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Waterborne Polyurethane Dispersions with New

Sustainable Solvent

The uniquely functional cosolvent N-methylpyrrolidone (NMP) is well suited for use in waterborne polyurethane dispersions (PUDs). The use of cosolvents during polyurethane dispersion production is often necessary to enable a smooth reaction between the hydrophilic diol components [e.g., dimethylolpropionic acid (DMPA)] and the more hydrophobic polyurethane prepolymer. In addition, the cosolvent used during the PUD production phase remains in the system and later becomes a useful coalescing solvent when the PUD is applied as a coating to a substrate. The utility of NMP is diminished by the negative health effects of NMP exposure, and for many years the industry has sought an effective and safer substitute for NMP. Taminco, now a subsidiary of Eastman Chemical Company, has identified and developed the needed replacement, TamiSolve® NxG. It is a more effective cosolvent than NMP and it also exhibits an improved Health, Environment and Safety (HES) profile relative to NMP.

HES Profiles

Waterborne PUDs are used as coatings, adhesives, sealants and elastomers. Waterborne PUD-based coatings display excellent adhesion to challenging substrates like plastic and metal. Dried/cured PUD coatings have excellent mechanical properties and environmental resistance, and waterborne PUD-based coatings are becoming the coatings of choice for demanding applications like floor coatings, as well as those used in industrial environments. Application of waterborne PUD coatings and adhesives can expose the applicator to volatile compounds that are emitted from the formulation. Therefore, the HES profile of the formulation's ingredients is very

TABLE 1 » HES summary of Tamisolve NxG.

Test	Test Method	Test Result
Acute toxicity (LD50/oral/rat)	OECD 423	300-2000 mg/kg
Acute dermal toxicity	OECD 402	>2000 mg/kg
Skin and eye irritation	OECD 404/405	Irritant
Sensitization	OECD 429	Negative*
Mutagenicity	OECD 471/476/487	Not mutagenic
Repeated dose toxicity (90 days)	OECD 408	NOAEL = 500 mg/kg/d
Developmental toxicity	OECD 414	Negative
Aquatic toxicity (EC50/48 h/Daphnia)	OECD 202	>100 mg/L
Algae growth inhibition (EC50)	OECD 201	>160 mg/L
Acute toxicity to fish (EC50)	OECD 203	>100 mg/L
Aquatic toxicity (Daphnia reproduction)	OECD 211	NOEC 100 mg/L
Biodegradability	OECD 302B	Inherently biodegradable
Bio-accumulation	OECD 117/EC A.8	Log Pow = 1.265

* Testing not complete

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important. In addition, the atmosphere is also exposed to the VOC content emitted from an applied PUD-based coating and/or adhesive. Obviously, the use of safer solvents, and in lower amounts, markedly improves the HES profile of a given PUD-based product.

A summary of the HES profile of Tamisolve NxG is provided in Table 1. Testing has shown that this new solvent has a good environmental impact profile and does not display genotoxicity. Most importantly, unlike NMP and NEP, TamiSolve NxG is not classified for developmental toxicity. Replacing NMP or NEP with TamiSolve NxG can reduce the overall health and environmental impact of cosolvent in a polyurethane dispersion formula.

Performance in PUDs

Reduced Water Solubilizing/Dispersing Entity Needed

The high solvency of TamiSolve NxG for polyurethane prepolymers delivers excellent processing and dispersion of the prepolymer into the water phase. The high solvency coupled with its water dispersibility as a cosolvent significantly aids in the dispersion of the polyurethane solids in water. The effects are far superior to NMP, and, in many cases, NxG will allow for a significant reduction in the required amount of hydrophilic entity content (e.g., dimethylolpropionic acid, DMPA) in the polymer backbone. This can provide unique formulation flexibility that is not available when using NMP or NEP. Also, the use of this product provides formulation cost advantages since more expensive DMPA-type monomers can be replaced with a lower-cost option.

To demonstrate the improved processing afforded by TamiSolve NxG and its ability to reduce the required level of DMPA for acceptable dispersion, two equivalent polyurethane preparations were made. One used TamiSolve NxG as a cosolvent and the second used NMP. A description of these comparative systems and the resulting process and product parameters are shown in Tables 2 and 3.

As noted in these two tables, the NxG-based polyurethane prepolymer was easy to produce and showed a clean, semi-translucent appearance, while the NMP-based prepolymer was more difficult to disperse and showed heavy flocculation. These results demonstrate that polyurethane prepolymers, using the new dispersion solvent, can be made at lower levels of DMPA compared to those using NMP as a solvent.

Enhanced Coalescence

Tamisolve NxG offers exceptional solvency for both polyurethane prepolymers and fully formed PUD backbones. Compared to NMP and NEP, it offers significantly improved coalescence of PUD films, and this can enable significant VOC reduction due to the lower cosolvent demand for a required degree of coalescence. Due to its improved coalescing ability, formulators may now use alternative, less-objectionable coalescing cosolvents in conjunction with TamiSolve NxG. This gives formulators more flexibility in formulating to achieve optimal dry times and application

TABLE 2 » System stochiometry.

Raw Material	Equivalent Wt	(X)	Equivalents	(=)	Equiv. Charge
H12MDI*	131.15		1.50		196.73
3000 MW hexanediol adipate	1584.75		0.50		792.38
DMPA (dimethylolpropionic acid)	67.10		0.50		33.55
DABCO T-9 catalyst	100 ppm				0.100
Cosolvent to 85% solids					180.47
					1203.23

(1.50-1.00)(4200)/1203.23 = 1.745% NCO theoretical
(33.55/134)(4500)/1203.23 = 0.936% COOH theoretical
*H12MDI is (4,4′-methylene dicyclohexyl diisocyanate)

TABLE 3 » Process and product parameters.

Processing Steps	TamiSolve NxG Results	NMP Results
1. Charge all ingredients with mixing.		
2. Heat to 89 °C. Cook at ≈ 90 °C until conversion of isocyanate is complete. Record accurate residual NCO%.	1.70% NCO	1.68% NCO
3. Cool to 78 °C. Record Brookfield viscosity of prepolymer.	30,000 cps	21,000 cps
4. To a separate dispersion kettle, charge water at 23-24 °C to equal 35% batch solids.		
5. Charge 0.99 equivalents TEA (triethylamine) to prepolymer.		
6. Charge prepolymer to water in dispersion kettle. Record observations.	NxG prepolymer disperses with ease. Starts opaque white and clears to semi-trans/opaque. 280 cps viscosity @ 32 °C	NMP prepolymer disperses with great difficulty. Flocculant upon entering water. Very slow feed required. Opaque white with flocculant.
7. Charge 35% hydrazine to 0.92 equivalent charge.		
	Resulting Dispersion Characteristics	
Appearance	Clean, semi-translucent/opaque liquid	Opaque liquid with heavy sedimentation
Viscosity	400 cps	380 cps
Average particle size	0.045 microns	0.081 microns
pH	7.98	7.99
Total solids content	35.28%	35.49%
Heat age (7 days @ 49 °C)	Clean	Heavy sedimentation/separation

properties. Even when equal levels of NxG, as compared to NMP or NEP, are used, the NxG systems still exhibit more rapid comparative dry to touch times with exceptional solvency and improved film formation.

To demonstrate the improved solvency, three equivalent polyurethane preparations were made. One used NxG as a cosolvent and the other two used NMP and NEP respectfully. A description of these comparative systems and the resulting process and product parameters are shown in Tables 4 and 5.

Because each of the above systems demonstrated poor coalescence at RT as manufactured, it was shown that not enough solvent was present. To determine the comparative amount of test cosolvent that is required to achieve coalescence of the PUD backbone when applied at 10 wet mil film and dried at 20 °C, appropriate cosolvent was back added to each system. A description of these comparative systems and the resulting product parameters are shown in Table 6.

The experimental data in Table 6 demonstrates that, whether used as the sole solvent or in combination with another cosolvent, PUD formulations with NxG show improved coalescence compared to formulations made with NMP or NEP. The data also shows that NxG allows for well-coalesced films at lower total solvent levels.

Conclusions

TamiSolve NxG is a true process equivalent to NMP, the benchmark for PUD cosolvent performance. It is supplied with polyurethane-grade moisture content and offers a clean/pure reaction medium that is free of polyisocyanate-reactive contaminants. NxG has low vapor pressure, and high flash and boiling points for processing that allows normal polyurethane cook temperature cycling and high exotherm processing (if desired). Just like NMP, it offers very slightly basic curing conditions that gently enhance the reactivity of the polyisocyanate. And it demonstrates excellent solvency for DMPA, yielding smooth dissolution and subsequent reaction. The comparative viscosities of NxG-containing prepolymers are typically higher than the equivalent NMP-based systems. Unlike the plasticizers and glycol ethers, it is a true processing match for NMP.

The new solvent demonstrates no permanent plasticizing effects beyond what would be considered normal for an NMP-based system. Due to the strong solvent coupling

TABLE 4 » System stochiometry.

Raw Material	Equivalent wt.	(X)	Equivalents (=)	Equiv. charge
H12MDI	131.15		1.70	222.96
500BA MW butanediol adipate	1584.75		0.67	176.67
TMP (trimethylolpropane)	44.67		0.03	1.34
DMPA	67.10		0.30	20.13
CosCat 83	100 ppm			0.042
Cosolvent to 85% solids				74.32
				495.462

(1.70-0.70)(4200)/475.332 = 8.84% 1st stage NCO
(1.70-1.00)(4200)/495.462 = 5.93% Final NCO
(20.13/134)(4500)/495.462 = 1.36% COOH

TABLE 5 » Process and product parameters.

Processing Steps	NMP Results	NxG Results	NEP Results
1. Charge H12MDI, 500BA, solvent and TMP with mixing.			
2. Heat to 80 °C. Charge CosCat, allow to cool to 95 °C; Record accurate 1st stage NCO%.	8.59% NCO	8.31% NCO	8.62% NCO
3. Charge DMPA, cook at 85-95 °C to theoretical NCO% of 5.93 or below. Record accurate NCO%.	5.91% NCO	5.68% NCO	5.69% NCO
4. Cool to 77 °C. Record Brookfield viscosity of prepolymer.	5,500 cps	8,500 cps	8,500 cps
5. To a separate dispersion kettle, charge water at 23-24 °C to equal 33% batch solids.			
6. Charge 0.98 equivalents TEA (triethylamine) to prepolymer.			
7. Charge prepolymer to water in dispersion kettle. Record observations.	Easy dispersion. Starts white/translucent and clears to semi-translucent	Easy dispersion. Starts white/translucent and clears to semi-translucent	Easy dispersion. Starts white/translucent and clears to semi-translucent
8. Charge 35% hydrazine to 0.92 equivalent charge.			
Resulting Dispersion Characteristics			
Viscosity	40 cps	110 cps	60 cps
pH	8.59	8.56	8.53
Total solids content	33%	33%	33%
RT coalescence	Poor	Poor	Poor

TABLE 6 » Results after cosolvent was back added.

Test Subset 1 (Single Cosolvent Coalescence)	**NMP**	**NxG**	**NEP**
Base PUD system as above @ 33% TSC	100 parts	100 parts	100 parts
Flow additive**	0.50 parts	0.50 parts	0.50 parts
Additional noted solvent for coalescence	6.00 parts	1.75 parts	7.00 parts
New theoretical PUD solids content	30.985%	32.274%	30.698%
Total solvent required for coalescence	11.69 parts	7.44 parts	12.69 parts
Total solvent as % of PUD solids	37.73%	23.05%	41.34%
König hardness: 7 wet mils film applied via Bird Bar to Steel Q-Panels			
1 day air dry @ RT	39	33	58
5 day air dry @ RT	90	87	102
Oven dry 3′/150 °C	109	115	119
Gardner dry time: 6 wet mils coated to Mylar film (min)			
Dry to touch	38	8	35
Dust free	58	27	60
Dry through	66	28	70
Test Subset 2 (Dual Cosolvent Coalescence)	**NMP**	**NxG**	**NEP**
Base PUD system as above @ 33% TSC	100 parts	100 parts	100 parts
Flow additive**	0.50 parts	0.50 parts	0.50 parts
Additional solvent (NMP, NxG, or NEP as noted)	3.0 parts	3.0 parts	3.0 parts
Cosolvent 1	3.0 parts	3.0 parts	3.0 parts
Room temperature coalescence: 10 wet mil films @ RT applied to clear Mylar, air dried @ RT	Acceptable	Excellent	Acceptable - mudcracking in high spots
Particle size analysis, CPS (disk centrifuge)	0.03 microns	0.03 microns	0.03 microns
König Hardness: 7 wet mils film applied via Bird Bar to Steel Q-Panels			
1 day air dry @ RT	47	37	67
5 day air dry @ RT	94	96	105
Oven dry 3′ / 150 ºC	108	119	122
Gardner dry time: 6 wet mils coated to Mylar film (min)			
Dry to touch	17	12	20
Dust free	49	48	47
Dry through	53	52	53

** NOTE: TamiSolve NxG-based system demonstrated excellent wet and flow properties but both NMP and NEP systems demonstrated very poor wet and flow properties on Mylar and Lanetta cards. As a result, 0.5 parts of BYK 348 silicone flow aid was added to all systems to assist with flow out and determination of coalescence.

effect of NxG, systems produced using it will demonstrate a slightly slower hardness development upon air dry compared to NMP and NEP. Hardness differences are minimal but, in general, the NxG-based system will produce a film that reaches the equivalent hardness of a film produced by a "normal" NMP system in three days via air dry. After this slightly extended drying time, the NxG-based film will demonstrate superior hardness development compared to NMP. With an oven dry cycle, the NxG yields superior film hardness immediately when compared to an NMP-based equivalent system.

This new product is an innovative, next-generation sustainable solvent with excellent performance in a wide variety of waterborne PUD applications. It offers an improved safety, health and environmental profile compared to the traditionally used solvents NMP and NEP. NxG, NMP and NEP have been tested in PUD systems. The results of these tests show NxG provides similar viscosity control, improved coalescence ability and improved dispersibility of the final PUD system. NxG provides formulators the ability to reduce the solubilizing comonomer content (e.g., the amount of DMPA used) and/or the total cosolvent content while maintaining or improving the end-use properties of the PUD. It now gives PUD chemists the ability to formulate reduced VOC systems with equivalent or superior film formation, similar dry times and, in many cases, enhanced physical properties due to improved film formation and dispersibility. ■

For more information, visit www.tamisolvenxg.com.

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