NOVEL ACRYLIC PARTICLE TECHNOLOGY FOR HIGH PERFORMANCE LEATHER FINISHING

by

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Abstract

The Dow Chemical Company has developed a novel acrylic technology for use in leather finishing formulations. Products making use of this unique technology can deliver low gloss finishes with high optical clarity, soft-touch aesthetics and high physical performance. The key enabler in this technology is an acrylic particle that offers comparable gloss, "jetness" and performance properties to many commercially available inorganic and organic dulling materials. The technology is inherently solvent free, and is compatible with existing acrylic and polyurethane resin components as well as conventional cross-linking chemistries.

Resumen

The Dow Chemical Company ha desarrollado una nueva tecnología de acrílicos para su uso en formulaciones de acabados de cueros. Los productos que hacen uso de esta tecnología única pueden ofrecer acabados de bajo brillo con alta claridad óptica, suave al tacto y altos valores físicos. El elemento clave en esta tecnología es una partícula de acrílico que ofrece un brillo comparable, negros muy intensos, y altas propiedades a varios materiales mateantes orgánicos e inorgánicos disponibles en el mercado. La tecnología es inherentemente libre de solventes, y es compatible con componentes resínicos acrílicos y poliuretanicos como así con la química convencional de reticulantes.

Introduction

Dow Leather Solutions has a well-established history of delivering new acrylic, polyurethane, and silicone chemistries into the leather industry. The range of these technologies covers both wetend and finishing segments. In the wetend segment acrylic polymers are used to provide softening, light-fastness and strength to the crust.[1-4] In the finishing segment acrylic emulsions, polyurethane dispersions, and silicones are used for a myriad of application stages including fleshcoating, impregnation, and as components in basecoat and topcoat formulations. While there are several key chemistries common to both wetend and finishing, Dow Leather Solutions offers the broadest spectrum of complementary chemistries in finishing and on this basis a further description is provided. As a class of binders, acrylics are used for exceptional print, cut-through resistance, flexibility, soft feel, aesthetic value and resistance properties.[5] As a class of binders, polyurethane dispersions offer many of the same properties but with much higher toughness and durability. Silicones in general are added for abrasion endurance and feel. Overall these chemistries when combined can result in systems for most end uses in leather finishing.

The subject of this paper naturally refines the finishing segment to topcoat and more specifically to automotive upholstery topcoat though art describing similar technology pertaining to furniture upholstery topcoat has been previously presented.[6] Before describing the new technology being offered it is important to detail the composition of a topcoat designed for automotive upholstery. At this point it is critical to mention that even within one sub-segment of finishing (auto topcoat) there are many different needs and end use targets so the description provided accounts for only a general idea of the expected components and levels. A starting point formulation is provided in Table I.

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TABLE I
Automotive Topcoat Generic Description
Starting Point Formulation

Component	Amount
Water	Nominal to adjust for final total solids
Pigment (optional)	0 – 7%
Flow Control Agent	1 – 3%
Binder (PUD or Acrylic ~35% AI)	30 – 50%
Dulling Agent (~20% AI, binder free)	20 – 30%
Silicone Feel Additive (60% AI)	1 – 10%
Thickener	1 – 4%
Polyisocyanate Crosslinker (80% AI)	5 – 10%

The generic topcoat description details a relationship between the binder (PUD/Acrylic based), dulling agent and total formulation in which the sum of the binder and dulling agent components will nominally comprise approximately 60 – 70% of the total topcoat. This balance is critical to the final topcoat's aesthetics and overall performance characteristics. In addition, there is another ingredient that significantly contributes to film formation, aesthetics, and to some extent the final gloss, the polyisocyanate crosslinker.

Now that a basic understanding of an auto topcoat has been provided, focus on a particular component will help lead into a discussion of the applications properties and advantages of the present novel technology. The component of primary interest in this work is the dulling agent. The chemistry of dulling agents used in leather auto finishing has progressed over the years from featuring primarily an inorganic rich base (silica) moving towards an organically rich base (often referred to as polymeric dulling agents). The reason for this progression is ever more challenging performance requirements that necessitate step-change technology advancements, as the performance of older chemistries is inadequate to meet the new specifications. The contrast between inorganic and organic dulling agents is recognized in the industry[7] and summarized in Table II.

Inorganic dulling agents utililized for leather topcoat are generally recognized as brittle and porous, light scattering particles with high binder demand. An SEM micrograph of a typical inorganic dulling material is shown in Picture I. The friable nature of these particles is largely responsible for their poor burning performance. Conversely their porous structure enables them to interact strongly with the binder component thereby providing wear support. It is only at the coating surface where the unsupported particles are exposed to burnish testing, resulting in particle wear and resultant gloss increase. Within the film, these same particles act as reinforcing agents which is a function of their high surface area. Organic dulling agents, and more specifically, polyurethane particles are generally very soft (Table III) and able to trap incident light with minimal scattering. The softness of these particles is important, as their presence at the coating surface contributes to burnish resistance and conveys the soft-touch feel. Their low binder demand, resulting from their smooth surface morphology can lead to reduced wear but this can be offset by strategic selection of complementary topcoat binders.

Summary of the New Acrylic Topcoat Technology

Dow Leather Solutions has developed an acrylic particle that has found use in leather finishing in several segments including furniture and automotive topcoat. The particle itself was designed to be comparable to existing urethane chemistries in many ways such as Tg, particle size and particle size distribution (Table IV), morphology (Picture II) and for application properties such as gloss reduction, jetness, and soft-touch. In addition to targeting the aforementioned characteristics and performance features, another part of the design was to improve upon existing chemistries through an advantaged cost position and resistance properties inherent to acrylics; namely thermal and hydrolytic resistance, and UV stability.

TABLE II
Contrast between inorganic and organic Dulling Agents

Performance Attribute – Testing details follow	Inorganic Dulling Agent	Organic Dulling Agent
Gloss Reduction	Good but can become hazy at very low gloss levels (below 1.2)	Excellent can achieve gloss values below 1.2
Jetness/color	Diminishing at higher loading due to light scattering	Excellent shows true color
Touch	Drier, influenced more by the continuous film former	Soft touch, very warm
Burnish Resistance	Prone to polishing	Polish resistant
Wear support	High surface area, Acts as a reinforcing agent	Low surface area, Requires higher performance from continuous film former

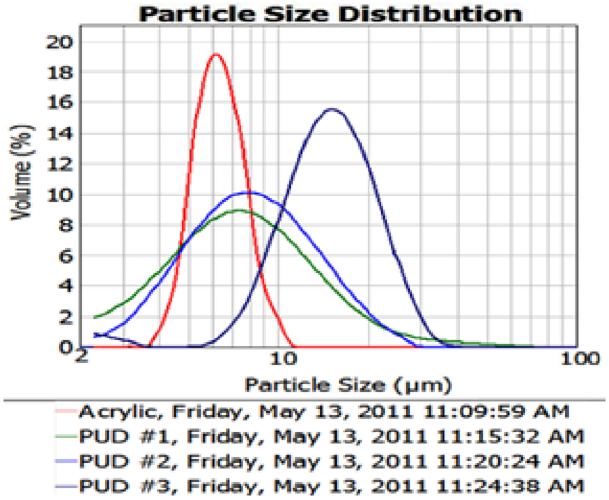
Gloss – Measured at 60° with a BYK-Gardner Micro-TriGlos (part# 5420)
Jetness/color – Measured using a spectrophotometer (X-rite USA model X-rite 8400, X-rite Color Master CM-2). Reflectance data captured using the spectral component included mode and under D65/10° observer conditions.
Touch – Primarily a side-by-side direct comparison, subjective.
Burnish Resistance – Measured with a Satra Footware Technology Center Model STM 421, 11.5 x 3.5 cm swatch from the finished crust is rubbed with a dry 1.5cm^2 felt pad for 2000 cycles with 1kg load.
Wear support – Can be measured in many ways, for example, Pilling, Wyzenbeek, Taber, and Gakushin wear tests.

TABLE III
Differential Scanning Calorimetry (Tg) for several organic dulling agents

Reference	Mid-point °C
New Acrylic Particle	-40
PUD #1	-62
PUD #2	-34
PUD #3	-21

Values measured on a DSC Q2000
Conditions:
- Preheat: 20°C/min, isothermal for 5 min, Equilibrate at-150°C, isothermal for 2 min
- Data: Ramp 20°C/min to 150°C

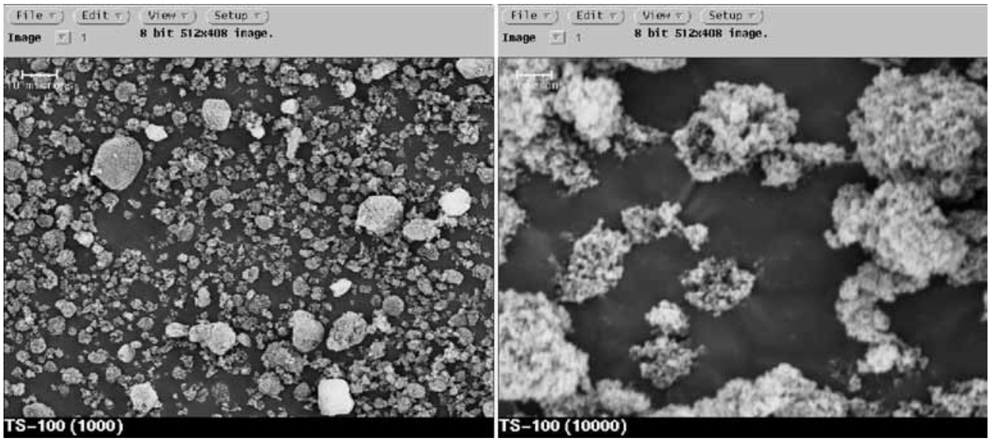
TABLE IV
Organic Dulling Agent Particle Size Distribution



	D(0.5)	d(0.9)
Acrylic	5.4	7.7
PUD #1	6.4	14.7
PUD #2	7.3	14.8
PUD #3	14.4	22.7

Details:
- Diameters in microns
- Malvern Mastersizer 2000 with 2000up Module

Picture I – Scanning Electron Micrograph



Fumed Silica

EXPERIMENTAL

Comparing Organic Particles

There are numerous urethane based particles in the leather industry, however, ascertaining the exact composition of a given material as supplied is challenging because most are formulated. To minimize the potential of making inconsistent comparisons, competitive materials studied in this experiment were sourced in a solid state at actives approaching 98% or higher. From the dry form, similar aqueous dispersions were made targeting 32.4% total solids to support all future trials.

To make a direct comparison for dulling efficiency, a combination of some common binders with polymeric dulling agents was needed to build the film required to measure gloss. A stable acrylic binder was selected and a blend of 50% bead on binder solids was prepared and applied to Lenata Card Form 1B at a 1.5 mil thickness via a bird applicator. The blends were carefully prepared and dried under the same conditions, 5 minutes at 185oF. The resultant gloss and delta L values can be found in Table V.

The L* value is the Black/White color space in the CIE L*a*b color system. An L* of 0 indicates complete blackness, whereas an L* of 100 indicates pure white. Delta L is the measured difference between the individual components and the reference. Measurement details are found in Table 2.

Finish Formulation and Crust Preparation

The effect of organic dulling components on the appearance, flex, and wear of automotive topcoats was studied. All testing was conducted on commercially available corrected grain crust. The undercoats used for this work are described in Table VI. The topcoats used are described in Table VII. Two different clear topcoats were tested, one based on an all acrylic continuous film former and another based on an all urethane continuous film former. The leather processing steps follow.

Process sequence:

- Basecoat spray application - coverage 4.0 – 5.0 dry grams/ft^2
- Dry 5 minute at 185°F, allowed to rest 6 hrs ambient
- Emboss with Honda Crunch Plate, 300 bar, 95°C, 5 second dwell
- Colorcoat spray application - coverage 1.2 – 1.5 dry grams/ft^2
- Dry 5 minutes at 185°F, rest overnight ambient
- Topcoat spray application - coverage 0.8 – 1.0 dry grams/ft^2
- Dry 5 minutes at 185°F

TABLE V
Gloss and Delta Values at Equal Bead Loading in Acrylic Latex

	Neat Binder	Acrylic	PUD #1	PUD #2	PUD #3
60° Gloss	80.1	1.3	1.5	1.6	1.1
Delta L Values	Reference	0.36	0.60	0.44	-.027

STD +/- 0.2 units. Testing details for gloss reference in Table II.

Picture II – Scanning Electron Micrographs

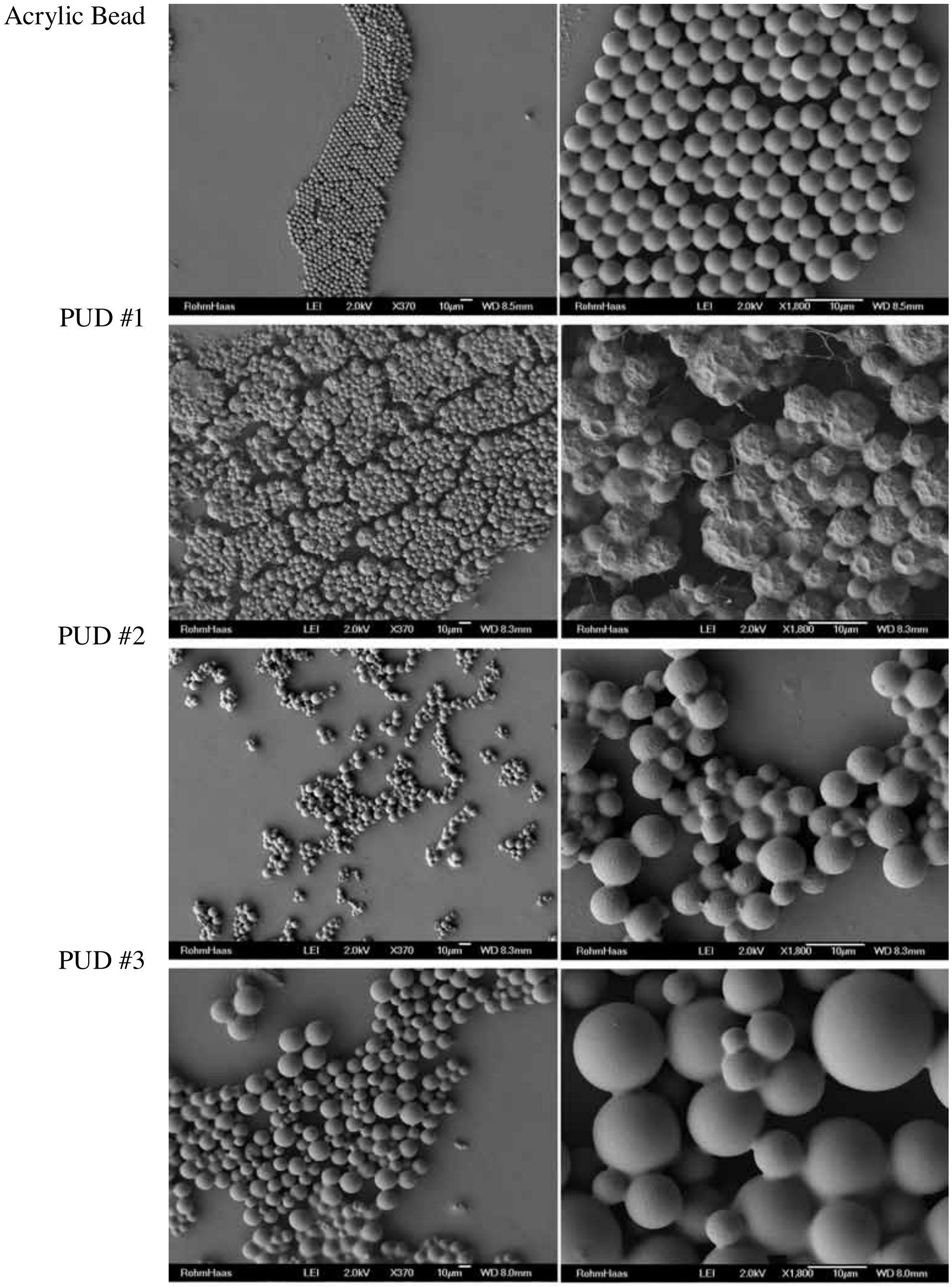


TABLE VI
Undercoat Formulations

Component	**Basecoat**	**Colorcoat**
	Weight in grams	
Water	120	90
Basecoat Acrylic 1	100	---
Basecoat Urethane Dispersion 1	250	100
Basecoat Urethane Dispersion 2	100	100
Unbound dulling agent	130	60
Softening Agent	100	50
Pigment (Black)	150	100
50% Polyisocyanate Crosslinker	30	30
Post added Thickener 1	20	20
Urethane Bound dulling agent	---	250
Topcoat Urethane Dispersion 1	---	50
Topcoat Acrylic 1	---	150
Total Solids	26.7%	23.2%
Zahn cup #2 viscosity	25+/- 2 seconds	

TABLE VII
Topcoat Formulation

Component	**Silica Based Acrylic Control Standard A**	**Samples B – E**	**Silica Based Urethane Control Standard F**	**Samples G – J**
	Weight in grams			
Water	185	185	205	205
Topcoat Acrylic 1	200	200	---	---
Topcoat Urethane Dispersion 1	---	---	200	200
Acrylic Bound Dulling Agent	430	320	---	---
Urethane Bound Dulling Agent	---	---	410	300
Flow Agent	10	10	10	10
Silicone Feel Agent	70	70	70	70
32.4% Organic Dulling Agent	---	**110**	---	**110**
80% Polyisocyanate Crosslinker	80	80	80	80
Post Added Thickener	25	25	25	25
Total	1000	1000	1000	1000
Total Topcoat Solids	30.0 %	31.0 %	29.9 %	30.9 %
Zahn cup #2 viscosity	25 +/- 2 seconds			

TABLE VIII
All Acrylic Application Properties

	A	B	C	D	E
	Appearance				
60° Gloss	1.5	1.4	1.4	1.3	1.2
Delta L/Delta E*	0.37/1.01	0.11/0.77	0.28/0.90	0.11/0.85	0.19/0.87
	Flexibility				
Bally 100k	Pass in duplicate	Pass in duplicate	Pass in duplicate	Pass in duplicate	Pass in duplicate
Cold Crack -10°C/30k	Good, crazing	Fair, trace micro cracking	Very Good, no crazing or micro cracks	Fair, trace micro cracking	Fair, trace micro cracking
	Wear				
Burnish**	2	3	3	3	2
Gakushin	All samples matched or exceed Control A				
Taber H-18	All Pass, no differentiation				
Taber CS-10	All Pass, no differentiation				

*Delta E was measured as described in Table 2 and is a color match measurement. The lower the value, the better the match. Values below 0.5 are considered to be a match. Delta E was measured using the unfinished Colorcoat as the reference.
**Burnish rating 1 = lowest rating with high degree of polishing, 5 = highest rating with low degree of polishing

These are typical properties, not to be construed as specifications.

TABLE IX
All Urethane Application Properties

	F	G	H	I	J
	Appearance				
60° Gloss	1.4	1.4	1.3	1.3	1.1
Delta L/Delta E*	0.69/1.00	0.58/0.82	0.69/0.93	0.37/0.71	0.20/0.59
	Flexibility				
Bally 100k	Pass in duplicate	Pass in duplicate	Pass in duplicate	Pass in duplicate	Pass in duplicate
Cold Crack					
-10°C/30k	Very Good no crazing or micro cracks	Good, trace crazing	Very Good, no crazing or micro cracks	Very Good, no crazing or micro cracks	Very Good, no crazing or micro cracks
	Wear				
Burnish**	2	5	4	5	3
Gakushin	All samples matched or exceed Control A				
Taber H-18	All Pass, no differentiation				
Taber CS-10	All Pass, no differentiation				

*Delta E was measured as described in Table 2 and is a color match measurement. The lower the value, the better the match. Values below 0.5 are considered to be a match. Delta E was measured using the unfinished Colorcoat as the reference.
**Burnish rating 1 = lowest rating with high degree of polishing, 5 = highest rating with low degree of polishing

These are typical properties, not to be construed as specifications.

Appearance

After the color coated crusts were finished and allowed to equilibrate for 48hrs, Gloss and Color measurements were made. The testing details for gloss were referenced in Table II. For the color comparisons, the colorcoat absent any topcoat was used as the reference. CIE L*a*b color system was used to objectively make comparisons.

Flexibility

The finished samples were subject to two types of Bally tests. For testing at ambient conditions a Bally flexometer (Otto Specht company model 2397) was used. For testing at low temperature (-10°C) conditions a Low Temp Flexometer (Giuliani model G6FN) was used.

Wear Performance

The finished samples were subjected to four types of wear testing. For burnishing, the details are found in Table II. For Gakushin, a Schap Model 200255 was used. It was equipped with No. 6 duck cloth, 1kg total head weight, and a stroke rate of 30 cycles/min. For the Taber abrasion test, Model 5150 Abrader was used equipped with either an H-18 or CS-10 wheels depending on the respective tests. For the H-18 test, the head weight was 0.5kg and the duration was 500 cycles. For the CS-10 test, the head weight was 1kg and the duration was 5000 cycles with resurfacing every 1000 cycles.

In addition to the application tests referenced previously, many tests exist that measure resistance properties including thermal, hydrolytic, and UV stability. When conducting these tests, it is often the case that the crust itself either will not pass or at a minimum imparts changes that significantly alter the measured or perceived performance of the coating. Separately, as mentioned earlier, topcoats can be formulated to target many different end-use requirements including resistance properties. To minimize the potential for crust or formulary

TABLE X
SAE J 1885 Weatherometer Exposure on Black Lenata Card Form 1B

60° Gloss

	Neat Binder	Acrylic	PUD #1	PUD #2	PUD #3
Initial	80.1	1.3	1.5	1.6	1.1
225kJ	73.7	1.6	5.0	16.9	10.9
488Kj	N/A*	1.9	9.5	15.6	5.6**

*The card for the neat binder degraded after 488 Kj.
**The film for PUD #3 significantly degraded leading to a low gloss reading.

Note: STD is +/-10%. Film prepared as described for Table V

TABLE XI
Various Resistance Tests on Clear Duralar 0.007 inch Sheeting

60° Gloss

Resistance Test	Neat Binder	Acrylic	PUD #1	PUD #2	PUD #3
Ambient	157.0	13.2	11.2	10.0	10.5
Thermal 7 days/70°C	129.0	11.7	11.1	9.8	10.2
Hydrolysis 70%RH/7days/70°C	148.0	13.2	10.9	9.4	10.2
SAE J 1885 225kJ Exposure	130.0	12.9	9.7	13.5	20.5
SAE J 1885 488Kj Exposure	147.0	13.5	10.7	20.9	18.4

Resistance Testing

Hydrolysis testing was carried out in a Hotpack environmental chamber at the conditions specified.
Weatherometer testing was carried out in a Ci65, type BH, Atlas Company testing chamber at the conditions specified.

related variables to confound the testing outcome, a simple approach was used to study resistance properties. As in the case of the very first gloss and Delta L assessment reported in Table V, a single binder known to be very stable to degradation of resistance properties was used to bind the various organic dulling agents at high loading (50% on binder) to an impervious substrate. The resulting system served as a carrier to enable rigorous thermal, hydrolytic, and UV testing to be conducted on the individual materials.

RESULTS AND DISCUSSION

In this systematic study, an acrylic based polymeric dulling agent was evaluated against commercially available urethane based comparatives. The logic of this approach was to benchmark performance of this new material as a neat particle and also within application tests typical to the Leather industry. For key performance properties, newly developed materials should be equal to or better than the commercially used materials.

In the introduction, several key physical characteristics were described. Features such as Tg, particle size and distribution, and morphology where offered. The Tg relates to softness which is a function of the soft touch property of the organic systems. All of the materials tested were fairly low in Tg yet low tack. In terms of particle size and distribution, a peak width comparison of the majority peak in all of the samples finds the acrylic based material sharpest suggesting that the distribution is over a narrower range than in all other instances. This is also apparent in the scanning electron micrographs. The acrylic based material is very uniform in distribution and very smooth on the surface. The surface smoothness, though not measured quantitatively, is apparent in the aesthetic feel of the topcoats. In the case of the urethane dulling agent with the largest particle size, PUD #3, the feel is possibly too waxy to be desirable.

Appearance

The appearance performance property is comprised of a gloss and a color component. Gloss was first compared in Table V, in which all of the samples were tested similarly and exhibit a comparable gloss. This is also true for the topcoat work that enabled comparisons in both all-acrylic (Table VIII) and all-urethane (Table IX) continuous binder systems. Although black was the only color tested, contrasting the Delta L and Delta E values suggested that the acrylic agent was a top performer in the all-acrylic system and also a good performer in the all-urethane system. It is important to note that the low gloss values attributed to PUD #3 in the urethane system correlated with feel that was possibly too waxy. In fact, the large particle size of this sample may cause particles to protrude excessively out of the film depending on the application. Particles in excess of 15 microns are beyond typical film thickness found in automotive topcoat finishes.

Flexibility

Two different tests were used to gauge flex performance, one was run at ambient temperature for 100,000 cycles and another was run at -10°C for 30,000 cycles. All of the systems passed flex testing. There were minor differences related to crazing or micro-cracks in the topcoat, but generally all samples were similarly rated as a pass.

Wear

There were four different wear tests conducted on the topcoat series. The first one, burnish, found the polymeric dulling agents as a group superior to silica as expected. It was also noted that the acrylic dulling agent exhibited a slight advantage in burnishing resistance in the all-urethane system. Regarding the Gakushin, Taber (H-18) and Taber (CS-10) tests, all the samples passed similarly, with performance at least matching the control standard which utilized silica as the sole matting agent.

Resistance

Applied to black Leneta card (Table X) all of the urethane-based dulling agents melted during weatherometer testing. This result was confirmed quantitatively through increases in 60° gloss, and qualitatively by touch, as it was noted that these same films became much tackier after exposure. This was not observed independently in either thermal or hydrolysis testing but was confirmed for PUD #2 and #3 on Duralar cards in Table XI.

OVERALL CONCLUSIONS

A new acrylic based dulling agent comparable to existing urethane-based dulling agents has been developed. Using this new technology, it has been shown that high performance automotive testing specifications can be met. A new class of chemistry for high performance finishing is now commercially available offering many of the same benefits as existing chemistries with the added benefit of improved weatherometer performance.

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