Aqueous Acrylic-Polyurethane Hybrid Dispersions and Their Use in Industrial Coatings

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Acrylic and polyurethane aqueous dispersions have been used extensively in coating applications, both independently and as physical blends. The resulting coatings display a balance of properties from the inherent characteristics of acrylics and polyurethanes. Nonetheless, these properties often fall short of those predicted from the traditional "rule of mixtures." In contrast, a process has been developed whereby acrylic monomers and urethane prepolymers are intimately mixed and mutually polymerized in an aqueous dispersion, thereby resulting in "hybrid" polymer dispersions. This process causes an interpentrating network (IPN) of the polymers which subsequently display unique properties compared to standard acrylic, polyurethane, or macroscopically blended acrylic/urethane dispersions. These properties appear to be directly attributable to the acrylic-polyurethane hybrid morphology.

INTRODUCTION

Over the past decade and probably into the next century, the coatings industry will have experienced a revolutionary period of technological change. A major contributor to this surge is increasing concern for health, safety, and the environment. Just as the industrial revolution of the 1800s was caused in part by the need for improved production and manufacturing techniques for a growing population, the recent advances in coatings technology have been "pulled" by the need for less hazardous and non-toxic materials. Reducing volatile organic compounds (VOCs) in paints and coatings is of particular interest due to their adverse effects on the environment. Nonetheless, the performance attributes of traditional solvent-based coatings, which in many cases were more than adequate, are still desired. In order to meet this demand of lower VOCs with acceptable performance, research and development of low VOC coatings, especially waterborne, high-solids, and powder, has escalated dramatically. This paper discusses an improvement in waterborne coatings technology through the development and application of acrylic-polyurethane hybrid dispersions. Unlike simple physical blends which have distinct acrylic and polyurethane domains, the hybrids form an interpenetrating network (IPN) of acrylic and urethane polymer chains at the molecular level. As will be discussed in the following, this approach offers unique advantages to the coatings formulator and applicator.

BACKGROUND

Two of the most popular vehicles for water-based coating systems are acrylic and polyurethane dispersions.[1-5] Since the introduction of acrylic polymers in the 1950s, they have been widely used as binders in interior and exterior architectural coatings. Yet their use in industrial applications, which are more demanding, was limited due to their relatively poor chemical resistance and mechanical properties compared to high performance solvent-based coatings. This limitation has changed over the past 10 to 20 years mainly because of the combined improvements in polymer synthesis and coating formulation. The addition of co-solvents which perform as coalescing aids has allowed the use of higher molecular weight acrylics (MW > 10^6), which are stronger, harder, and less permeable than earlier versions. Unlike solvent-based systems, waterborne latex vehicles allow these higher molecular weight polymers to be used without adverse viscosity effects. In addition, surfactants and defoamers are being utilized which enhance pigment dispersion and stability; allow good application, flow, and leveling; and improve opacity, gloss, and color.[6]

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Table 1—Comparison of Acrylic and Polyurethane Dispersion Properties[9]

Acrylic	Urethane
Advantages	
Non-yellowing	Solvent resistance
Outdoor resistant	Mechanical stability
Broad adhesion characteristics	Film forming properties
Compatibility with other ingredients	Gloss
Pigmentability	Less thermoplastic
Shear stability	Elongation/tensile strength
Thickener response	Wide scope for variations of composition and properties
Relative low price	Toughness
Disadvantages	
Thermoplasticity	Cost
Film formation	Limited outdoor durability
Coalescence/plasticizers	pH stability
Mechanical properties	Presence of NMP/MEK/TEA
Chemical resistance	Adhesion
	Compatibility

These improvements have allowed formulators of industrial coatings to take advantage of the positive attributes of acrylic resins: good weathering properties, well understood structure-property relationships, and relatively low cost.

In the mid-1970s, aqueous polyurethane dispersions (PUDs) were considered exotic and their use was sparse. Since that time, both technological advancements and environmental issues have caused their commercial application to become widespread. This is especially true in some industrial applications which were previously dominated by solvent-based counterparts. Early polyurethane dispersions were relatively unstable and experienced film formation problems. They required external surfactant additives for dispersion stabilization and substrate wetting. Unfortunately, these additives also rendered the resulting coatings susceptible to damage by water. As waterborne polyurethane technology evolved, this deficiency was addressed by incorporating stabilizing anionic, cationic, and non-ionic groups directly onto the polymer chain. Most commonly today, anionic stabilization is obtained by reacting carboxylic acid functionality directly onto the backbone. Generally, these waterborne polyurethanes are one-component, fully reacted thermoplastics. It recently has been confirmed that coatings from these waterborne dispersions display the same hard/soft domain morphology as their solvent-borne counterparts.[7,8] This morphology, along with the chemical structure of the polyurethane backbone, is greatly responsible for their unique and versatile properties. Therefore, it is not surprising that the waterborne versions can provide properties such as chemical, solvent, abrasion, and scratch resistance, as well as flexibility and toughness. However, these properties are obtained at the expense of increased cost. *Table* 1 provides a more thorough listing of advantages and disadvantages of both acrylic and polyurethane dispersions.

Table 2—Applications of Polyurethane/Acrylic Blends[9]

PVC ink and coatings
Wood flooring (gym, bowling)
Furniture lacquers
Parquet lacquers
Cork lacquers
Decorative paints
Automotive cosmetic black
Plastic and metal coatings
Industrial joinery
Floor polishes
Adhesives
Screen printing ink
Business machine coatings

In order to take advantage of the beneficial properties of each of these waterborne resins, it has become popular to physically mix them.[9] In many cases, this allows a compromise between the superior performance properties of the polyurethane and the lower cost of the acrylic. *Table* 2 is a partial listing of applications utilizing acrylic-polyurethane blends. Although some benefits have been obtained from this approach, properties of the resulting physical blends do not match up to expected values as predicted from the simple "rule of mixtures." For example, *Figure* 1 illustrates the tensile strength of 100% acrylic, 100% polyurethane, a 50/50 blend, and a 50/50 hybrid. From the arithmetic rule of mixtures,[10] one might expect the 50/50 blend to have a tensile strength residing on the line attaching the two pure materials (i.e., approximately 4200 psi). However, as illustrated by the graph, the actual strength of the blend is considerably less, ~2900 psi.[11] Similar effects have been observed with other mechanical and chemical resistance properties. The reasons for these types of undesired effects with blends have not been well defined but certainly the inhomogeneity caused by separate acrylic and polyurethane domains is a contributor. These areas may have excessive internal stresses and/or incomplete coalescence which will cause increased permeability and reduced cohesive strength.

An alternative approach to physically mixing acrylic and polyurethane dispersions is to form a dispersion of particles, each consisting of intimately entangled acrylic and polyurethane chains. This is accomplished by *in situ* polymerization of the respective monomers and prepolymers which have been previously mixed, thereby forming "hybrid" particles. The key to this process is that the polymerization mechanisms for these polymers are different; that is, polyurethane is formed by step growth polymerization and acrylic is formed by free radical, chain growth polymerization. A comparison of these respective processes is illustrated in *Figure* 2.

It should be noted that the hybrid process described is not designed to be co-polymerization where the acrylic and urethane segments are attached directly through primary bonds, nor is it a blend with large acrylic and polyurethane domains. This process appears to result in acrylic and polyurethane chains which are intimately mixed at the molecular level and presumably held together with numerous entanglements and secondary intermolecular bonding forces. However, it is possible that a minor extent of grafting between urethane and acrylic chains does occur, and this would increase the stability of the system. One benefit of this process is the increased tensile strength of the resulting materials as compared to its blended counterpart mentioned (*Figure* 1). In the case of the hybrid material, its tensile strength is approximately 5900 psi, well above that of the blend and the value predicted by the rule of mixtures. In fact, it is nearly as high as that of the 100% polyurethane. The effect of improved performance of hybrids over physical blends also is apparent with other properties such as toughness, durability, and chemical/solvent resistance. To investigate the use of these hybrid materials in coating applications, five commercially available aqueous dispersions were characterized and compared: an acrylic, a polyurethane, and three acrylic-polyurethane hybrids. In addition, one of the hybrids was formulated into a topcoat and evaluated along with a commercially available acrylic topcoat.

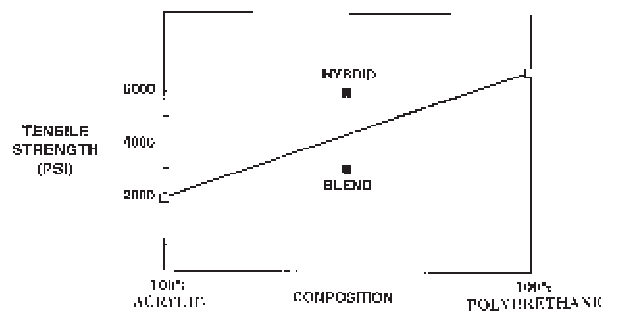

Figure 1—Performance of hybrid polymer.

EXPERIMENTAL

Materials

The acrylic, polyurethane, and hybrid dispersions evaluated in this study (*Table* 3) were designated AC1, PU1, H560, H570, and H580, respectively. The acrylic and polyurethane dispersions were prepared using the common commercial process. Details of the hybrid dispersion process are described in references 12 and 13. All five dispersions were evaluated as clear coatings without the use of co-solvents or additives. As an example of a formulated system, the H570 dispersion was used in a control topcoat formula (*Table* 4). The pigmented coating was prepared by first adding the surfactants to the hybrid dispersion in a one liter glass jar while under mild agitation. After 15 min, the defoamer was added and the mixture was agitated for an additional 15 min. The titanium dioxide was mixed into the dispersion which was then stirred for 15 min. At this time, the jar was filled half-way with five mm diameter glass shot. The jar was then sealed and placed on a paint shaker for 30 min, after which the coating was poured through a fine paint filter. An additive package containing ultraviolet absorber, light stabilizer, and carrier solvent was post added under mild agitation. The resulting paint had a Hegman fineness-of-grind (ASTM D 1210) greater than seven. This coating was compared to a commercially available waterborne acrylic topcoat.

Procedures

Unformulated (neat) dispersions, along with the pigmented topcoats, were applied to steel and aluminum

Table 3—Typical Properties of Aqueous Acrylic-Polyurethane Hybrid Dispersions

	H560	H570	H580	AC1	PU1
Appearance	Milky white	Milky white	Milky white	Milky white	Milky white
Viscosity					
Brookfield (cP)	100	50	37.5	25	26
Ford 4 (sec)	27	21	18	—	—
Nonvolatiles (% by weight)	42-44	42-44	42-44	50	30
Organic solvent content (% NMP)	6-8	6-8	6-8	0	—
Water content (%)	49-51	49-51	49-51	50	—
VOC as supplied					
g/L	150	150	150	0	—
lbs/gal	1.3	1.3	1.3	0	—
Dispersion density					
g/ml	1.0	1.0	1.1	1.1	1.1
lbs/gal	8.6	8.6	8.7	8.7	8.9
Bulking value (gal/lbs)	0.116	0.116	0.115	0.115	0.112
pH	7.5-8.5	7.5-8.5	7.5-8.5	9.0	8.0
Refractive index (of polymer film)	1.53	1.49	1.50	—	—
Particle charge	Anionic	Anionic	Anionic	—	Anionic
Particle size	Colloidal	Colloidal	Colloida	Colloidal	Colloidal

Table 4—White Topcoat Composition and Formulation Parameters

Component	% by Weight	Supplier
Hybridur 570	74.23	Air Products
Surfynol 465	0.23	Air Products
Aerosol OT-75 surfactant	0.23	American Cyanamid
Foamaster VF	0.31	Henkel
Titanium dioxide, R960	21.90	DuPont
Texanol	1.85	Eastman
Tinuvin 384	0.50	Ciba Geigy
Tinuvin 292	0.75	Ciba Geigy

Formulation Parameters

Density	1.24g/ml
VOC	<165 g/L
Pigment volume concentration	15%
Weight percent solids	54.5%
Volume percent solids	45.6%
Viscosity	
Brookfield	163 cps
Ford 4	24 sec
pH	8.5

Table 5—Coating Test Procedures

Property	Procedure
Storage stability (pigment setting)	ASTM D 869
60° gloss	ASTM D 523
Color	ASTM D 2244
Contrast ratio	ASTM D 2805
Adhesion	
Tape adhesion	ASTM D 3359
Scrape adhesion	ASTM D 2197
Impact and flexibility	
Gardner impact	ASTM D 2784
G.E. impact	Federal Test Method 6226 in Federal Standard 141B
Mandrel bend	ASTM D 1737
Hardness	
Pencil	ASTM D 3363
Persoz pendulum	ASTM D 4366
Solvent resistance (double rub)	ASTM D 4752
Xenon arc weatherometer	ASTM G26
QUV (UV-B & condensation)	ASTM G53

specimens to a dry film thickness of 50 ± 5 microns using conventional air spray. The steel panels were cold rolled 1020 steel with a zinc phosphate treatment (Bonderite 952) and a chromate sealer (Parkoline 60). The aluminum specimens were 2024-T3 with a chromate conversion coating (Alodine 1200), except for the aluminum impact and flexibility specimens which were 2024-0 temper with a chromic acid anodize treatment and hot water seal (military specification MIL-A-8625, Type I). The coatings were dried for 10 days at 21°C and 50% relative humidity prior to testing.

The applied coatings were characterized for optical, mechanical, and environmental exposure properties using the procedures listed in *Table* 5. In addition, liquid retains of the pigmented coatings were evaluated for pigment settling and storage stability under ambient conditions according to ASTM D 869.

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) were performed to characterize the thermal response properties of coatings from the acrylic-polyurethane dispersions. In order to eliminate water and organic solvent effects, unformulated samples of all three dispersions were prepared by allowing the samples to cure for 10 days at ambient conditions and subsequently placing them in a vacuum until a constant weight was obtained. A DuPont 2100 thermal analyzer was used for the TGA and DSC.

TGA was performed from room temperature to 600°C at a heating rate of 10°C/min. To look at the oxidation of the samples, they were run with both an air purge (100 cc/min) and nitrogen, respectively.

DSC was performed with nitrogen purging the cell (50 cc/min) and at a heating rate of 10°C/min from –100° to 200°C. In order to investigate potential morphological changes during heating, a sample of each material was subjected to this heating, quench cooled to –100°C, and reheated to 250°C.

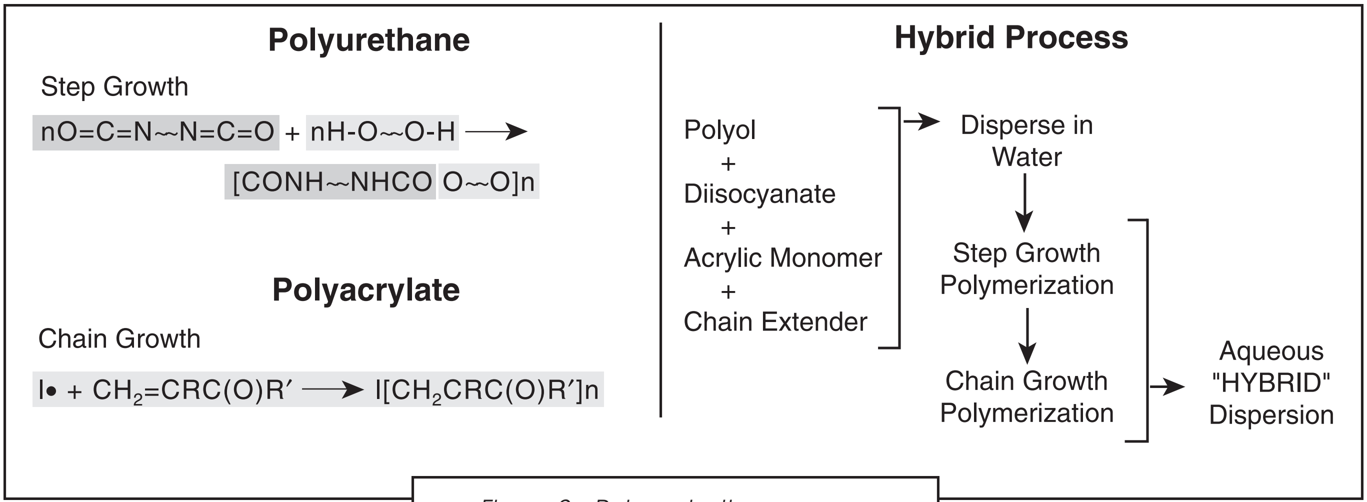

Figure 2—Polymerization processes.

DMA was performed in a tensile dynamic mode using a Rheometrics solids analyzer (RSA II) with a thin film fixture. The films were analyzed in a temperature range from –150° to 250°C. The samples were not preconditioned with regard to humidity prior to the acquisition of data. Data was obtained every 6°C. To ensure isothermal conditions, a one-minute temperature soak time was used. All measurements were made in a dry nitrogen atmosphere.

Coatings from the unpigmented hybrids and the TiO_2 pigmented version (*Table* 4) were inspected using scanning electron microscopy (SEM) and atomic force microscopy (AFM). AFM is a relatively new technique which allows three-dimensional imaging of a surface by using a "scanning probe" with a tip of molecular dimensions. More details on this technique are provided in references 14-16.

AFM was performed using a Digital Instruments Nanoscope III. The one cm square samples were mounted onto steel pucks with double stick tape. After cleaning with a gentle nitrogen purge to remove dust particles, samples were characterized in air. A 0.36 N/m cantilever was used, and a silicone nitride "oxide sharpened" probe tip from Digital Instruments was used to image the coatings. In the imaging experiments, forces of 50 to 80 nN were used. The AFM calibration technique is described in detail in reference 17.

SEM specimens were prepared by applying a one nm coating of platinum on the surface of the coating with an ion beam sputterer. The platinum coating was applied to help minimize electron beam damage to the specimen and also to enhance the secondary electron signal used to form the image. The samples were imaged at 2 kV accelerating voltage in a JEOL JSM-6300F field emission scanning electron microscope. Coating surface views were observed with the hybrid coatings on the metal substrate. Cross-sections were obtained by immersing free-standing films in liquid nitrogen, then quickly snapping the brittle film to produce a fracture surface.

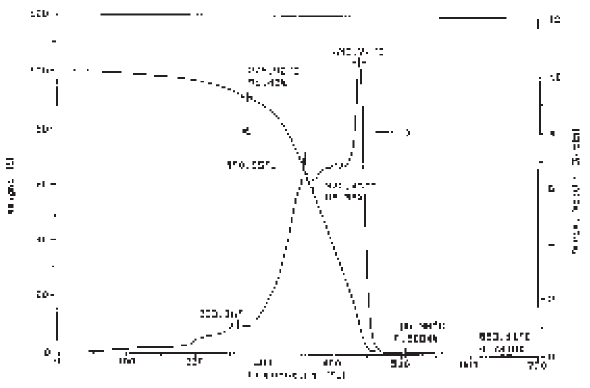

Figure 3—TGA response for H570.

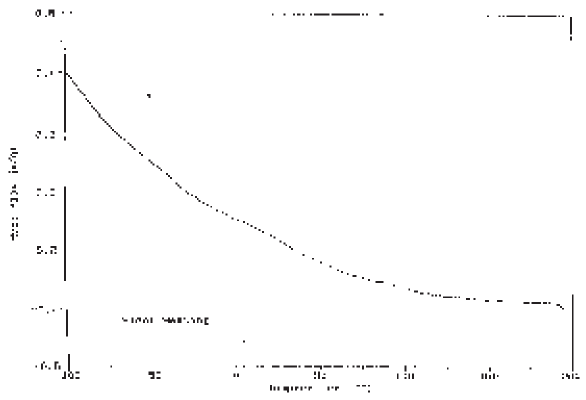

Figure 4—DSC response for H570 (first heating).

RESULTS AND DISCUSSION

Thermal Properties

In general, the thermal response of the H560, H570, and H580 hybrids had similar trends in both TGA and DSC. *Figures* 3 and 4 illustrate TGA and DSC results for H570. TGA response in both air and nitrogen (not shown) indicate good thermal stability with no appreciable weight loss until well above 200°C. As expected for this intimate mixture, the DSC curve (*Figure* 4) is stable (although the baseline does curve) with no clear indication of a distinct glass transition temperature. Taking this same DSC sample, quench cooling and reheating resulted in a similar DSC response. This quenching-reheating process was performed to determine if the first heating process caused substantial morphological changes such as segregation of the acrylic and polyurethane chains in the sample and the results indicate that this did not occur.

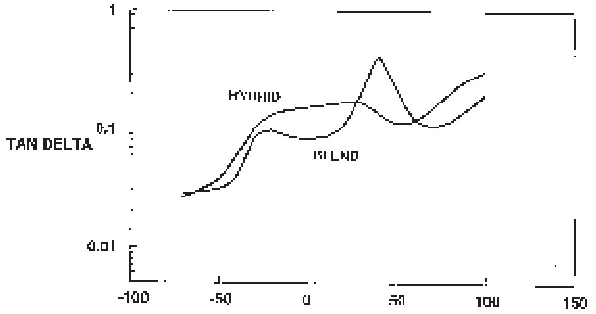

Figure 5—Dynamic mechanical spectroscopy of hybrid polymer.

Figure 5 illustrates the DMA response (tan δ) of the H570 hybrid compared to that of a 50/50 acrylic-poly-

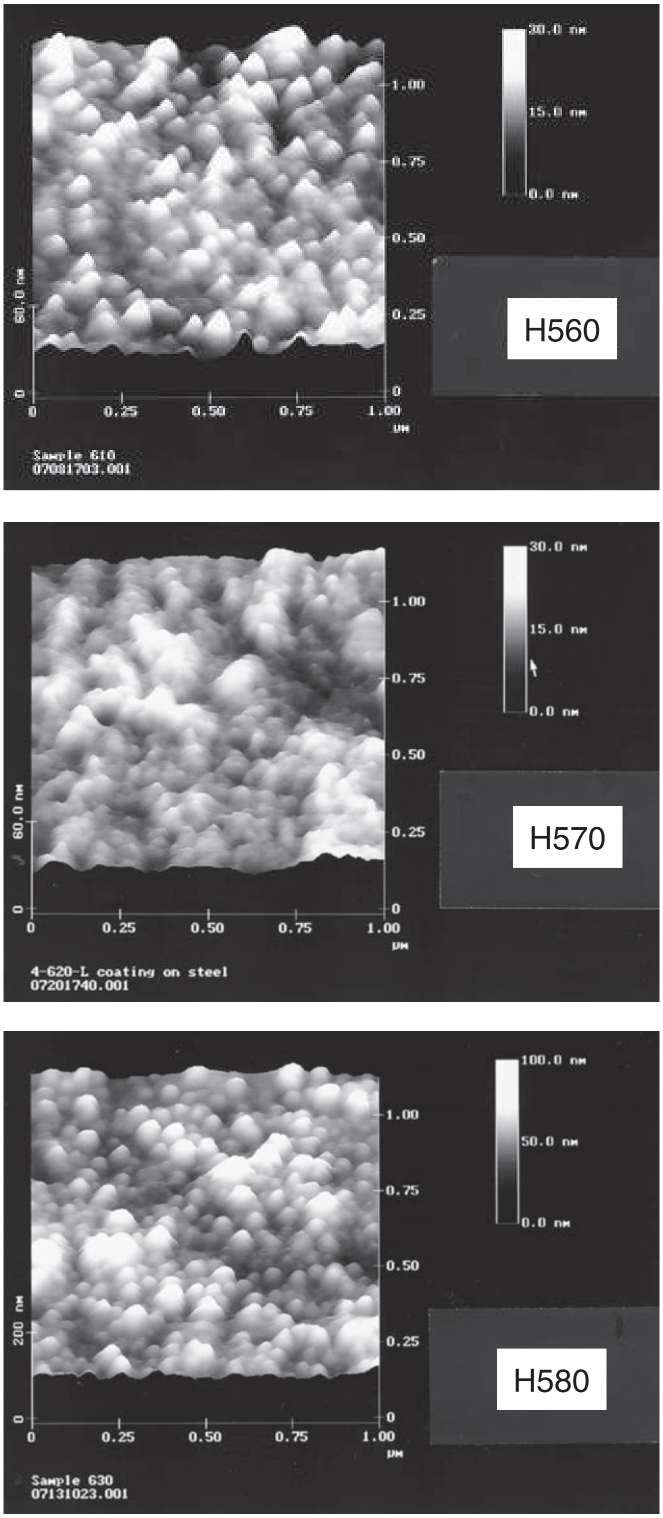

Figure 6—Atomic force microscopy (AFM) of unpigmented coatings.

urethane blend.[11] The physical blend clearly displays two glass transition peaks, indicating two distinct morphological domains, one for the polyurethane and another for the acrylic. In contrast, the hybrid displays one broad glass transition region from –20° to 35°C, and a storage modulus, E′, well above 10^9 dynes/cm^2. These DMA results are indicative of a more homogeneous and mechanically compatible material than a physical blend.

The broad glass transition range in both DSC and DMA, along with an understanding of the polymer synthesis and dispersion procedures, provides strong evidence that the acrylic and polyurethane chains are intimately entangled as opposed to a simple physical blend with larger acrylic-rich and polyurethane-rich domains. This effect with blends has been observed with numerous systems.[18] In addition, the fact that annealing the hybrid specimen caused no discernible changes according to DSC is also supporting evidence. Finally, the coating property data described later in this paper is consistent with this proposed morphology.

Surface Topography

Figures 6 and 7 illustrate a comparison of SEM and AFM images for all three unpigmented hybrid coatings. The main observation from these micrographs is the surface topography which consists of protrusions and depressions less than 100 nm in width. It would appear that the protrusions correlate with individual particles (diameter = 40 to 80 nm) which were dispersed in the aqueous medium prior to application and drying. Analysis of these micrographs indicates varying extents of coalescence (at ambient laboratory conditions, without coalescing aids): H570 > H560 > H580. In order to quantify this effect, average particle height, surface roughness, and surface area were determined from the AFM images (*Table* 6). It is clear from this data that H580 has higher protrusions and a rougher surface as associated with less complete coalescence. The H580 also had more protruding particles per coating surface area (particle density) than both H560 and H570. This is expected since H580 is formed from a harder acrylic polymer, and it typically requires co-solvent or higher temperature to aid coalescence and film formation. As will be illustrated in the presentation and discussion of coating properties, H560 and H570 displayed acceptable film formation. Since H580 is a harder material, addition of 5-10% co-solvent is recommended for improved coalescence and film formation.

Figure 8 is an SEM micrograph of the TiO_2 pigmented H570. The most important observation in this micrograph is that the titanium dioxide particles appear to be well dispersed with good pigment-binder interaction. No cracks are apparent in the matrix or at the matrix-pigment interface. A fracture surface cross-sectional view with SEM agrees with these results.

Clear Coating Properties

Film properties of the unformulated (clear) coatings are listed in *Table* 7. All five clear coatings were transparent and had a 60° gloss of over 90. These optical properties illustrate that all of the coatings had a high quality appearance, indicating homogeneity throughout the coatings and relatively good film formation. In contrast, coatings from many physical blends of polymers have a hazy or milky white appearance as a result of resin incompatibility and different refractive indexes between polymer domains.

Mechanical property results on both steel and aluminum substrates (*Table* 7) indicate that the hybrids have good adhesion and a wide range of flexibility and hardness. With all of the hybrid coatings, the tape test adhesion rating was a 5A (no removal) and the scrape adhesion value (the force required to scrape the coating from the surface) was ≥ 3 kg which typically is adequate for industrial coating applications. The Gardner indirect impact values were all greater than 160 in.-lbs, except for the H580 which was considerably less. Nonetheless, the G.E. impact and mandrel bend flexibility results on aluminum were all impressive, 60% elongation and 0.125 in. mandrel bend, respectively. These mechanical property results illustrate that H580 is harder but more brittle than both H560 and H570. This is understandable considering that the acrylic portion of the H580 is harder than that in H560 and H570. Comparing these results to those obtained for the acrylic (AC1) and polyurethane (PU1) dispersions, the results indicate that the acrylic is moderately hard yet it is very brittle as evidenced by low impact strength and elongation. The polyurethane coating has mechanical properties which are more comparable to those exhibited by the hybrid coatings; it is moderately hard with good impact flexibility. The scrape adhesion values for all of the coatings followed the trend:

$$\text{AC1} < \text{H560} \sim \text{H570} < \text{H580} < \text{PU1}$$

Interestingly, this is the trend that one might expect for film toughness, which is reasonable considering the mode of failure when attempting to scrape a coating from its substrate by using increasing loads (weights). A softer material will be easily gouged and the scraping stylus will cut through to the substrate, while a brittle material will crack and flake off the substrate. Traditionally, coatings with a balance of strength and flexibility (indicative of toughness) do well in this test.

The MEK and toluene solvent resistance of all three hybrid coatings was greater than 100 double rubs (*Table* 7). In fact, even at 200 double rubs, the only evidence of solvent effects was a decrease in gloss (slight marring) of the coatings' surfaces. In contrast, the solvent resistance of both the polyurethane and acrylic coatings was poor. Considering these results with respect to those for the hybrids, it may be somewhat surprising that the hybrids perform noticeably better in solvent resistance since one may expect that the solvent would attack the most susceptible polymer in the hybrid. However, as with mechanical properties, chemical resistance appears to undergo a synergistic effect with the hybrid process.

Pigmented Coating Properties

Results for the pigmented hybrid and acrylic coatings are provided in *Table* 8. The 60° gloss values were 64 for

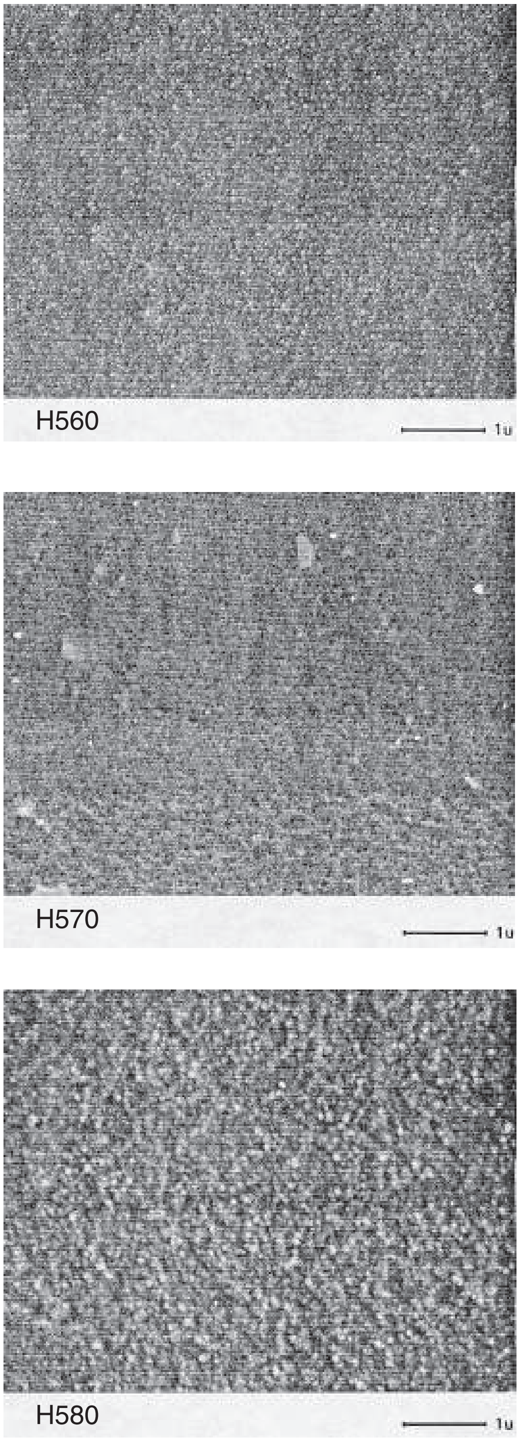

Figure 7—SEM micrographs of unpigmented coatings (x20,000).

Table 6—Summary of AFM Observations

	H560	H570	H580
Average particle height (nm)	10	11	28
Surface roughness	2.7	3.1	7.7
Surface area (%) (100%=flat)	104	103	116

the acrylic and 70-75 for the hybrid topcoats. These values are relatively low for a desired high-gloss finish; however, they are indicative of many waterborne topcoats which rarely have gloss values exceeding 80. It should be noted that pigmenting both the H570 and the acrylic resulted in a substantial reduction of gloss. Although it is well documented that waterborne coatings normally have poorer gloss than their solvent-borne counterparts due to wetting and leveling effects,[19] it was not clear from SEM and AFM why this occurred with the TiO_2 pigmented H570 coating. Braun recently illustrated that even nanometer-range roughness at the coating surface can dramatically decrease gloss.[20,21] It would seem likely that these effects are all interrelated and the cause for gloss reduction in these and other waterborne coatings. It should be noted that the hybrid formulation is considered a “suggested starting point formulation,” and it has not been optimized for optical properties. Addition of dispersing aids and use of a grade of titanium dioxide specifically designed for optimum gloss effects in aqueous systems may increase the 60° gloss properties of pigmented hybrid coatings to greater than 80.[22] These formulation optimization efforts currently are underway. Both pigmented coatings had a contrast ratio of > 0.90 and a whiteness index > 80 at a thickness of 50 microns, which is good considering the low titanium dioxide pigment volume concentration (15%) of the hybrid topcoat. (PVC of acrylic topcoat was unknown.)

Concerning mechanical properties of the pigmented coatings, the addition of titanium dioxide at the given concentrations appears to improve hardness without detrimental effects on toughness or flexibility. Although the pendulum hardness of the pigmented H570 is less than that of the clear H570, it is believed that this is simply due to a minor increase in surface friction from pigmentation. The scrape adhesion and pencil hardness of the pigmented material compared with that of the clear coating agree with this explanation. Comparing the hybrid and acrylic topcoats, the mechanical properties are somewhat comparable, both having moderate hardness and good flexibility. The improvement in flexibility of the acrylic topcoat over the clear acrylic may be due to the incorporation of plasticizers or co-solvents for better coalescence. However, the solvent resistance results are indicative of those obtained for the clear coatings with the hybrid clearly displaying better resistance properties than the acrylic.

The accelerated weatherability of the hybrid topcoat was tested by exposing specimens in both xenon arc weatherometer and QUV (UV-B bulbs and condensation) chambers for 1000 hr, respectively. Gloss, color, and G.E. impact were measured before and after the exposures. The retention of these properties is listed in *Table* 8. For both exposures, gloss retention was above 90% and color change (ΔE) was 0.9 and 1.6, respectively. The G.E. impact was 60% elongation prior to exposure in the Weatherometer and 40% after exposure. Since this is a step-function test (i.e., 10, 20, 40, and 60%), the retention of impact elongation is listed as between 67 and 100%. All of the optical, mechanical, and exposure results presented and discussed illustrate that the hybrid materials form moderately hard yet tough, flexible, adherent, weatherable, and solvent-resistant coatings.

Finally, a retain sample of the formulated white topcoat was kept at laboratory conditions and periodically

Table 7—Properties of Clear (Unpigmented) Coatings

	Unformulated Clear				
	H560	H570	H580	AC1	PU1
Properties over Steel					
60° gloss	>90	>90	>90	>90	>90
Drying time (min)					
Dry hard	<30	<30	<30	<30	<30
Tape adhesion (1-5, worst-best)	5	5	5	5	5
Scrape adhesion (Kg)	3	3	5	0.5	5.5
Gardner impact (in. lbs) (indirect)	≥160	≥160	36	60	≥160
Pencil hardness	2B	F	2H	F	B
Pendulum hardness (cycles)	157	165	225	113	103
Solvent resistance (double rubs)					
MEK	>100	>100	>100	<25	<75
Toluene	>100	>100	>100	<25	–100
Properties over Aluminum					
Tape adhesion	5	5	5	5	0
Scrape adhesion (Kg)	3	3	3	1.5	2.5
G.E. impact (% elongation)	≥60	≥60	≥60	0.5	≥60
Mandrel bend (in)	≤0.125	≤0.125	≤0.125	≤0.125	≤0.125

VOC of all coatings ≤165 g/L (1.3 lbs/gal).
Dry film thickness = 50 ± 5 microns.

evaluated for storage stability and especially pigment setting according to ASTM D 869. Ten months after milling, the wet coating was homogeneous with no significant pigment setting or hard compaction, an ASTM D 869 rating of eight. This result also provides evidence of good pigment-vehicle interaction. In many cases, waterborne coatings require a dispersing aid to obtain this type of interaction and acceptable pigment dispersion stability. The coating property results illustrate that the acrylic-polyurethane hybrid dispersions offer unique advantages in the formulation of industrial coatings.

Table 8—Properties of TiO_2 Pigmented Topcoats

	Hybrid	Acrylic
Properties over Steel		
60° gloss	>70	64
Drying time (min)		
Set-to-touch	15	15
Tack free	20	20
Dry hard	30	30
Contrast ratio	>0.90	>0.90
Tape adhesion (1-5, worst-best)	5	5
Scrape adhesion (Kg)	4	2.5
Gardner impact (in. lbs) (indirect)	≥160	≥160
Pencil hardness	H	H
Pendulum hardness (cycles)	140	194
Solvent resistance (double rubs)		
MEK	>100	<25
Toulene	>100	<25
Properties over Aluminum		
Tape adhesion	5	5
Scrape adhesion	3	<2
G.E. impact (% elongation)	≥60	≥60
Mandrel bend (in)	≤0.125	≤0.125
Xenon arc		
Gloss retention (%)	94.1	—
Color change (ΔE)	0.9	—
G.E. impact retention (%)	67-100	—
QUV		
Gloss retention (%)	92.1	—
Color change (ΔE)	1.6	—

SUMMARY AND CONCLUSIONS

Acrylic and polyurethane aqueous dispersions have been used extensively in coatings applications, both providing respective advantages and disadvantages. Generally, the acrylics have moderate properties and are less expensive, while polyurethanes provide better performance properties at a significantly higher cost. Physical blends of acrylics and urethanes have been used to obtain a cost-performance compromise; however, the properties of these blends normally are less than those predicted from the rule of mixtures.

In order to obtain a cost/performance advantage, aqueous acrylic-polyurethane hybrid dispersions have been developed by mixing urethane prepolymers and acrylic monomers, dispersing the mixture in water, and mutually polymerizing the prepolymers and monomers, respectively. This *in situ* polymerization results in a colloidal dispersion of individual particles containing acrylic and polyurethane polymer chains which are intimately entangled. This molecular level mixing is demonstrated by broad glass transition ranges (> 50°C) which are indicative of an interpenetrating network of acrylic and polyurethane polymer chains as opposed to larger individual acrylic- and polyurethane-rich domains.

Coatings from the unpigmented dispersions formed transparent films with good adhesion, flexibility, and hardness. Impact flexibility ranged from 36 to 160 in.-lbs while pencil hardness ranged from 2B to 2H. In general, the flexibility trend was H560 ~ H570 > H580, while coating hardness had the reverse trend. All three coatings displayed fairly good solvent resistance by withstanding 100 double rubs with MEK and toluene, respectively. The titanium dioxide pigmented H570 was harder than the unpigmented version (H vs. F) while still being flexible and tough (> 160 in.-lbs reverse impact). At 2 mils dry film thickness, it had a contrast ratio of greater than 0.90. Finally, 10 months after milling, a retain of this pigmented version had no pigment compacting. Extended exposure studies of these coatings are underway. From the data obtained, the acrylic-polyurethane hybrid dispersions provide the coatings formulator with an attractive alternative in the development of waterborne coatings for industrial applications.

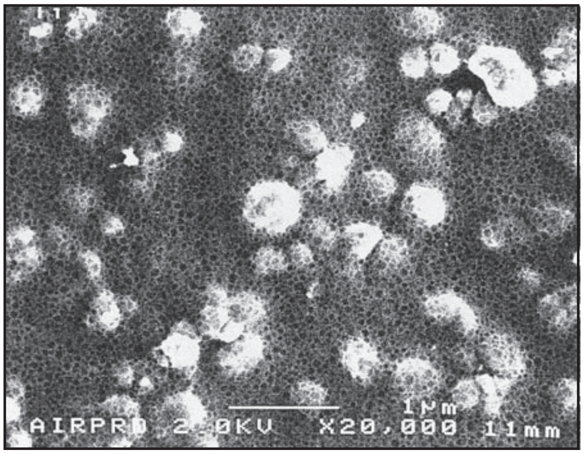

Figure 8—Scanning electron micrograph of titanium dioxide pigmented H570 (x20,000).

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