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Synthesis and Coating Properties of Novel Waterborne Polyurethane Dispersions

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A series of novel waterborne polyurethane dispersions were prepared by non-isocyanate chemistry and their properties in cured coating formulations were studied. The combination of free film surface analysis by infrared spectroscopy, solvent swelling studies and stress-strain analysis reveal more homogeneous network formation in films of these polyurethane dispersions, as compared to polyurethane dispersions prepared via isocyanate processes. The novel polyurethane dispersions are solvent-free and were formulated into coatings which are low in volatile organic content, and fit the need for water-based resins that conform to current government regulations. It was also discovered that one of the polyurethane dispersions possesses unique wetting characteristics, and functions as an efficient dispersing resin for a variety of inorganic and organic pigments.

INTRODUCTION

Waterborne polyurethane dispersions (PUR) find use in many industrial coating applications. Certain applications involve the use of waterborne polyurethanes as uncrosslinked thermoplastic coatings. In many other areas where solvent resistance and improved coating performance properties are essential, it is possible to achieve crosslinking with a polyisocyanate, an amino-formaldehyde crosslinker or other crosslinking agent (1-5). Coatings cured with amino-formaldehyde (melamine) resins find widespread use, and are advantageous because they are stable in a one-package system. Typical commercial solvent-borne polyurethane coatings are relatively high in solvent content and do not qualify in low volatile organic content (VOC) applications. There is currently a great need for low or near zero VOC coating systems due to current government regulations. For this reason, there is an increased interest in developing waterborne resin technology that meets new environmental standards (6).

Most conventional PUR dispersions are high molecular weight ionic polymers which are commonly prepared by one of two processes: the polyurethane is polymerized in solvent then dispersed in water, or an isocyanate terminated pre-polymer is prepared in the melt or in an aprotic solvent, and is then chain extended with a diamine in the water phase in the presence of a neutralizing tertiary amine (7,8). Urethane dispersions are also prepared through the attachment of polyoxyethylene side chains that enable the polymer to be dispersed in water utilizing a non-

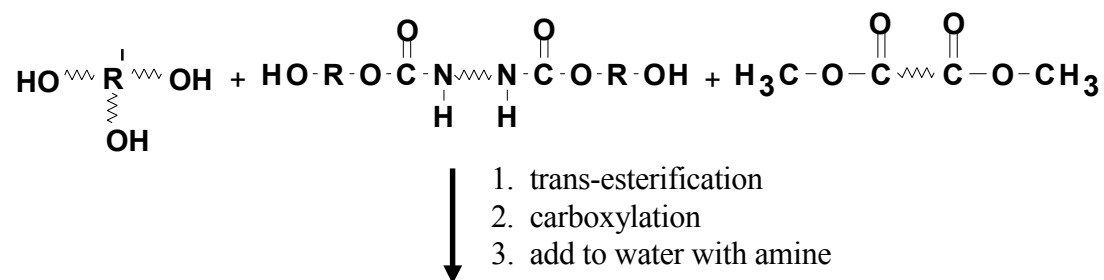
ionic mechanism (9). We have prepared novel low MW hydroxy/carboxy functional polyurethane dispersions through the use of non-isocyanate chemistry (10,11,12). When crosslinked with a melamine resin these PUR dispersions produce films of more uniform structure and crosslink density. Due to the higher reactivity of the hydroxyl groups with the melamine resin, there is a substantial reduction of the melamine self-condensation reaction. Extensive melamine self-condensation reaction is associated with a reduction in the performance properties of the resultant coating (13). The present study demonstrates the film properties and network formation of these novel low MW dispersions cured with a melamine resin.

One of the emerging alternative technologies is the use of a water-dispersible polyisocyanate as a crosslinker for hydroxy functional water-based resins (14-17). The concept involves the modification of a polyisocyanate crosslinker with water soluble moieties, and dispersing the crosslinker in a water-based resin formulation, while attempting to minimize the amount of time the crosslinker is in direct contact with water. One of the objectives is to reduce the amount of side reaction of isocyanate with water, which generates carbon dioxide, and can cause imperfections as the formulation dries to a finished coating (18). One of the four novel polyurethane dispersions developed in our series is designed for crosslinking with a water dispersible polyisocyanate.

EXPERIMENTAL

Materials

The four hydroxy/carboxy functional PUR dispersions (XM-2311, XM-2312, XM-4310 and XM-4316) were prepared by a non-isocyanate process. Physical characteristics are given in Table 1 and the synthetic scheme is shown in Figure 1. The polymers were synthesized by first reacting the diester with the polyol in the presence of an organometallic catalyst at 200° - 220°C in vacuo. Methanol is the byproduct of the trans-esterification reaction. Next, a hydroxy-functional urethane diol was added, and propylene glycol was removed in vacuo at 180°C. The hydroxy-functional urethane diol was previously prepared by a non-isocyanate process utilizing the reaction between a cyclic carbonate and a diamine. The resin was then carboxy-functionalized and dispersed in water with the aid of a neutralizing tertiary amine (Figure 1). Number average molecular weights for the PUR dispersions were in the 3000 - 4000 g/mol range.



(HO)_x polyurethane (COO A)_y (R, R' and $\sim \sim \sim$ = aliphatic groups)

Figure 1. Synthesis of waterborne anionic polyurethane dispersion by a non-isocyanate process.

The XM-2311 PUR was also prepared in an oligomeric form (1,500 g/mol) for use as a pigment dispersing resin. Comparisons of a melamine-cured PUR were made to a PUR (designated XP-7) prepared by a conventional isocyanate process. Two polyurethane dispersions, designated XP-7 and XP-4, were prepared by the conventional prepolymer isocyanate process given in Figure 2. As seen in the reaction scheme, this process actually produces a polyurethane-urea polymer,

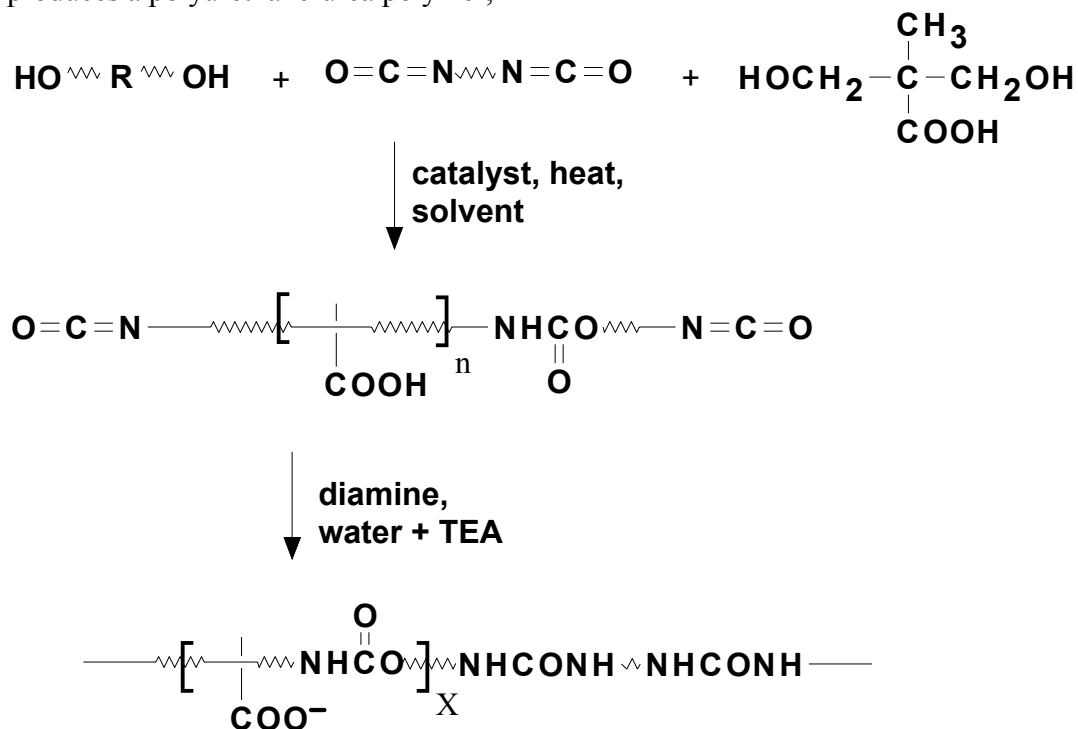


Figure 2. Synthesis of conventional waterborne polyurethane dispersion by the isocyanate prepolymer process.

Although such polymers are typically abbreviated as polyurethanes. The chain extension reaction of the isocyanate terminated polyurethane with the diamine forms the urea moiety.

The melamine resin (crosslinker) used in this study was a commercially available version of hexakis(methoxymethyl)melamine (HMMM), which has a degree of polymerization of about 1.5, an average molecular weight of 554 and an average theoretical functionality of 8.3. The waterborne (WB) acrylic dispersion used for formulating was Acrysol WS-68 from Rohm and Haas, a hydroxy/carboxy functional resin. A water-dispersible polyisocyanate from Bayer Corporation (Bayhydur XP-7007, a modified aliphatic isocyanate trimer) was used for crosslinking XM-4316 in one study, and another PUR prepared via isocyanate chemistry (designated XP-4) was used for further comparison to XM-4316. Pigments were obtained from commercial suppliers such as Bayer, Cabot, DuPont and BASF.

Coating Formulations

The PUR dispersions were formulated with 10 to 35% HMMM on total resin solids, and catalyzed with 1% of amine-blocked p-toluenesulfonic acid. Coatings were cast on Bonderite 1000 iron-phosphated cold-rolled steel panels at a 25 micron (1.0 mil) dry film thickness, and were cured for 20 minutes at 120°C and at 150°C. Pigmented films were cured at 150°C for 15 minutes. Coatings prepared with the water-dispersible isocyanate were cured at ambient temperature for two weeks (21°C \pm 2°), and also cured at 80°C for 30 minutes. Coated panels were tested for dry film thickness (DFT), pencil and Knoop hardness (KHN), König hardness, cross-hatch adhesion, direct and reverse impact resistance, MEK (methyl ethyl ketone) double rubs, and gloss (60° and 20°) in accordance with ASTM procedures.

Surface analysis was performed by using Fourier Transform Infrared Analysis Attenuated Total Reflectance Spectroscopy (FT-IR ATR). An IBM Model IR44 instrument was used with a Spectra Tech zinc selenide reflectance attachment. Stress-strain analysis of coating free films was performed on an Instron Model 1011 materials tester. Particle size measurements were made with a Leeds and Northrup Microtrac Model UPA 150 instrument. Cured coatings were tested for abrasion resistance on a Taber Abraser Model 5130 using CS-17 abrasive wheels in accordance with ASTM D4060. All abrasion data were normalized to wear index values based on 1000 cycles. Gloss measurements were obtained with a Byk-Gardner Multi-Gloss meter. Molecular weight values were obtained by size exclusion chromatography on a Waters 510 system with a Waters 410 refractive index detector, and values are relative to polystyrene standards. The system was operated at 30°C using tetrahydrofuran as the eluent at a flow rate of 1.0 ml/min.

RESULTS AND DISCUSSION

Polyurethane Dispersion Properties and Resin Design

The basic physical properties of all six dispersions are given in Table 1. All but the XP-7 and XP-4 dispersions were prepared using the non-isocyanate synthetic process. These two dispersions were prepared by the conventional diisocyanate prepolymer process. Note that these two dispersions also contain solvent, which is 1-Methyl-2-pyrrolidinone (commonly named N-methyl-pyrrolidone). The solvent is present during the isocyanate prepolymer synthesis step for viscosity reduction. The presence of the solvent increases the VOC of the final coating formulation. The polyurethane dispersions prepared by the non-isocyanate process (XM type) do not require any solvent during synthesis, and thus yield coatings with much lower VOC levels.

Different neutralizing amines were chosen to prepare the anionic dispersions depending on the end-use application and on the nature of the resin backbone. Triethylamine (TEA) has traditionally been used for conventional PUR's due to its high basicity and high volatility at ambient temperature. We have found that N-methylmorpholine (NMM) yields a dispersion with superior shelf stability and rather unique colloidal behavior. A mixed amine approach of diisopropanolamine (DIOPA) and TEA was used for XM-2311 because of an enhancement in colloidal stability. Dimethylethanolamine (DMEA) was useful in certain instances, but is not desirable for use with water dispersible isocyanates due to its reactive hydroxyl functionality.

The XM type PUR dispersions have particle size values that are typical for waterborne polyurethanes. Amongst the XM PUR's, the largest particle size was obtained with the resin with the lowest level of carboxyl functionality. Such is expected due to the larger hydrophobic particle center associated with less carboxyl groups on the exterior of the particle.

In varying the type of comonomer components in the transesterification reaction, different final film properties were obtained. One variable that was employed was the balance between diesters and polyols of straight-chain alkyl type and cycloaliphatic type. The introduction of a cycloaliphatic diester or diol provided a convenient means of increasing the glass transition temperature (T_g) of the polymers. The increase in polymer T_g resulted in an increase in the final cured film hardness. The XM polymer T_g increases in the order of XM-2311<XM-2312<XM-4310<XM-4316. Polymer XM-4316 has the highest level of cycloaliphatic segment, and only XM-2311 has no cycloaliphatic segments. XM-2312 and XM-4310 have the same base resin composition, and only differ in acid number (amount of carboxyl functionality). Table 2 gives some of the coating properties when the dispersions are cured with 25% HMMM and 1% blocked acid catalyst (both on total resin solids) at 150°C. The introduction of 10% XM-2311 results in a softening of the films and also yields a coating with greater impact resistance (flexibility).

PROPERTY	XM-2311	XM-2312	XM-4310	XM-4316	XP-7	XP-4
Method of synthesis*	NI	NI	NI	NI	I	I
Nonvolatile, 60 min., 110°C	43.8	36.0	40.9	42.0	36.0	40
Brookfield viscosity, cP, 25°C	1720	700	506	2300	650	300
Acid number, on solids	60	30	45	45	7.5	32
Hydroxyl number, on solids	33	70	65	75	0	56
Number Avg. MW	1500	3100	3100	3000	30000	3750
pH of dispersion	8.4	8.3	8.4	7.4	8.1	7.5
Particle size, mean, nm	11	61	15	24	66	23
Solvent content, %	0	0	0	0	5	10
Neutralizing amine	TEA & DIOPA	DIOPA	DMEA	NMM	TEA	TEA

* I = isocyanate process; NI = non-isocyanate process

Table 1. Physical characteristics of waterborne polyurethane dispersions.

PROPERTIES	XM-4310	XM-4316	XM-4310 (WITH 10% XM-2311)	XM-4316 (WITH 10% XM-2311)
Knoop hardness, KHN ₂₅	12.1	16.2	10.0	13.1
Konig hardness, sec.	128	145	109	130
Direct impact resistance, in.lb	120	120	160	160
Tensile strength, psi	3000	6500	-----	-----
Elongation, %	15	4	-----	-----

Table 2. Coating properties of PUR dispersions cured with HMMM.

Coating Properties

The film property results of the XM-2312 / HMMM system (Table 3) clearly indicate that the optimum level of HMMM crosslinker is 25 to 30%. At this level there is no loss in impact resistance while the film retains acceptable elongation. The optimum film cured at the 25 to 30% HMMM level has an excellent balance of hardness and flexibility, which is usually difficult to achieve considering the tendency for the melamine resin to self condense (crosslink) and form brittle films. These findings provide evidence for a more uniformly crosslinked network. At the 35% HMMM level there is a drastic loss in film elongation along with a reduction in direct impact resistance. At this point, the theoretical amount of HMMM required is exceeded leading to self HMMM reaction, which leads to embrittlement of the film. Excellent compatibility of the resin and the HMMM crosslinker is evidenced in the high gloss values for the clear-coat films.

HMMM %	KNOOP HARD.	DIRECT IMPACT (IN*LB)	MEK 2X RUBS	GLOSS 60°, %	MAX. TENSILE (PSI)	% ELONG.
10	2.7	>160	35	>90	----	----
15	3.0	>160	120	>90	1000	32
20	5.0	>160	>200	>90	2350	34
25	9.4	>160	>200	>90	2800	14
30	15.0	>160	>200	>90	3550	13
35	18.0	140	>200	>90	3450	2

Table 3. Coating properties of XM-2312 PUR cured with HMMM at 150°C.

In a second coating system, XM-4310 was evaluated as a modifier for an acrylic resin. The XM-4310 resin imparted significant improvements to the performance properties of a white thermoset acrylic coating, as shown in Table 4. The XM-4310 was used at a 16 weight percent level on total resin solids, with an HMMM content of 20 weight percent. The coating was compared to the acrylic with the same HMMM level. The HMMM level was adjusted (lower than standard 25 - 30%) in this case because the acrylic requires a lower HMMM level. The white pigment (DuPont R-900) was initially dispersed in the acrylic resin, then let-back with the acrylic or PUR/acrylic. Both formulations were catalyzed with only 0.2 weight percent of blocked p-toluenesulfonic acid, and the final pigment to binder ratio was 0.63 to 1.0. The formulations required less catalyst than the clear-coat PUR/HMMM formulations. The final solids of both formulations was 42.5%.

Improvements were found in flexibility, chemical resistance, and in salt spray resistance. Increased abrasion resistance of the film occurred upon introduction of the XM-4310. It is clear that the introduction of urethane character into an acrylic coating provides benefits in abrasion resistance, which will enhance the long term durability of the coating. The fact that the MEK resistance increased upon introduction of the XM-4310 provides evidence for the formation of a more highly crosslinked network. The XM-4310 has the available primary hydroxy functionality for curing with the HMMM. The acrylic polymer has a much higher molecular weight than the XM-4310 polyurethane. Thus, the molecular diffusion of acrylic polymer chains is slower, affecting the availability of the hydroxyl reactive sites.

Test panels were prepared for weathering under a constant salt-spray environment for 250 hours in accordance with ASTM D117. At the conclusion of the test the acrylic coating was completely rusted whereas the coating modified with the XM-4310 PUR had only 3 mm of rust creep. Therefore, it is shown that by modifying the acrylic coating with XM-4310 that a number of coating performance advantages are realized. The VOC for this system may be further reduced since some of the cosolvents present are required for the acrylic component. We have found that the use of the XM type dispersions for modifying acrylics enhances film formation (film coalescence) of the coatings, thus requiring less cosolvent to accomplish this function, leading to a favorable reduction in VOC.

Mechanical & Appearance Properties	Acrylic / HMMM	Acrylic / XM-4310 / HMMM
Pencil Hardness	4H	4H
Knoop Hardness	19.7	15.3
Direct Impact (inch*lb)	60	120
Reverse Impact (inch*lb)	< 5	60
Gloss, 60°, %	94	92
Gloss, 20°, %	79	75
MEK Double Rubs	155	>200
Taber Abrasion Wear Index	620	412
Salt Spray, Creep in mm (250 Hours exposure)	99% rusted	3

Table 4. Coating properties of acrylic and PUR/acrylic cured with HMMM at 150°C (white pigmented).

A series of coatings were prepared where various resins were melamine cured on test panels, and tested for abrasion resistance. The resins were used alone; not as modifying resins for other systems. The Taber abrasion wear index data is given in Table 5. The lower the wear index number, the more abrasion resistant the coating, and testing was performed as indicated in ASTM D4060. The XM-4310/HMMM coating is the most abrasion resistant coating tested when compared to other melamine cured waterborne polyurethane, acrylic, and polyester coatings.

WB resin cured with HMMM	Taber Abrasion Wear Index
XM-4310 PUR	87
conventional PUR (XP-4 type)	335
acrylic	620
polyester	646

Table 5. Taber abrasion data for various waterborne resins cured with HMMM at 150°C.

Waterborne Polyurethane Dispersions As Pigment Dispersing Resins

The starting point in any water-based coating application is the initial dispersing of the pigment in water. In designing a polyurethane dispersion that functions as an efficient pigment wetting resin, certain design features were implemented. A high degree of branching is present, along with hydroxyl functionality and increased levels of urethane and carboxyl functionality. The presence of all three of these moieties in the same molecule, along with the proper resin molecular weight distribution, allow the groups to work synergistically to “wet” the pigment’s surface. XM-2311 dispersed a wide range of organic and inorganic pigments, and readily dispersed pigments that are traditionally considered difficult to disperse in water (phthalo blue, perylene red). Base pastes were readily prepared by ball-mill grinding the pigment in XM-2311 and deionized water. Such pastes were stable for up to one year when stored at ambient temperature.

One of the key attributes of XM-2311 is that it functions as the sole pigment dispersing vehicle, not requiring the use of any additional dispersing resin. Table 6 illustrates the formulas used to disperse a number of pigments with XM-2311. Note that the phthalo green pigment loading is very high, at a level of 3 to 1 pigment to binder (P/B) ratio. An effort was made to obtain the highest loading level for this pigment as a way to illustrate the fact that XM-2311 is efficient in wetting pigment. Many of the other formula P/B values can likely be increased as well, and only the green-pigmented formula has been optimized thus far.

Material	Carbon Black	Phthalo Blue	Perylene Red	Phthalo Green	TiO₂ White
XM-2311	36.2	48.3	48.3	37.1	28.7
Pigment	15.0	21.0	21.0	48.7	68.2
Water	45.1	30.7	30.7	14.2	3.1
DMEA	3.7	-----	-----	-----	-----
TOTAL	100.0	100.0	100.0	100.0	100.0
Resin Solids, WT %	15	21	21	16	12.3
Pigment/binder	1/1	1/1	1/1	3/1	5.5/1

Table 6. Low molecular weight PUR used to disperse various pigments.

The TiO₂ (white) pigment required only 10-15 minutes of dispersing time on a Cowles disperser. The dispersing ability of the XM-2311 PUR was compared to other commercially available acrylic and alkyd resins, as well as a commonly used surfactant system. It was determined that the other commercial systems required longer grind times in dispersing the TiO₂ pigment. A shorter grind time is desirable from an industrial standpoint due to the lower cost associated with the more efficient process. The carbon black pigment required some pre-neutralization with DMEA. The grind pastes generated high-performance coatings when formulated and cured with XM-4310 and HMMM. The grind pastes were also successfully formulated into a number of other commercially available resin vehicles. The XM-2311 grind pastes were compatible with waterborne acrylic, alkyd, polyester, and polyurethane resins, indicating a “universality” of the XM-2311 PUR and its broad use in water-based systems. A

coating formulation was prepared whereby XM-2311 was used to grind the phthalo blue pigment, and was combined with the XM-4310 PUR and melamine. The formulation was cast on B-1000 steel panels, and cured at 150°C for 20 minutes. The properties of the coating are given in Table 7, which exhibit an excellent combination of flexibility, chemical resistance and high gloss.

PROPERTIES	CURED COATING
Pencil Hardness	H-2H
Knoop Hardness	4.1
Direct Impact (in.lb)	>160
Reverse Impact (in*lb)	>160
Gloss, 60 degree, %	91
Gloss, 20 degree, %	78
MEK Double Rubs	>200

Table 7. Coating properties of phthalo-blue pigmented XM-2311 / XM-4310 system cured at 150°C with HMMM.

Curing Polyurethane Dispersions with Water-Dispersible Isocyanates

XM-4316 proved to be readily crosslinkable at ambient temperature with a water-dispersible polyisocyanate. One of the inherent drawbacks of this new technology is the formation of carbon dioxide due to the side reaction of isocyanate with water. When an isocyanate reacts with water, the products are a urea linkage (via an amine intermediate) and carbon dioxide. The carbon dioxide formation is problematic in that it causes imperfections in the coating during cure, such as blistering and pin-hole formation. An excess of isocyanate relative to polymer hydroxyl functionality is recommended due to this side reaction. It is quite common to prepare such water-based formulations with a 2.0/1.0 isocyanate to hydroxy-polymer mole ratio.

One way to minimize such effects is to prepare the PUR with a neutralizing amine that does not function as an efficient catalyst for the isocyanate/water reaction. The use of N-methylmorpholine (NMM) as the neutralizing amine for the XM-4316 PUR proved to be beneficial in this respect. NMM is a weaker base than most other tertiary amines, and is not a strong catalyst for the side reaction of isocyanate and water (19,20,21). The use of triethylamine in this case is not favored, due to its strong basicity and ability to catalyze the isocyanate/water side reaction. Triethylamine is the most commonly used amine for neutralizing commercial PUR dispersions. The pK_a values for triethylamine and N-methylmorpholine are 10.75 and 7.38, respectively, at 25°C. Triethylamine has a rate constant 7.4 times greater than N-methylmorpholine in catalyzing the reaction between phenyl isocyanate and n-butanol. Formulation characteristics and clear-coat film properties are given in Table 8 for the XM-4316 PUR cured with a water-dispersible polyisocyanate.

PROPERTY	AMBIENT CURE	80°C, 30 MIN
NCO / OH ratio	1.7 / 1.0	1.7 / 1.0
Theoretical VOC, gram/liter	89	89
pH	7.5	7.5
Dry time, set to touch (hours)	0.25	----
Surface dry, hours	2.25	----
Through-dry, hours	5.75	----
Film thickness, microns	25	25
Konig hardness, sec	41	70
MEK double rubs	90	160
Direct impact resistance, in.lb	>160	>160
Gloss, 60°, 20°, %	>90, >90	>90, >90

Table 8. Properties of PUR cured with water-dispersible polyisocyanate.

The high gloss values indicate that there is no problem of entrained carbon dioxide in the coating system. The film has acceptable hardness and solvent resistance upon ambient curing, and these values are much improved upon a low-temperature bake cycle. Ambient cured panels were tested two weeks after initial film casting. The improvement in MEK resistance for the low-bake coating indicates the formation of a more highly crosslinked network. Since the low-bake cycle allows for faster water release from the film, there is less time for the side reaction of water and isocyanate to take place. Therefore, the isocyanate/PUR reaction is favored, leading to optimum crosslink formation. After mixing the XM-4316 PUR and the water-dispersible polyisocyanate the formulation has a pot-life of 4 to 6 hours, without undergoing any excessive foaming.

In comparison, when formulating the XP-4 PUR into a similar formulation, the use of cosolvents was required to obtain acceptable film formation and coating gloss. As a result an almost three-fold increase in VOC level resulted (255 grams/liter), thus favoring the formulation with the XM-4316 PUR for VOC reduction.

Stress-Strain Analysis

Figures 3 and 4 show the stress-strain behavior of the free films of the XM-2312 and the conventional PUR (designated XP-7) cured with the HMMM crosslinker at 120°C. The extension ratio is defined as the ratio of the extended sample length to the original sample length. The conventional PUR (XP-7) behaves in a two-phase fashion, undergoing an initial rapid increase in stress accompanied by very little elongation, indicating behavior of a more highly crosslinked phase. Next, there is a steady elongation of the sample.

In considering all of the other experimental evidence thus far, it is likely that the rapid increase in tensile strength is related to the HMMM self-crosslinked network, followed by the elongation of the uncrosslinked polyurethane phase. The 30,000 g/mol PUR can exhibit such a distinct elongation profile because the resin itself is thermoplastic. Conversely, the XM-2312 film undergoes a more uniform change in its stress-strain relationship, providing evidence for a more homogeneous network. Such behavior is more closely related to the ideal (theoretical)

stress-strain curve given in Figure 5, which is derived from the classical relationship (11) relating retractive stress of an elastomer during deformation (elongation).

As seen in Figure 3, once the level of HMMM is exceeded (see 35% curve) beyond the amount needed for proper crosslinking, the same effect becomes noticeable in the XM-2312 film. Although less HMMM is required for curing the XP-7 resin, it is clear that even at the 10% level (Figure 4) the two phase stress-strain behavior is observed. Theoretical HMMM resin levels are determined from the total available hydroxyl and carboxyl functionality in the polymers. The theoretical molecular weight per crosslink point is 561 g/mol for XM-2312 and 7480 g/mol for the XP-7 polymer. The stress-strain data provide evidence of the formation of a more uniform and homogeneous network in the XM-2312 cured film. Network homogeneity translates to improved mechanical and performance properties of the resultant coating.

In our earlier work (22), we demonstrated the same stress-strain behavior in cured films of the XP-4 polymer. In this instance, the water-dispersible isocyanate was used as the crosslinking agent. The XP-4 polymer is prepared by an isocyanate process, and is close to the molecular weight of the XM-2312 and XM-4316 polymers (see Table 1), thus eliminating PUR molecular weight as a variable. Similar two-phase behavior was demonstrated by the cured XP-4 polymer, whereas the XM-4316 system exhibits a stress-strain curve more closely resembling an ideal system.

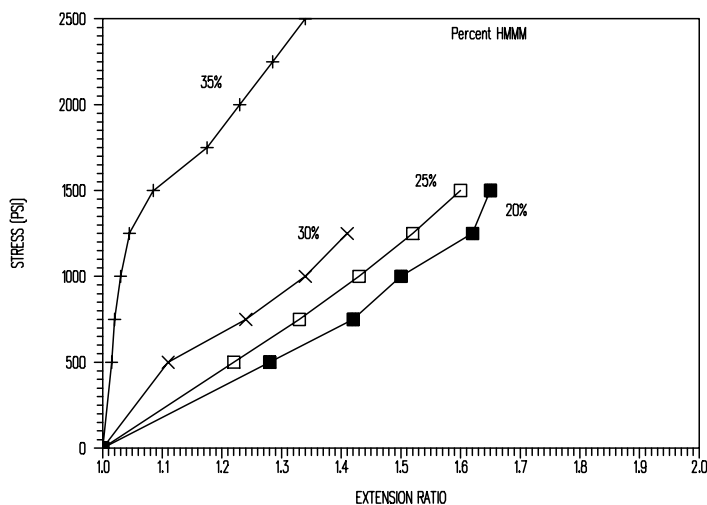


Figure 3. Stress-strain curves for XM-2312 PUR cured with various levels of HMMM.

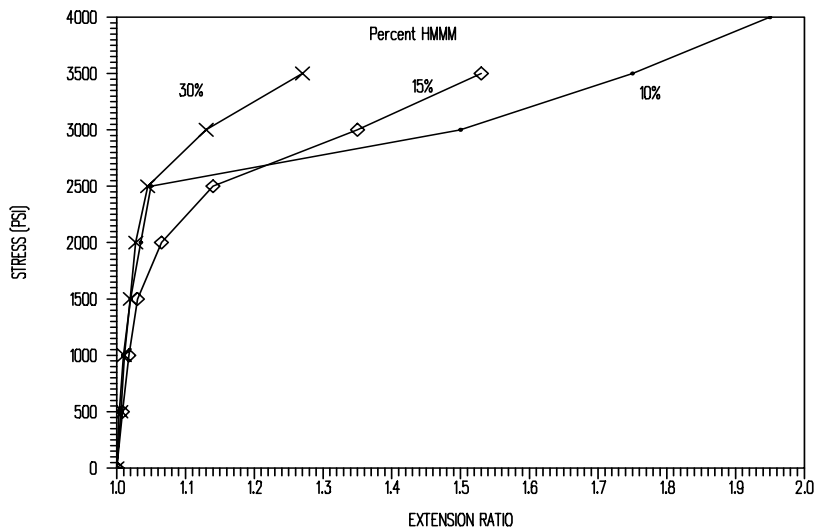


Figure 4. Stress-strain curves for XP-7 PUR cured with various levels of HMMM.

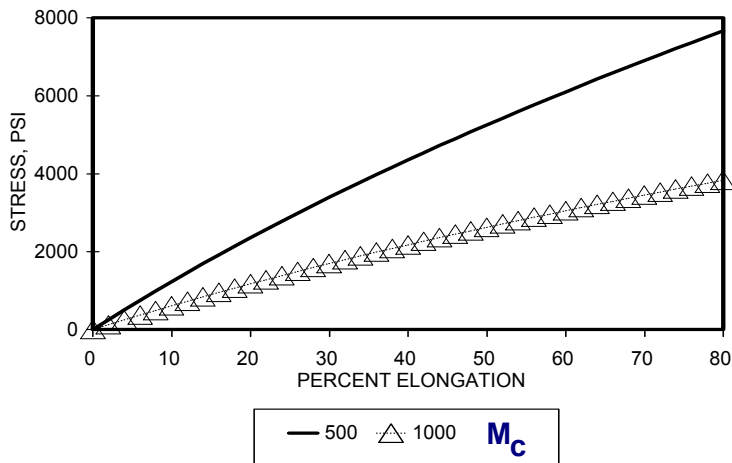


Figure 5. Theoretical stress-strain curves at different molecular weight per crosslink values for an ideal network.

Free Film Solvent Swelling Experiments

Swelling experiments of the HMMM crosslinked free films was performed using methylene chloride as the swelling solvent. The Flory-Rehner equation (Equation 1) was employed to calculate the crosslink density of the films (23).

$$-\left[\ln(1 - \nu_2) + \nu_2 + \chi_1(\nu_2)^2\right] = \nu_1 n \left[(\nu_2)^{1/3} - \nu_2/2\right] \quad \text{Equation 1.}$$

The value v_2 is the volume fraction of polymer in the swollen mass, V_1 is the molar volume of the swelling solvent, χ_1 is the Flory-Huggins polymer-solvent dimensionless interaction term, and n is the number of active chain segments per unit volume. The quantity n equals ρ/M_c , where ρ is the density and M_c is the molecular weight between crosslinks. Published data for the interaction term (or parameter) in chlorinated solvents indicates a value in the range of 0.4 - 0.5 (24). In this study, an interaction parameter of 0.5 was used. The value of the molar volume of methylene chloride is 64.22 ml/mol. A previously reported method was used for the solvent swelling study where the dimensions of the film were accurately measured before and after swelling (11).

Figures 6 and 7 illustrate the data in graph form. Three different curves are shown in each figure. One curve is for the measured (actual) crosslink density values, one is for the calculated HMMM/polymer values, and one is for the values calculated for the scenario where the HMMM cures with the polymer and with itself (remaining curing by self-condensation of HMMM). This last scenario occurs if there is insufficient hydroxyl functionality present to cure with the HMMM (25). The XM-2312 film has measured crosslink density values that are close to the calculated values. However, the XP-7 film has measured crosslink density values that are closer to the values calculated for self-condensed HMMM. The data clearly show that the XM-2312 film has more ideal behavior and that the XP-7 film has a two-phase composition, with one phase composed of mostly HMMM self-crosslinked material. The presence of such material is known to lead to brittle coatings and reduced coating performance.

The isocyanate prepolymer process allows for the chain extension of an isocyanate terminated prepolymer with a diamine, such that any hydroxyl end groups are present at approximately one per 30,000 molecular weight unit. Therefore, the XP-7 polymer has little or no pendant hydroxy functionality by virtue of its method of synthesis (see Table 1), and thus can not obtain a lower M_c without the occurrence of the melamine self-condensation reaction. As indicated earlier, the carboxyl groups may participate in crosslinking with HMMM, but this process occurs at a much slower rate and is less likely to occur.

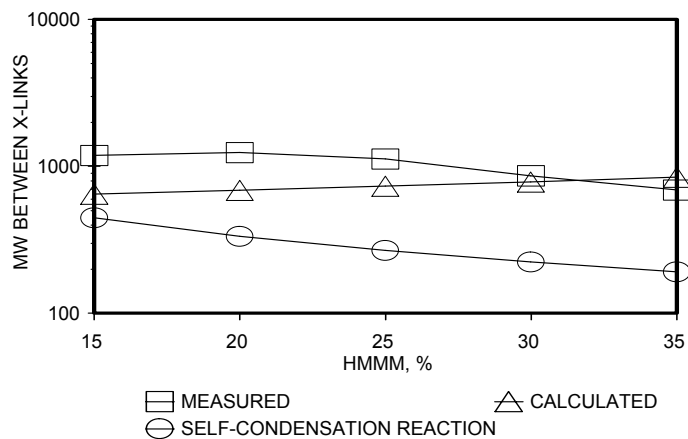


Figure 6. The XM-2312 / HMMM free film crosslink density data.

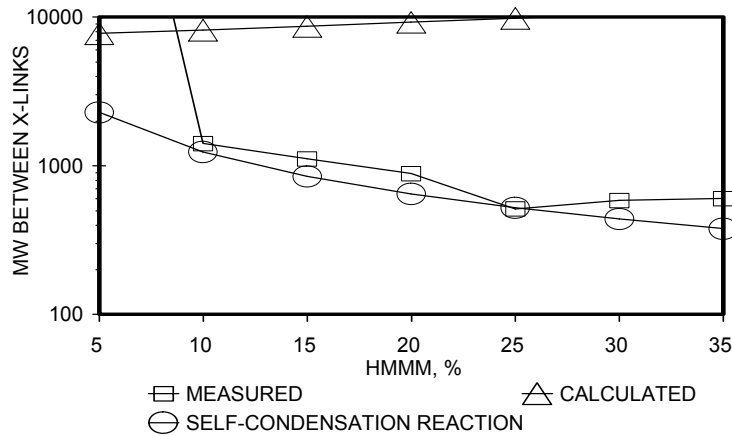


Figure 7. The XP-7 / HMMM free film crosslink density data.

FT-IR ATR Analysis of Free Films

Surface analysis of the cured coating free films by FT-IR ATR proved to be very useful in comparing the relative concentrations of HMMM at the film-air interface, which is an indirect measure of film homogeneity and network formation. The spectra are given in Figure 8. A comparison was made between the XM-2312 and the XP-7 films cured with 30% HMMM at 150°C.

The IR band of interest is the out-of-plane deformation of the HMMM triazine ring which occurs at 815 cm^{-1} (26). All of the spectra were baseline corrected so that they may be compared. The individual polymers (XM-2312 and XP-7) did not have any absorptions in the region of interest, thus eliminating any interference problems. The depth of penetration of the IR beam is given by Equation 2, where λ_0 is the wavelength of the infrared radiation, n_1 is the refractive index of the ATR crystal,

$$d_p = \lambda_0 / 2 \pi n_1 (\sin^2 \theta - n_{21}^2)^{1/2} \quad \text{Equation 2.}$$

θ is the angle of incidence and n_{21} is the ratio of refractive indices of the sample and the ATR crystal (27). Using Equation 2, the depth of penetration at 815 cm^{-1} is 3.5 microns at the film-air interface. The films prepared for this study were 25 microns in total thickness.

The surface spectra indicate a significant increase in the HMMM absorption for the XP-7 film, indicating a higher HMMM content on the film surface, and a less homogeneous film. Our studies indicate a level of HMMM twice that on the surface than is theoretically present in bulk for the XP-7 coating. Conversely, the XM-2312 coating had the expected level of HMMM at the surface. Unreacted melamine resin tends to migrate to the film-air interface and self react if there are a lack of hydroxyl functional groups available for crosslinking (28). Such a self-

crosslinked melamine network functions only as a temporary barrier. Once abraded or degraded under weathering conditions the exposed coating has reduced performance characteristics. These results provide further evidence that the XM-2312 type resin yields coatings that have a more homogeneous composition, which ultimately leads to coatings with improved performance and weathering resistant properties.

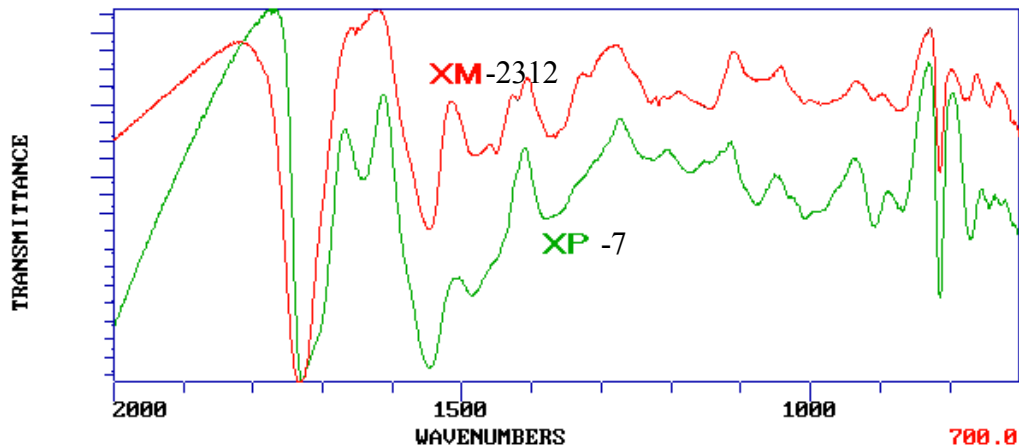


Figure 8. FT-IR ATR spectra of XM-2312 and XP-7 films cured with 30 weight percent HMMM at 150°C.

Summary

Low VOC coatings with superior performance properties are obtained when formulating with the waterborne polyurethane dispersions, XM-2311, XM-2312, XM-4310 and XM-4316. The polyurethanes are prepared by non-isocyanate chemistry which eliminates the exposure hazards of working with isocyanate raw materials. The XM-2311 PUR functions as a highly efficient pigment dispersing resin by virtue of the presence of hydroxyl, carboxyl and urethane functionality. The proper molecular weight and degree of branching incorporated into the resin design also enables the resin to effectively “wet” pigment surfaces, and not undergo any mechanical (shear) degradation. Other acrylic type dispersing agents are subject to shear degradation during the dispersion process due to the higher molecular weight values. Also, there is no need for the use of solvents or surfactants in dispersing the pigments with XM-2311. These additives are often necessary in using other waterborne resins to disperse pigments. XM-2311 is able to disperse a wide variety of pigments, both inorganic and organic types, which is unique among conventional dispersing resins.

The XM-2312 PUR coating cured with melamine has a VOC level of 46 grams/liter (0.38 lb/gallon), and the two-component formulation of the XM-4316 PUR with the water-dispersible isocyanate has a level of 89 grams/liter (0.74 lb/gallon). These VOC levels are well below the current government regulation limits and yield coatings which are considered environmentally friendly. Recent advances in the water-dispersible isocyanate technology have made it possible for us to prepare formulations at VOC levels of less than 50 grams/liter with the XM-4316 PUR.

The use of the XM-4310 PUR as a modifying resin in an acrylic/melamine coating imparts performance advantages in flexibility, abrasion resistance and in salt-spray weathering

resistance. The XM-4310 PUR also has the highest abrasion resistance when compared to other waterborne resin types cured with the same melamine coating system.

The combination of stress-strain analysis, solvent swelling studies, and surface FTIR ATR provides evidence for more uniform network formation in the coatings prepared from the XM type polyurethanes. It is clear that the formation of a more uniform network leads to coatings with improved performance properties.

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Abbreviations

WB	waterborne
PUR	waterborne polyurethane dispersion
VOC	volatile organic content
HMMM	hexakis(methoxymethyl)melamine crosslinker
melamine	hexakis(methoxymethyl)melamine crosslinker
DMEA	dimethylethanolamine
TEA	triethylamine
NMM	N-methylmorpholine
DIOPAD	diisopropanolamine
P/B	pigment to binder ratio
M_c	molecular weight per crosslink
XM	waterborne polyurethane dispersion prepared by non-isocyanate synthetic route
XP	waterborne polyurethane dispersion prepared by conventional isocyanate prepolymer synthetic route
cP	centipoise, a unit of viscosity
P/B	pigment to binder ratio
MEK	methyl ethyl ketone
cosolvent	coalescing solvent (solvent used to achieve film coalescence)
MW	molecular weight
ASTM	American Society for Testing and Materials

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