Hybrid vigour

Waterborne urethane-acrylics combine high performance with low VOC content

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Urethane-acrylic hybrid polymer dispersions (HPDs) offer an excellent cost/performance balance, but usually have a high content of N-methylpyrrolidone (NMP) solvent. New regulations make it desirable to eliminate this material. However, solvent-free high-performance HPDs have now been developed. Novel gemini surfactants reduce their MFFT significantly, creating high-performance coating formulations with volatile organic content (VOC) of less than 100 g/l.

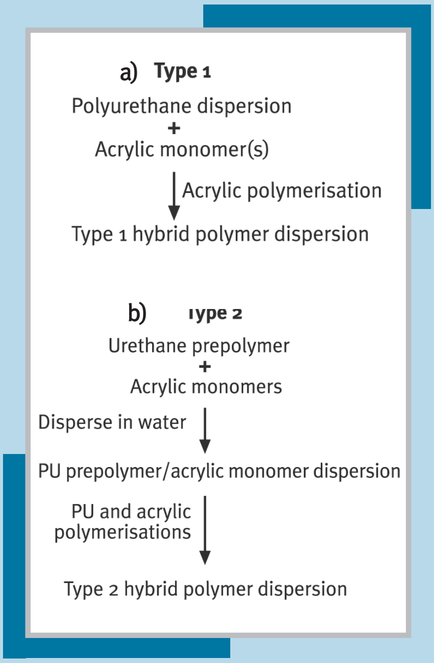

Figure 1: Simplified process flow diagram for preparation of type 1 and type 2 urethane/acrylic hybrid

Thermoplastic polyurethanes are well known for their excellent balance of mechanical toughness and chemical resistance [1, 2]. Because of regulatory pressures, waterborne versions (polyurethane dispersions or PUDs) of these resins are becoming increasingly popular choices as binders for a variety of one-component coatings for wood (floors and furniture), plastic (business machine housings), leather, metal, and concrete. Their superior physical and chemical properties have been attributed to a combination of their molecular structure and hard/soft domain morphology [3, 4]. PUDs are relatively expensive. Formulators have sought to reduce the cost of their aliphatic PUD-based coatings by blending the PUD with much less expensive acrylic polymer emulsions. Unfortunately, the acrylic emulsions tend to reduce the overall performance of the binder. The reduction in performance can be lower than would be predicted from an arithmetic rule of mixtures [5, 6].

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One possible reason for this behaviour is that, on a molecular level, the acrylic polymers are not soluble in the polyurethane polymers. Therefore, the polymers remain phase-separated during film formation. The resultant phase morphology is probably at least partly responsible for this diminished performance behaviour. In order to take advantage of the potential cost reduction afforded by the acrylics and maintain a greater share of the advantageous PUD properties, so-called "hybrid" systems were developed. The hybrids incorporate both urethane and acrylic polymers into the same dispersion. As outlined in the simplified process flow diagram (*Figure 1*), there are generally two methods for preparing HPDs (Type 1 and Type 2).

Two ways to make a hybrid

For Type 1 hybrids, a PUD is first prepared, acrylic monomers are added to the PUD, and the acrylic polymer is formed in the presence of the PUD [7]. To prepare Type 2 hybrids, a polyurethane prepolymer is formed, the acrylic monomers are added to the prepolymer, the mixture is dispersed in water, and the urethane and acrylic polymerisations are completed concurrently [8]. As mentioned previously, the rationale for preparing the hybrids was to improve performance relative to a simple blend. In *Figure 2*, the tensile strengths of films prepared from the individual polymers (i.e., a blend) and the two hybrid types are compared to that predicted by a linear rule of mixtures. The blend and the hybrids contain equal amounts of the same urethane and acrylic polymers. As expected, the urethane polymer had a significantly higher tensile strength than the acrylic polymer. Interestingly, the tensile strength of the blend was found to be lower than that predicted by the simple averaging rule. The Type 1 hybrid system showed slightly higher tensile strength than predicted. Remarkably, the Type 2 hybrid was found to have a tensile strength approximately equal to that of the polyurethane. Similar results for other properties have been reported as well [5]. This evidence strongly suggests that the phase morphology of a urethane/acrylic polymer system has a significant influence on its ultimate performance.

NMP plays a key role in polyurethane dispersions

Typically, PUDs and HPDs contain NMP, which is required to dissolve dimethylolpropionic acid (DMPA), an acid-containing diol that is incorporated into the polyurethane polymers to stabilise the dis-

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persions after neutralisation with a tertiary amine. Being a relatively high boiling solvent, NMP cannot readily be removed from the process and remains in the final dispersion product. Although the amount of NMP can vary according to the product, typical NMP levels are 10% to 15% for PUDs and 3% to 8% for hybrids, based on total dispersion weight. In a final formulated product such as a coating, NMP is beneficial as a coalescing solvent for film formation. Unfortunately, NMP contributes to VOC (Volatile Organic Content), and is also under regulatory pressure because of worker safety issues. Thus, a need exists for NMP-free HPDs that still provide the outstanding performance that is expected of their NMP-containing counterparts.

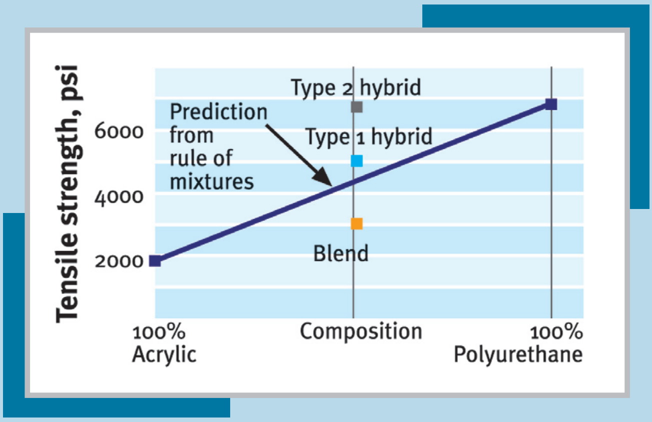

Figure 2: Tensile strengths of free films prepared from a simple blend and HPDs compared with theoretical values

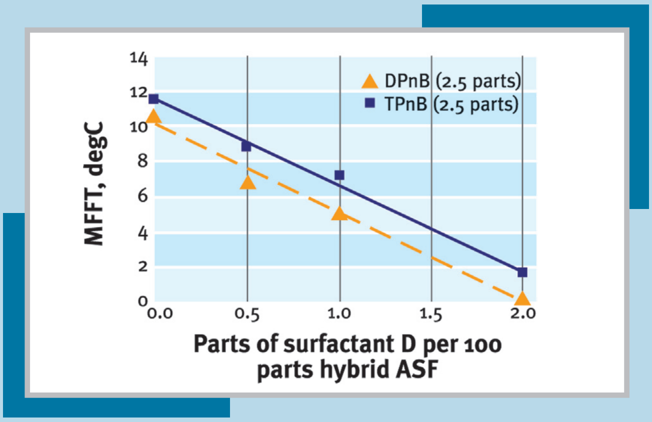

Figure 3: Effect of gemini alkane diol surfactant on MFFT

Regulations put continuing pressure on VOC levels

There continues to be a strong regulatory demand to reduce the amount of VOC in paints and coatings. In accordance with the VOC limits recently announced by the South Coast Air Quality Management District (SCAQMD) in California, many industrial coatings will be limited in VOC to less than 100 g/l. The VOC of most conventional PUDs and HPDs which are currently being used for industrial coatings is at least 160 g/l because NMP levels are typically 15% for PUDs and 3% to 8% for hybrids. Those polymer dispersions cannot be used to formulate coatings with a VOC of less than 100 g/l.

The purpose of this study was to develop waterborne coating formulations based on new NMP- and solvent-free HPDs that would have the performance required in many coatings applications while limiting added coalescing solvents to a level of less than 100 g/l. Since it is known that surfactants can reduce the minimum film-forming temperature (MFFT), and thereby improve coalescence, the use of novel surfactants which do not contribute VOCs to coating formulations was studied as a means to achieve the <100 g/l target.

Experimental

Polymer composition and properties

The typical properties of the solvent-containing (hybrids A and B) and NMP-free

Table 1: Typical characteristics of type 2 hybrid polymer dispersions

Property	Hybrid A [a]	Hybrid B [b]	Hybrid ASF [c]	Hybrid BSF [d]
Viscosity, cP, 25°C, Brookfield	50 - 150	50 - 150	50 - 150	50 - 150
Non-volatiles, % by weight	39 - 41	39 - 41	39 - 41	39 - 41
Solvent	6% NMP	6% NMP	<0.2% acetone	<0.2% acetone
VOC, g/l (lbs/gal) *	160 (1.33)	164 (1.37)	30 (0.25)	24 (0.20)
pH	7.5 - 9.0	7.5 - 9.0	7.5 - 9.0	7.5 - 9.0
Acid number, mg KOH/g **	14.5	14.5	16.0	14.5
T_g range, °C ***	-35 to 35	-35 to 100	-35 to 35	-35 to 100
Particle diameter (wt. avg.), nm	75 - 85	75 - 85	75 - 85	75 - 85
Residual acrylic monomer, ppm	500	500	50 - 200	10 - 50

[a], [b], [c], [d] Refer to Appendix A for material identification.

* VOC includes contribution from the triethylamine (neutralizing amine, ca 1% by weight). Acetone was not included in the VOC calculation.

** Calculated on a solids basis.

*** T_g estimated from DMA measurements (breadth of tan δ peak) and polymer compositions.

(hybrids ASF and BSF) HPDs used in this study are given in *Table 1*. The letter designations (i.e., A or B) refer to the analogous polymer compositions, and the suffix "SF" indicates the solvent-free version. The composition of the urethane (aliphatic) portion was identical for all of the hybrid polymers. The acrylic polymer composition was kept the same for the hybrid B variants, while the monomer ratios were varied within the A series. Nevertheless, the acrylic polymers had approximately the same theoretical T_g within a given series (either A or B). The ratio of urethane to acrylic was approximately the same for each HPD.

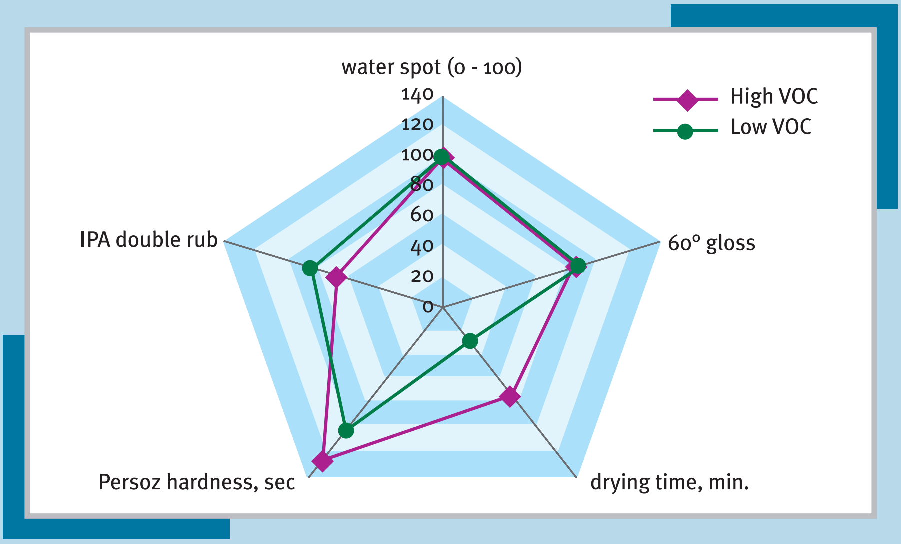

Figure 4: Low-VOC coating properties (room temperature drying)

Formulations
High VOC: hybrid A (100) + ester alcohol (2.1) + DPnB (2.4); calculated VOC = 250 g/l
Low VOC: hybrid ASF (100) + TPnB (2.5) + surfactant D (2.0); calculated VOC = 93 g/l

Notes on test procedures
Water spot test: 0 = completely dissolved
100 = no effect
Drying time: time for complete drying

Test procedures

Coating properties were tested over cold-rolled steel with a zinc phosphate treatment ("Bonderite 952"), untreated cold-rolled steel, or on sealed-paper charts (from Leneta Co.). The coatings were applied using a #60 wire-wound draw-down rod and were allowed to dry at 20°C and 50% relative humidity for 7 days.

For the elevated temperature tests, the coating specimens were put into an oven at 85°C for 3 minutes. Depending on the formulation, the dried film thickness ranged from 30 μm (1.2 mil) to 76 μm (3.0 mil). Coating performance was evaluated in accordance with standard ASTM methods. Spot tests were performed on clear coatings applied by drawdown on sealed-paper charts. The coatings were dried for 24 hours at room temperature (ca 25°C), and the spots (2-3 cm wide) were rated after exposure to each reagent for 1 hour. The reagent spots were covered during the exposure to prevent evaporation. Prior to evaluating the coating, the reagent spots were removed by lightly patting with a clean paper towel.

Table 2: Surfactant effects on hybrid coating formulations

Surfactant Surfactant class	A [e] Nonyl phenol	B [f] DOSS *	C [g] DOSS *	D [h] Gemini alkane diol	E [i] Gemini alkyl ester
Viscosity, cps	370	100	1700	56	50
Appearance	Pass	Pass	Pass	Pass	Pass
Water spot test (1hr)	Pass	Pass	Pass	Pass	Pass
Persoz hardness, sec.	98	117	89	101	94
IPA double rub	32	40	40	85	65
APE-free**	No	Yes	Yes	Yes	Yes
Volatile content of surfactant ***	0.5%	14%	7%	6%	2%
Calculated VOC of Coating, g/l	93	94	93	94	93
Remarks	9 mole	Dissolved in isopropyl alcohol	Dissolved in ethanol		

Test formulation: hybrid ASF (100) + TPnB (2.5) + surfactant (2.0).
Drying conditions: 7 days @ 20°C, 50% R.H.
[e], [f], [g], [h], [i] Refer to Appendix A for material identification.
* DOSS: dioctyl sulfosuccinate, sodium salt
** APE: alkyl phenol ethoxylate
*** Typical values described in suppliers' brochures

Table 3: Comparison of effects of different solvents on hybrid ASF

Coating properties	Solvent type and test results				
	DMM*	Ester alcohol* [j]	TPM*	DPnB*	TPnB*
MFFT, °C	5.1	2.9	2.1	0.4	0.8
Persoz hardness	90	87	82	102	94
Water spot resistance **(4 days R.T. drying)	1	2	6	7	10

Test Formulation: hybrid ASF (100) + surfactant E (2.0) + solvent (2.5)

* DMM: Dipropylene glycol dimethyl ether, TPM: Tripropylene glycol methyl ether, DPnB: Dipropylene glycol n-butyl ether, TPnB: Tripropylene glycol n-butyl ether.

[j] Refer to Appendix A for material identification. (Trimethylpentanediol monoisobutyrate).

** Rating key: 10 = no effect; 5 = moderate: swelling, softening, 0 = completely dissolved

Refining the formulations for optimum results

Calculating the maximum allowable solvent content

Although hybrid ASF will form a continuous film by itself, it is essential to add a certain amount of solvent to get satisfactory coating performance such as hardness, gloss, impact strength, etc. The amount of solvent, however, should be limited by the target VOC of 100 g/l. Including the VOC of hybrid ASF, the VOC is calculated to be 93 g/l with 2.5 parts of solvent. Since there might be small additional contributions to VOC from surfactants and other additives, 2.5 parts of solvent are used in this study to allow a small margin for error.

Appendix A: List of materials used in formulations and their suppliers

Key	Material	Supplier
a	„Hybridur 570“ polymer dispersion	Air Products
b	„Hybridur 580“ polymer dispersion	Air Products
c	„Hybridur 870“ polymer dispersion	Air Products
d	„Hybridur 878“ polymer dispersion	Air Products
e	„Igepal CO 630“	Stepan
f	„Agnique DOS 44IP“	Cognis
g	„Aerosol OT 75%“ surfactant	Cytec
h	„EnviroGem AD01“	Air Products
i	„EnviroGem AE02“	Air Products
j	„Texanol“ ester alcohol	Eastman
k	„Coat-O-Sil 1770“	GE Silicones

Gemini surfactants show best overall performance

In order to find an optimum surfactant to improve the coalescence of hybrid ASF, several different classes of surfactants were evaluated. The results are given in *Table 2*. Surfactants A (nonyl phenol ethoxylate) and C (sodium dioctyl sulfosuccinate) showed quite a large viscosity increase. Surfactant B (sodium dioctyl sulfosuccinate), showed good compatibility and hardness, but lacked resistance to IPA (isopropyl alcohol).

The gemini surfactants D and E showed the best overall performance, and did not substantially increase the total VOC since they do not contain solvent. Surfactant D yielded a clear coating which showed excellent IPA resistance.

Alcohol resistance is a common requirement of many industrial finishes, and lack of resistance to alcohols is a common weakness in PUD-based thermoplastic coatings. In most of this study the gemini alkane diol (surfactant D) was therefore employed. In certain tests the gemini alkane diol type surfactant (surfactant E), was used in the formulations, as it gave similar results. However, it should be noted that as an ester, this surfactant may undergo hydrolysis reactions, especially in high pH formulations, and therefore its stability should be carefully tested in formulations intended for commercial use.

Solvent selection affects hardness and resistance

In order to characterise and understand the coalescing efficiency of various solvents in HPD formulations, MFFTs, hardness and water spot resistance were determined. The results are given in *Table 3*. In this test, the water spot test was conducted after 4 days curing to check the difference more clearly. Water spot resistance of the test formulation was optimal with TPnB (tripropylene glycol n-butyl ether). As shown in *Figure 3*, the amount of gemini surfactant reduces the MFFT of the test formulations. The MFFT of neat hybrid ASF was 25.8°C [9]. It dropped to around 10°C with 2.5 parts of DPnB (dipropylene glycol n-butyl ether), and to 8°C with TPnB. Adding 2 parts of surfactant E reduced the MFFT to <1°C in both formulations.

Low-VOC formulation provides good properties

Based on the above results of preliminary tests, a low-VOC coating test formulation consisting of hybrid ASF (100) + TPnB (2.5) + surfactant D (2.0) was used for further testing. The VOC of this test formulation is about 93 g/l, allowing room to use small amounts of other volatile additives and still remain below the VOC limit of 100 g/l. Five coating performance properties of this low-VOC formulation are compared to those obtained from the standard high-VOC formulation based on hybrid A, which is given as a starting point by the supplier.

As shown in *Figure 4*, the low-VOC formulation has equivalent properties in water spot resistance and 60° gloss. IPA double rubs improve in the low VOC formulation. The drying time for complete curing of the low-VOC coating is 28 minutes, which is faster than the high-VOC time of 72 min. This is the result of the relatively slow evaporation rate of NMP. On the other hand, the Persoz hardness of the low-VOC coating, 94 seconds, is a little lower than

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that of high-VOC, 124 seconds. This result is due to slight T_g depression by the surfactant.

Blending resins improves hardness

The hardness of the low-VOC formulation can be improved by blending hybrid ASF with a high-T_g NMP-free HPD, hybrid BSF. As described in *Table 2*, BSF has a T_g range of -35 to about 100°C so that its hardness is much higher than ASF. Actually, this product was developed for very high hardness applications such as plastic film coatings and wood coatings. The two solvent-free hybrids exhibit excellent compatibility. Addition of 20% of high-T_g HPD increases the Persoz hardness to 109 sec. for the blend while the other properties are comparable to those of Hybrid ASF. The hardness can be further increased by the addition of more BSF, but more solvent will be needed to maintain a satisfactory level of coalescence.

Crosslinking enhances chemical resistance

Another way to improve performance is through use of crosslinking agents. The HPDs described in this paper contain carboxylic acid groups, which serve as a convenient functional group through which a film can be crosslinked. Indeed, the resistance properties of coatings based on hybrid A have been found to be improved when crosslinked with an epoxy-silane crosslinker, β-(3,4-epoxycyclohexyl)ethyltriethoxysilane (a cycloaliphatic epoxy-silane, listed as **k** in Appendix A). High-VOC formulations which are shelf-stable (at least 6 months) have been developed [10]. Incorporation of this crosslinker with a 7-day room temperature cure increased IPA double rubs from 65 to 180. There were also improvements in chemical resistance to a variety of reagents.

Hybrids offer a new way to optimise performance

New NMP-free waterborne, high performance, urethane-acrylic HPDs have been developed to meet market needs for lower VOC coating formulations. Coatings based on NMP-free HPDs provide properties comparable to their NMP-containing counterparts. In order to develop coating formulations with a total VOC of less than 100 g/l, a number of solvents and surfactants were evaluated to find the best coalescing aids.

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A gemini alkane diol type surfactant and tripropylene glycol n-butyl ether (TPnB) were selected in preliminary screening tests to be further evaluated in test coating formulations. Coating formulations meeting the stated VOC target exhibited coating properties comparable to those of much higher VOC coating formulations. Although the low VOC formulation was slightly softer when compared with the higher VOC analogue, its hardness was improved by blending with a higher T_g NMP-free HPD. The chemical resistance of low-VOC coatings was enhanced through the use of an epoxy-silane crosslinker. ■

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Results at a glance

- New NMP-free waterborne, high performance, urethane-acrylic hybrid polymer dispersions (HPDs) have been developed to meet market requirements for lower VOC coating formulations free of the N-methyl pyrrolidone (NMP) normally present in these materials.
- Coatings based on these NMP-free HPDs provide properties comparable to their NMP-containing counterparts.
- A number of solvents and surfactants were evaluated in order to develop coating formulations with total VOC of less than 100 g/l. A gemini alkane diol type surfactant and tripropylene glycol n-butyl ether (TPnB) were selected for further evaluation.
- Coating formulations meeting the stated VOC target exhibited coating properties comparable to those of much higher VOC coating formulations.
- Although the low VOC formulation was slightly softer, its hardness was improved by blending with a higher Tg NMP-free HPD. The chemical resistance of low-VOC coatings was enhanced through the use of an epoxy-silane crosslinker.

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