A	4A	4A
Wet Adhesion (24 h, D3359)	4A	4A	4A
Impact (D/R in-lb)	160/160	160/160	160/160
MEK rubs	100+	100+	100+
60° Gloss	92.6	94.7	95.3
Gloss Retention (1000 h, UV-B313)	92%	88%	97%

Plural Component Application

Application trials of the two sample formulations were conducted at Graco, Inc. Engineering Labs in Franklin Park, IL. The pump used was a Graco Bulldog 206-740 fixed at a 1:1 volume mix ratio with a 32:1 air/fluid pump ratio. This set-up utilizes equivalent volume dual pistons which fill on the up-stroke and empty on the down stroke. The reacting materials were pumped directly from 5 gallon pails, through in-line heaters and 60 mesh filters, and could be recirculated through this cycle to heat the material fully. The fluid lines to the mixing manifold were resistively heated. The mixing element was a 3/8" diameter static mixer with 30 elements. Both formulations were easily pumped at temperatures from 120°F to 150°F. The appearance and properties of the applied material also indicated excellent mixing of the reactive components. Applied films were smooth and uniform, and coating film performance was as expected. The coatings were applied by airless (517, 617, and 619 tips) and high pressure air-assisted airless (608 cap, 100 psi atomizing pressure) methods. Applications characteristics were fair. The near-zero VOC, polyester-based formulation atomized better than the higher solids acrylic formulation; however, both formulations showed some tailing. Larger tips and slightly higher application temperatures may have improved the spray pattern, but the trial was limited in the amount of available formulated paint at this writing.

CONCLUSIONS

The development of low oligomer content isocyanate terminated prepolymers (diisocyanate/polyol adducts) has introduced a new option in formulating very high NVM two component urethane coatings. The low solvent demand of these prepolymers and their rapid viscosity decrease with increasing temperature has allowed the use of this type of material for the first time in high performance, plural component applied coatings. The higher equivalent weight of these prepolymers allows the formulator to develop paints at a 1:1 volume mix ratio. These formulations showed good handling and excellent mixing properties. Coatings applied by airless and air-assisted airless methods showed fair atomization and excellent flow out. The performance of these coatings is as good as, or better than, high mix ratio polyisocyanate-based control formulations.

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