

# Solvent-Free Urethane-Acrylic Hybrid Polymers for Coatings

by Ernest C. Galgoci,<sup>†</sup> Charles R. Hegedus, Frederick H. Walker, Daniel J. Tempel, Frank R. Pepe, Kenneth A. Yoxheimer, and Alan S. Boyce

Air Products and Chemicals, Inc.\*

rethane-acrylic hybrid polymer dispersions (HPDs) can offer cost/performance advantages over common HK coating materials such as polyurethane dispersions (PUDs), acrylic emulsions, and blends thereof. One disadvantage of both PUDs and HPDs is the inclusion of N-methylpyrrolidone (NMP) solvent, which is commonly a necessary processing solvent included at levels ranging from about 3 to 15%. Since NMP has recently been added to California's Proposition 65 list and has generally become objectionable for use in Europe, it has become desirable to eliminate NMP from these products. Consequently, solvent-free versions of FIPDs have been developed that, despite the lack of NMP used in their preparation, have been found to perform favorably compared to analogous solvent-containing polymers (both hybrid and PUD). Like their solvent-containing counterparts, the outstanding properties of the new solvent-free versions are apparently due to their true hybrid nature, which is analogous to an interpreticating network (HPN) as indicated by a broad glass transition temperature range. Although the NMP-free versions still require coalescing solvents for adequate film formation, they offer greater flexibility in choosing alternate solvents when formulating high performance contings.

## BACKGROUND

Thermoplastic polyurethanes are well known for their excellent balance of mechanical toughness and chemical resistance.<sup>19</sup> Unfortunately, the solventbased versions require exceedingly high levels of VOC for application by conventional coating techniques. The waterborne versions (polyurethane dispersions or PUDs) require significantly lower VOC and are, therefore, 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.<sup>9,0</sup>

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7700 Hamilton Blvd., Allentown, PA 18195.

Author to whom correspondence should be addressed. Email: galgococi@airproducts.com.

In general, PUDs are prepared by reacting an excess of diisocyanate with a polyol, dispersing the resulting prepolymer in water, and completing the reaction by adding a water-soluble diamine to consume the residual isocyanate and, thereby, chain-extend the prepolymer to a high molecular weight. The dispersed PUD particles are usually anionically stabilized, which is commonly accomplished by incorporating a carboxylic acid-functional polyol into the backbone of the Figure 1—Simplified process flow diagram for preparation of Type 1 and Type 2 Hybrids.

Туре 1	Type 2
Polyurethane Dispersion	Urothane Prepolymer
-1	+
Acrylic Manamer(s)	Acrylic Monomers
Acrylic Polymeri∠ation	Disperse in Water
Type 1 Hybrid Polymer Dispersion	PU Propolymer/Acrylic Monomer Dispersion
	PU and Acrylic Polymerizations
	Type 2 Hybrid Dispersion

polyurethane and neutralizing the acid groups with a tertiary amine. Thus, in many cases, no external surfactants are present to contribute adversely to the water sensitivity of PUD-based coatings.

PUDs are available in both aromatic and aliphatic varieties. Aromatic PUDs are not suitable for applicatious requiring low yellowing and, therefore, the aliphatic PUDs are required for such cases where exposure to direct or indirect sunlight occurs.

Unfortunately, one of the main disadvantages of the aliphatic PUDs is their relatively high cost. As a result, formulators have sought ways to reduce the costs of their coatings. The most popular strategy is to blend the PUD with an acrylic polymer emulsion that costs less than one-half of a standard aliphatic PUD. Although the acrylics reduce the system cost, they also reduce the overall performance of the binder. The reduction in performance can be lower than what would be predicted from an arithmetic rule of mixtures.<sup>11,1°</sup> One possible reason for this behavior is that, on a molecular level, the acrylic polymers are not soluble in the polymethane polymers. Therefore, the polymers remain phase-separated during film formation. Arguably, the resultant phase morphology is at least partly responsible for the diminished performance behavior.

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 have been developed. The hybrids incorporate both the urethane and the 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). 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.<sup>13</sup> 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 polymerizations are completed concurrently.<sup>14,15</sup> improved molecular compatibility versus simple blending. The improved compatibility is demonstrated by the dynamic mechanical analysis (DMA) data that is shown in Figure 2. The simple blend has two distinct tan delta ( $\tan \delta$ ) peaks, which correspond to the glass transition temperatures (T<sub>a</sub>) for the phase-separated urethane and acrylic polymers. The hybrid prepared from the first method previously described also shows two T<sub>a</sub> peaks, but the peaks have become somewhat broader, which is indicative of some limited molecular mixing. In contrast, a Type 2 hybrid, in which the urethane prepolymer and acrylic monomers are homogeneously mixed prior to dispersion and subsequent polymerization, exhibits only a single, very broad tan ô peak. The single peak, which spans the temperature range between the theoretical T<sub>s</sub>s of the urethane and acrylic polymers, is strong evidence for a significant amount of polymer-polymer mixing, in which, presumably, the different polymer molecules are intertwined similar to that of an interpenetrating network (IPN). Possibly, the improved compatibility for the hybrids

The urethane and actylic polymers in HPDs exhibit



Figure 2—DMA data comparing a simple blend with HPDs.

Figure 3—Tensile strengths of free films prepared from a simple blood and HPDs.<sup>11.12</sup>



(especially Type 2) is at least partly the result of some molecular-level grafting of the two polymers.

As mentioned previously, the rationale for preparing the hybrids was to improve the performance relative to a simple blend. In *Figure 3*, 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 actylic 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. On the other hand, the hybrid systems showed higher tensile strengths 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.<sup>11</sup> One interpretation is that the phase morphology of a urethane/acrylic polymer system has a significant influence on the ultimate performance.

Typically, PUDs and HPDs are prepared using an aprotic solvent such as N-methylpyrrolidone (NMP). The NMP is required in the polyurethane prepolymer step to dissolve the dimethylolpropionic acid (DMPA), which is a crystalline carboxylic acid polyol that is virtually insoluble in the polyol-diisocyanate mixture that reacts to form the urethane prepolymer. Being a relatively high boiling solvent, NMP cannot be readily removed from the process and, thus, remains in the finaldispersion 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. In the final product, NMP is beneficial as a coalescing solvent for film formation. Conversely, NMP and high levels of residual acrylic monomers are undesired due to their odor and, in the case of NMP, its regulatory status (e.g., inclusion on California's Proposition 65). Therefore, there is a market need for NMP-free, low residual monomer HPDs that meet those requirements and still provide outstanding performance that is comparable to that of their NMP-containing counterparts.

In this article, the properties and performance of new, NMP solvent-free, Type 2 urethane acrylic HPDs are discussed.

## EXPERIMENTAL

Solvent-containing (Hybrids A and B) and solventfree (Hybrids Asp and Bsp) HPDs were prepared accord-

## Table 1---- Typical Characteristics of the Type 2 Hybrid Polymer Dispersions Evaluated

Property	Hybrid Aª	Hybrid 8 <sup>5</sup>	Hybrid A <sub>sp</sub> e	Hybrid B <sub>SF</sub> <sup>d</sup>
Appearance	Opaque, Slight Milky	Opague, Slight Milky	Opaque, Slight Milky	Opaque, Slight Milky
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 content, % by weight	5	6	<0.2	<0.1
Solvent	NMP	NMP	Acetone	Acetone
VDC, g/L (¿b/gal) <sup>e</sup>	160 (1.33)	164 (1.37)	30 (0.25)	24 (0,20)
Density, g/ml (lb/gal)	1.03 (8.60)	1.64 (8.70)	1.05 (8.76)	1.07 (8.93)
pH	7.5-9.0	7.5-9.0	7.5-9.0	7.5-9.0
Acid number, mg KOH/gf	14.5	14.5	16.0	14.5
T, range, °C <sup>u</sup>	-35 to 35	-35 to 100	-35 to 35	-35 to 100
Neutralizing amine <sup>b</sup>	TFA	TEA	TEA	DMEA
Particle diameter (wt. avg.), nm	75-85	75-85 <sup>i</sup>	75-85	75-85'
Residual acrylic monomer, ppm	500 <sup>i</sup>	500	50-200 <sup>i</sup>	10–50 <sup>i</sup>
Particle charge	Anionic	Anionic	Anionic	Anionic

 $\{a,b,c,d\}$  Refer to Appendix C for material identification. (c) WiC incluses contribution from the heutratizing comme (-0.75 averagint).

(I) Calculated on a solies peris. (a) I<sub>4</sub>s estimated from DNA measurements (treadth of tan A prick) and polymor compositions.
 (b) TDA = triatny's mine, UNIFA = dimethyled sustaining.

(f) Notical values.

# Table 2----Test Methods Used to Evaluate the Performance Characteristics of the Coatings

Property	ASTM Test Procedure
Adhesion, dry and wet tabe	
Dry time	
Rexipility (mandrei bend)	D 1737
Gloss	
Hardness (Persoz)	D 4366
Humidity resistance (Cleveland)	
Immersion resistance	
Impact resistance,	D 2794
Solvent resistance (dnuble rubs)	D 4752
Tensile properties	BE8 D
Minimum film formation Lengerature	D 2364

ing to the procedures outlined previously.<sup>14,15</sup> The letter designations (i.e., A or B) refer to the analogous polymer compositions, and the subscript "SF" indicates the solvent-free version. The typical properties of the HPDs used in this study are provided in *Table* 1. 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<sub>g</sub> within a given series (ci-ther A or B). The amount of either urethane or acrylic was about 50% for each HPD. With the exception of dimethylethanolamine (DMEA) for Hybrid B<sub>SD</sub> the neutralizing amine used was triethylamine (TEA).

Coating formulations (*Appendix* A) were prepared using standard techniques. Coating properties were tested over cold-rolled steel with a zinc phosphate treatment (Bonderite 952), untreated cold-rolled steel, or on sealed-paper charts (Leneta Co.). The coatings were applied using a #60 wire-wound drawdown rod and were allowed to dry at 21 °C (70 °F) and 50% relative humidity for seven days. Depending on the formulation, the dried film thickness ranged from 30  $\mu$ m (1.2 mil) to 76  $\mu$ m (3.0 mil).

The standard test methods listed in *Table* 2 were used to evaluate coating performance. Spot tests were performed on clear coatings applied by drawdown on sealed-paper charts. The coatings were dried for 24 hours at room temperature ( $\sim 25$ °C), and the spots (2  $\cdot 3$  cm wide) were rated after exposure to each reagent for one 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.

DMA data was obtained on clear resin coatings

(Appendix A) using a Rheometrics Solids Analyzer RSA II (Rheometric Scientific) in a tensile dynamic mode with a thin film fixture. The films were analyzed over the temperature range from -150°C to 150°C. The samples were not preconditioned with regard to humidity prior to data acquisition, but dry nitrogen was used as the atmosphere during the measurements. Data were acquired at intervals of 6°C; a one-minute soak time was used at each measurement temperature to ensure isothermal equilibration. MFFT results were obtained using a Minimum Film Formation Temperature Bar Model MFFT-90 (Rhopoint Instrumentation Ltd.). Films were applied by drawdown to a wet film thickness of 152 µm (6 mils). Tensile data were obtained on clear films that had an average thickness of ~152 µm (6 mils) and were dried at 21 °C (70°F) and 50% relative humidity (RH) for seven days. The crosshead speed used was 5.1 cm/min (2 in./min) and the temperature was 23°C (73°F) with 50% RH. Particle size determinations were made using an LA-910 Laser Scattering Particle Size Distribution Analyzer (Horiba).

# RESULTS AND DISCUSSION

## **Dispersion Properties**

With the obvious exception of VOC and residual monomer levels, the physical property data as provided in *Table* 1 are quite similar for all of the HPDs studied. Both the solvent-containing and the NMP-free versions exhibited similar viscosities at the same solids levels. Interestingly, the particle diameter distributions (*Figure* 4) and the respective means for the NMP-free dispersions were similar to those that contained NMP. All of the distributions were mono-modal with no particle diameters greater than 200 nm and weight-average particle diameters between 75 and 80 nm. The weight-average particle diameters (in nanometers) for the samples in *Figure* 4 were 81, 77, 79, and 78 for Hybrids A, B.

Figure 4—Particle size distributions for the hybrid polymer dispersions.



# Table 3-----MFFT ("C) Data for the HPDs

Additive (% wt.)	Hybrid A	Hybrid B	Hybrid A <sub>se</sub>	Hybrid B <sub>st</sub>
None	< -4.б		19,1	62.0
NMP (6%)	×	•	<0.0	18.3
DMM (6%)	×	×	-1.0	40.8
S-1 (2%)"	2	×	3.1	*
5-2 (2%)9	.,	*	5.5	*
5-3 (2%)'	+	*	10.9	*

"Vision was nee determined. 5-0, 5-2, and 5-3 are surfactants identified in Appendix C by sub-script letter.

 $\Lambda_{sp}$  and  $B_{sp}$  respectively. Since all of the hybrids have similar acid numbers and degrees of neutralization, the similarity in particle sizes suggests that, regardless of the NMP level (at least up to 6% by weight), the average particle diameter is determined by the zeta potential,16 In addition, the particle size distributions probably explain the similar viscosity-solids relation shown for these HPDs. Because of the lack of NMP and the low residual monomer levels, the NMP-free HPDs have very low odor compared to the solvent containing versions.

#### Film Formation Characteristics

Film formation characteristics of Type 2 hybrid polymers have been reported previously for systems. containing NMP solvent.17 Our experience with Hybrids A and B has shown that ultimate performance is impacted by particle coalescence which, of course, is greatly influenced by the type and amount of co solvent used. Both Hybrids A and B, which contain NMP, formed clear films (from drawdowns) at room temperature (~25°C). Hybrid A<sub>SP</sub> formed a clear but non-continuous (cracked) film, whereas Hybrid Ber formed a white, flaky film, which is indicative of poor coalescence. Films prepared using co-solvents (formulations in Appendix A) were clear and continuous.

In order to characterize and understand the effects of co-solvents and additives, minimum film-formation temperatures (MFFTs) were determined for the NMPfree HPDs; the results are provided in *Table* 3. In line with the drawdown observations, both of the neat solvent-containing products had MFFTs below 0°C,

## Table 4----Tensile Properties for the Hybrid Polymers

Polymer	Strength, psi	Elongation, %	Modulus, 10 <sup>s</sup> psi	
Hybrid A	2433 ± 458	236 ± 76	30 ± 11	
Hybrid Asp	2576 ± 650	245 ± 12	38 ± 11	
Hybrid B	$4552 \pm 450$	$15 \pm 8$	$115 \pm 59$	
Hybrid Ba	4407 ± 244	8 ± 0.4	$155 \pm 11$	

## Table 5----Chemical Spot Testing Results for Hybrids B and B<sub>sr</sub>

Chemical	Hybrid B	Hybrid B <sub>N</sub>
10% wt. NH.OH in water	10*	10
Clorox (5.25% wt. NaClO/water)	10	10
50% wt. ethanol in water	10	9
JPA	7	7
Commercial cleaner 1**	9	8
Commercial cleaner 2	8	8
Commerce, Clearer L = Fanta≂ik (S.C. Joh 109 (Clarret) 1472 (Clarret) 1472 (Clarret) 1472 (Clarret) 1472 (Clarret) 1473 (Clar	hrson): Commercia : swelling, softenin	:, cleaner 2 - Formula rg. and Afritaming; 0 =

whereas the NMP-free versions had, as expected, much higher METS. In the case of Hybrid B<sub>SD</sub> the MFFT was 62°C. The addition of co-solvents (6% by weight of either NMP or DMM-dipropylene glycol dimethyl ether} was found to significantly lower the MFFIs. Comparatively. NMP was shown to be somewhat more efficient (especially for Hybrid B<sub>sr</sub>) for lowering the MMFL Despite the addition of the co-solvents, the MFF1s for Hybrid  $B_{\delta b}$  were unexpectedly much higher than for Hybrid B. Perhaps, the order of addition has an effect on the coalescing efficiency of the co-solvent. Alternately, it may be that the formulations had not reached equilibrium prior to testing, although a sweatin time of between 1 to 5 days after preparation was employed. Another possibility is that some fundamental differences between the polymers or polymer morphology exist, although the DMA data to be discussed in the next sub-section does not seem to support this hypothesis.

Besides the co-solvents, several novel surfactants were tested in Hybrid A<sub>st</sub> as potentially ultra-low VOC coalescing agents. These surfactants are low volatility, alkyl ester-based products that are purported to have utility to reduce MFFTs. The results in Table 3 show that these surfactants do indeed significantly reduce the MFFIs. At a level of 2% by weight (total emulsion basis), the MFFT was found to drop by the amount of 8° to 16°C. Thus, the use of these surfactants may offer the potential to significantly lower VOCs in formulations developed from these materials.

## Clear Film Mechanical Properties

The dynamic and static (tensile) mechanical properties of the hybrid polymers were determined. Figures 5 and 6 compare the dynamic mechanical properties (storage modulus, E', and  $\tan \delta = E''$  [loss modulus]/E']. as a function of temperature. Below the  $T_{e}$  (~ -35 °C) of the urethane polymers (the same composition for all four hybrids), both series (A and B) of hybrids had E' values between about 2 to  $3 \times 10^{10}$  dyn/cm<sup>2</sup>. Above the

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Figure 5—Comparison of the DMA properties for Hybrids A and A<sub>st</sub>.

urethane  $T_g$  the E' values declined to about 10<sup>3</sup> dyn/cm<sup>2</sup> near the  $\Gamma_g$  of the individual acrylic polymers. Having the higher  $T_g$  acrylic polymers, the B-series did not reach an E' value of 10<sup>9</sup> dyn/cm<sup>2</sup> until > 100°C versus about 50°C for the A-series materials. The Hybrid A-series showed a pronounced rubbery plateau above the acrylic  $T_g$ s, whereas the B-series did not.

For the A-series polymers, the E' and tan  $\delta$  responses were similar, and both polymers showed very broad peaks in the tan  $\delta$  over the expected  $T_{c}$  ranges as listed in Table 1. Hybrid A<sub>se</sub> did have a somewhat higher E' over most of the temperature range studied. The B-series polymers showed comparable E' and tan 8 behavior, although Hybrid B<sub>sp</sub> did have a slightly higher E over most of the temperature range examined. However, unlike that for the A-series, there was no apparent tan  $\delta$  peak over the anticipated T<sub>a</sub> range. The tan δs did, however, show a steady increase with increasing temperature as the E' decreased. In general, both the solvent-containing and NMP-free versions displayed dynamic mechanical properties which would be expected if there were some molecular level mixing of the urethane and acrylic polymers.

The room temperature tensile mechanical properties of thin films of the hybrids are summarized in *Table 4*. Within a given series, the tensile properties were comFigure 6-Comparison of the DMA properties of Hybrids B and Bsr-



parable. As expected the A-series, having the lower  $T_g$  acrylic polymers, had lower tensile strengths and moduli but higher tensile elongations. The A-series polymers showed a relatively good balance of properties with high elongations (> 230%) and moderate tensile strengths.

### Coating Performance: B-Series Hybrids

The performance of Hybrids B and B<sub>SF</sub> was evaluated and compared using chemical spot tests; the results of which are provided in *Table 5*. Both hybrids showed comparable performance, as the spot test resistance was relatively good for both systems. Of the chemicals studied, isopropyl alcohol (JPA) showed the most effect on the coatings, and this could be a potential area for improvement.

#### Coating Performance: A-Series Hybrids

In *Table* 6, the performance properties of the A-series hybrids in clear and pigmented coatings (*Appendix* B for 1 and 2) are compared and benchmarked versus commercial NMP-containing PUDs, an HPD, a PUD/acrylic blend, and an acrylic. Coating properties for the NMPfree Hybrid A<sub>sr</sub> were similar to those of Hybrid A. Dry

## Table 6—Clear and Pigmented Costing Performance Property Comparison

Property/Formulation	1	2	35	4-	5"	6'	7"	8×
Dry-hard time, mis	40	40	40	30	30	25	>60	60
60° yloss	75-80	34	53	NA	NA	74	31	81
Reverse impact, inlb	160	160	160	160	160	28	4	72
IPA* double rubs	83	50	182	25	25	83	200	4D
MEK* double ruhs	>200	>200	200	25	25	90	115	<10
1000 br QUV-B, AE	<2	<2**	<2	NA	NA	2	1	3.5

key: 1 = Hybrid A: 2 = Hybrid AS 1; 3, 4, and 5 = D2Ds; 5 HPD; 7 FUD/acg/re blond: 8 = acg/in. Formulation 3 was a pigmented white costing and 4 and 6 were clear costings acced on recommengerions from the respective sourcies. Formetations 6, 7, and 8 were commercially available pairly. See Appendix C for insterial identifications. \* TPA = isopropyl alenter; M-K = methyl ettyl ketore.

\*\* CUV-A.

time, gloss, reverse impact resistance, MEK tesistance, and UV resistance of the NMP-free Hybrid  $A_{33}$  compared favorably to Hybrid A and the benchmarked commercial materials. The IPA resistance was better for Hybrid  $A_{sr}$  than that for three of the other systems tested. Interestingly, the commercial paints had comparatively much lower impact resistance.

## Further Study

A potential area for improvement of the NMP-free hybrids is their IPA resistance. Crosslinking of the HPDs through their carboxylic acid groups is a potential way to improve their resistance properties. Indeed, the resistance properties of acid-functional polymers have been found to be improved when crosslinked with an epoxy-silane crosslinker, β-(3,4-epoxycyclohexyl)ethyltriethoxysilane (a cycloaliphatic epoxy-silane).16,19 Shelf-stable (at least six months) formulations using Hybrid A have been formulated.20 The use of epoxysilane and other crosslinkers to improve the performance properties of NMP-free hybrids needs to be examined. Another market need is for lower cost formulations. Acrylics are often blended into PUDs for that purpose, and should be evaluated in the NMP-free HPDs.

# SUMMARY AND CONCLUSIONS

Waterborne, high-performance, urethane-acrylic HPDs have been developed to offer cost/performance. advantages over standard 1K coating materials such as polyurethane dispersions (PUDs), acrylic emulsions, and blends thereof. These so-called Type 2 hybrid polymers provide many of the benefits (e.g., superior mechanical properties and chemical resistance) of PUDs but at an intermediate cost between PUDs and low-cost acrylics. The Type 2 hybrid has an IPN-like polymer structure which is characterized by a broad glass transition temperature range as measured by DMA. The IPNlike structure is the result of the chemical composition. of the material and, particularly, the process by which the urethane and acrylic are polymerized together as a homogenous mixture that is dispersed as colloidal particles in water. The IPN-like morphology is apparently. responsible for the hybrid's outstanding properties, which would not be predicted from a simple, arithmetic rule of mixtures. New NMP-free HPDs have been developed to meet the market needs for lower odor products that comply with increasingly stringent regulations. The NMP-free HPDs have been shown to provide dispersion and coating properties comparable to their NMP-containing counterparts. Due to their lack of NMP and low residual monomer contents, both NMPfree HPDs were observed to have reduced odor, which

is obviously desirable from a health and safety perspective. In addition, the lack of NMP offers potential regulatory benefits (e.g., California Proposition 65). Because the performance of the HPD systems was found to compare favorably with other polymer systems (PUDs, HPD, and acrylic) evaluated, the possibility exists to replace or partially replace those types of polymers with HPDs.

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# Appendix A—Clear Coating Formulations and Formulation Properties.

(See Appendix C for list of materials and suppliers as indicated by superscripts.)

## Table A1—Clear Coating Formulation for Hybrid A

Material	Weight %
Pre-Mix: Mix a solution of the following Solvent <sup>e</sup>	5.98 0.40 0.21
Resin Blend: Add to the following with agitation Hybrid A <sup>a</sup>	79.76
Letdown: Dilute to brush and roll viscosity Water	13.65

#### Table A2—Clear Coating Formulation for Hybrid B

Material	Weight %
Pre-Mix: Mix a solution of the following Solvent <sup>e</sup>	11.93 0.40 0.21
<b>Resin Blend:</b> Add to the following with agitation Hybrid B <sup>b</sup>	79.51
Letdown: Dilute to brush and roll viscosity Water	7.95 100.00

### Table A3—Clear Coating Formulation for Hybrid Acc

Material	Weight %
Pre-Mix: Mix a solution of the following	
Solvent <sup>e</sup>	2.15
Solvent <sup>h</sup>	5.49
Solvent <sup>i</sup>	1.93
Surfactant <sup>f</sup>	0.05
Defoamer <sup>j</sup>	0.10
Resin Blend: Add to the following with agitation	
Hybrid A <sub>se</sub> <sup>c</sup>	90.28
Total	100.00

#### Table A4—Clear Coating Formulation for Hybrid B<sub>cc</sub>

Weight %
. 4.13
. 5.27
. 3.71
. 0.05
0.10

#### Resin Blend: Add to the following with agitation

Hybrid	$B_{SF}^{d}$	-	-	6		a	,		,	4	-	-			-	-	*	•	,	•		4	*	•	٤	R	86.74
Total			-					•			-	-				-										1	00.00

# Appendix B—Pigmented Coating Formulations and Formulation Properties.

(See Appendix C for list of materials and suppliers as indicated by superscripts)

Table B1—Pigmented Coating Prepared from Hybrid A (Formulation 1 in Table 5)				
Material			Gal	
Resin-Free Grind: Mi Water (deionized Pigment disperse Defoamer <sup>o</sup>	* the falls ) nL <sup>v</sup>	wing under mild agitation	until dissolved 	
Continue agitation и TiD <sub>2</sub> pigment <sup>1</sup>	inile eddî.	ng the pigment below	22.85	
Increase ≤peed to hi Do not excend 140°	gh and di F	sparse to Hegman $\ge$ 7 grim	n'.	
Reduce speed and an Water (defonized	ld the fol )	lowing with medium agitati	ion until blendea • • • • • • 2.03	
Blend: Mix the follow	ving in a	separate container until bli	ended	
Hybrid A <sup>a</sup>				
Pre-biend the next f strong agitation Surfactant <sup>1</sup> Solvent <sup>4</sup> Defoamer <sup>2</sup>	our ilems	before adding to the Hybri	d A with 0.13 1.67 1.50 0.03	
Final Blend: Slowly 2 mild agitation until Total	idd the re homogane	sin-free grind to the blend cous	and mix with	
Weight sorids, % Volume solids, % Viscosity, r.P	52.4 41.2 500	PVC, % VOC, .5/gal (g/l) Density, lb/gal (g/ml)	17.1 1.66 (199) 10.3 (1.23)	

Note: Properties reported are based on theoretical calculations.

īable B2—	-Pigmented	Coating	Prepared	from	Hybrid	A <sub>SF</sub>
	(formu	lation 2	in Table 6	)		

Material		We		
Resin-Free Grind: Mi Water (deionized Pigment dispersa Defoamer <sup>i</sup>	x the fo∬n  ) ant <sup>x</sup>	wing under mild agitati	on until dissolved 2.15 2.55 	
Continue agitation ( TiO <sub>p</sub> p <sup>i</sup> gment <sup>1</sup>	vinilə əddi)	ng the pigment below	21.24	
Increase speed to hi Do not exceed 140'	igh and di F	sperse to He <u>o</u> man≥ 7 g	rind.	
Reduce speed and an Water (defonized	dd the foll  )	iowing with medium agi	tation until blended	
Blend: Mix the follo	wing in a .	separate container until	blended	
Hybrid A <sub>SF</sub>				
Pre-blend the next i strong agitation Surfactant <sup>n</sup> Solvent <sup>h</sup> Solvent <sup>i</sup> Defuamer <sup>1</sup>	īve items .	before adding to the Hy	brid A <sub>SF</sub> with 0.06 	
Final Blend: Slowly a mild agitation until	add the ro homogene	sin-free grind to the blo pous	nd and mix with	
īotal			100.00	
Weight sulids, %	48.5	VOC, (b/gat (g/l)	1.65 (184)	

Note: Properties reported are based on theoretical calculations.

36.9

17.4

Density, lb/gal (g/ml) 10.1 (1.21)

# Appendix C---List of Materials and Suppliers.

Superscript Material	5upplier	Superscript	Material	Supplier
<ul> <li>a, Hybridur* 570 pulymer dispersion</li> <li>b, Hybridur* 580 polymer dispersion</li> <li>c, Hybridur* 870EV polymer dispersion</li> <li>d, Hybridur* 878 polymer dispersion</li> <li>e, Arcosolv* DPNB</li> <li>f, BYK*-346</li> <li>g, Surfynol* 0F-58 detoamer</li> <li>h, fexanol* ester acohoi</li> <li>j, BYK*-024</li> <li>k, Disperbyk*-190</li> <li>t, FI-Pure* R706</li> </ul>	Air Products Air Products Air Products Lyonder! BYK-Chemie Air Products Dow Cheminal Eastman: BYK Chemie BYK-Chemie BYK-Chemie DuPort	nDow oDee pEnvi qEnvi sNeol tWitz uWitz wPola xRast mair	anol <sup>®</sup> DPnB FO <sup>G</sup> PI-4 roGem <sup>®</sup> AE01 roGem <sup>®</sup> AE02 roGem <sup>®</sup> AE03 Rer <sup>®</sup> R960 subond <sup>©</sup> W-236 o white industrial coating Pac <sup>®</sup> R900D me <sup>®</sup> 700T -0 Lastic Gloss Acrylic (DTM) itenance finish	Dow Chemical Ultra Additives Air Products Air Products Air Products NenResins Bniroyal Chemical Wilko Paint NeoResins Shetwin Willfams MAB Paints

Volume solids, %

2VC. %