High Performance Acrylic Polymer Technology for Use in Leather Finishing Processes*

by

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Abstract

High performance topcoats designed for automotive and furniture upholstery are generally rich in polyurethane dispersion (PUD)-based binders. This binder technology has been used commercially for years because it offers a distinct combination of high abrasion resistance, flexibility, and tactile performance benefits. However, recent market trends place higher emphasis on performance properties that are challenging for these traditional finishing systems to achieve. Such properties include: dirt pick-up and dye transfer resistance, cleanability after soiling, as well as UV, hydrolytic, and thermal stability. Topcoats featuring acrylic-based binders are increasingly competitive due to intrinsic soiling resistance and stability properties; however, replacing more than approximately 25% of the polyurethane-based resin with acrylic-based resin can result in a noticeable loss in abrasion resistance or toughness.

The Dow Chemical Company has developed a novel acrylic binder technology designed to offer many of the same advantages of PUD binders, such as toughness, while retaining the enhanced soiling resistance and stability needed to address the stringent demands of today's market. This paper describes the performance properties attributed to this new binder technology through a systematic validation process.

Resumen

Tops de acabado de alto rendimiento diseñados para tapicería de automóviles y muebles son generalmente ricas en dispersión de poliuretano (PUD) a base de ligantes. Esta tecnología de ligantes se ha utilizado comercialmente durante años, ya que ofrece una combinación distintiva de alta resistencia a la abrasión, flexibilidad, y buen tacto. Sin embargo, las tendencias recientes del mercado ponen mayor énfasis en las propiedades de desempeño que son un reto a alcanzar por estos sistemas de acabado tradicionales. Tales propiedades incluyen: resistencia a la suciedad y a la transferencia de colorantes, facilidad de limpieza luego de ensuciarse, así como la estabilidad UV, hidrolítica y térmica. Los acabados de ligantes a base de acrílico son cada vez más competitivos debido a la resistencia intrínseca a la suciedad y sus propiedades de estabilidad; sin embargo, la sustitución de más de aproximadamente del 25% de la resina de poliuretano a base de resina de base acrílica puede resultar en una pérdida notable en la resistencia a la abrasión o tenacidad.

The Dow Chemical Company ha desarrollado una nueva tecnología de ligante acrílico diseñado para ofrecer muchas de las mismas ventajas de los ligantes PUD, tales como tenacidad, mientras que conserva una mejorada resistencia al ensuciamiento y estabilidad necesaria para hacer frente a las estrictas exigencias del mercado actual. Este artículo describe las propiedades de rendimiento atribuido a esta nueva tecnología de ligantes a través de un proceso de validación sistemática.

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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, lightfastness 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 a broad spectrum of complementary chemistries in finishing and on this basis a further description of these chemistries is provided. As a class of binders, acrylics are used for exceptional print, cut-through resistance, flexibility, soft feel, aesthetic value and resistance properties.[5-6] As a class of binders, polyurethane dispersions offer many of the same performance properties but with much higher toughness and durability. Silicones in general are added for abrasion resistance and feel. When properly combined, these chemistries can produce systems suitable for most end uses in leather finishing.

The subject matter of this paper applies to the topcoat segment of leather finishing and more specifically to the automotive upholstery topcoat segment, which is further divided into performance and anti-soiling topcoats. The performance topcoat realm is dominated by PUD binders while the anti-soiling topcoat is dominated by acrylic binders. However, both areas could benefit from higher performing acrylic binders. At this point, it is critical to mention that even within one sub-segment of finishing, whether the performance or anti-soiling area, there are many different needs and end use targets. For this reason, the descriptions provide only a general idea of the expected components and levels. Starting point formulations are provided in Tables I and II.

The generic automotive performance topcoat recipe displays a relationship between the binder(s) (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, which significantly contributes to film formation, aesthetics, and to some extent the final gloss, the polyisocyanate crosslinker.

The generic automotive anti-soiling topcoat recipe displays a relationship between the binder(s) (PUD/Acrylic-based), dulling agent and total formulation in which the sum of the binder (which is mostly acrylic) and dulling agent components will nominally comprise approximately 40 – 50% of the total topcoat. This is a much lower level than that utilized in the performance topcoat above. Additionally the polyisocyanate crosslinker content is lower because a product with lower isocyanate AI is chosen. This is done to introduce more water-miscible solvent into the formulation in order to enhance film formation. The balance of the formulation is made up of several different additives comprised primarily of fluoroalkyl acrylate. In the anti-soiling example, film formation is challenged because there is a high ratio of non-film former to film former. The negative effects of a low level of film forming binders are somewhat mitigated by the fact that a lower dry film add-on level is required (1.6g/ft^2 minimum for the performance topcoat, 0.5g/ft^2 minimum for the anti-soiling topcoat). While the anti-soiling topcoat must look and feel similar to the performance topcoat underneath, it is not required to pass all of the performance topcoat tests. Instead, the total system derives stain resistance and cleanability from the anti-soiling overspray, and other topcoat performance attributes from the conventional topcoat below.

Having established a basic understanding of automotive topcoats and the distinction between performance and anti-soiling coatings, a focus on a particular component, the binder,

TABLE I
Automotive Performance Topcoat Description

Component	Amount
Water	Nominal to adjust for final total solids
Pigment (optional)	0 – 7%
Flow Control Agent	1 – 3%
Binder (PUD and/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%

TABLE II
Automotive Anti-soiling Topcoat Description

Component	Amount
Water	Nominal to adjust for final total solids
Pigment (optional)	0 – 3%
Flow Control Agent	1 – 3%
Acrylic Bound Dulling Agent (~25% AI)	30 – 40%
Binder (PUD and/or Acrylic ~35% AI)	10 – 15%
Fluoroalkyl Acrylate Additive (~25% AI)	15 – 25%
Silicone Feel Additive (~50% AI)	5 – 10%
Silicone Feel Additive (~45% AI)	1 – 2%
Polyisocyanate Crosslinker (~50% AI)	5 – 10%

will help lead into a discussion of the applications properties and advantages of the present novel technology. The performance topcoat will be discussed first, followed by the anti-soiling topcoat. While the two topcoats are related in that they are both applied to light colored upholstery articles, with the anti-soiling topcoat applied on top of the performance topcoat, the composition and performance properties required differ significantly.

EXPERIMENTAL

Performance Topcoat

The performance topcoat binder component is generally very rich in polyurethane, sometimes contributing 100% of the binder. When present, acrylics have been limited to about 25% of the binder solids contribution. The high usage of polyurethane-based binder relates to the inherent toughness and flexibility properties attributed to this binder class. In comparison, traditional acrylic-based binders can be engineered to approximate polyurethane-based binders for toughness or flexibility but simultaneously achieving both is a technical challenge. Other properties attributed to polyurethane-based binders are low glass transition (T_g) values while maintaining low film tack at ambient to slightly elevated temperatures. In contrast, acrylic binders are generally high in Tg and low in film tack or the converse. Dow has developed a new class of acrylic-based binders that more closely approximate the performance characteristics ascribed to polyurethane-based binders and include a de-coupled relationship between T_g and film tack properties. The experiments that follow show performance topcoat applications data sets generated using these new acrylic binders.

Anti-soiling Topcoat

The binder component of the anti-soiling topcoat is generally very rich in acrylic due in part to the PUD binder's high affinity for the indigo dyes found in denim jeans. However, there are many different anti-soiling tests [7] and passing a majority of them requires not only an acrylic-rich coating but also a high level of silicone and/or fluro alkly acrylate additives. These components play a key role in anti-soiling performance but also add a significant cost burden. The primary driver for the present research is to develop a better acrylic for the performance topcoat while retaining or even improving acrylic anti-soiling performance. The performance of the novel acrylic technology in both performance and anti-soiling topcoats is presented below .

Summary of the New Acrylic Technology for the Performance Topcoat

Dow Leather Solutions has developed an acrylic-based binder technology that is designed for use in several leather finishing segments including high-end furniture and automotive. This binder technology is designed to be comparable to existing PUD binders in many ways, such as Tg (Table III), tack, gloss, rub fastness, flexibility, and wear. Though not part of the experimental design covered in this paper, properties inherent to acrylic chemistry such as thermal, hydrolytic, and UV resistance are within established expectations for the new binders described here, as well as a potential advantaged cost position when compared to PUDs.

MATERIALS AND METHODS

Finish and Formulations

The application properties of the new acrylic binders were studied in automotive performance topcoats. All testing was conducted on commercially available corrected grain crust. The undercoats used for this work are described in Table IV. The topcoats used are described in Table V. Two different topcoats were tested, one based on a single binder and another based on a 1:1 binder blend with 50% of the binder coming from a commercially supplied PUD-based bound dulling agent. The applications properties for the two performance topcoats can be found in Tables VI and VII, respectively. Additionally, application properties of the new acrylic binders were studied in

TABLE III
Differential Scanning Calorimetry (Tg) for several acrylic and PUD binders

Reference	Mid-point °C
Acrylic #1	-39
Acrylic #2	-43
Acrylic #3	-44
Acrylic #4	-47
PUD Polyester	-54
PUD Polyether/polycarbonate	-54

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
Undercoat Formulations

Component	Basecoat
Water	120
Flow Agent	10
Basecoat Acrylic 1	300
Basecoat Urethane Dispersion 1	100
Basecoat Urethane Dispersion 2	100
Unbound dulling agent	100
Softening Agent	100
Pigment	150
Post added Thickener 1	20
Total Solids	26.7%
Zahn cup #2 viscosity	25+/- 2 seconds

an automotive anti-soiling topcoat. The leather substrate used for this work is the same as described above. The overcoat was applied to the article labeled “Topcoat D” in Table VI. The topcoats used are described generically in Table II and the actual compositions differed only in the acrylic composition of the bound dulling agent. All other components were identical between comparison. The applications properties for the anti-soiling topcoat can be found in Table VIII. The leather processing steps are described below.

Process sequence:
- Basecoat #1 spray application - coverage 4.0 – 5.0 dry grams/ft^2
- Dry 5 minutes at 185°F, allow to rest 6 hrs at ambient conditions
- Emboss with Honda Crunch plate, 300 bar, 95°C, 5 second dwell
- Basecoat #2 spray application - coverage 1.2 – 1.5 dry grams/ft^2
- Dry 5 minutes at 185°F, rest overnight at ambient conditions
- Topcoat spray application 2x - coverage of each: 0.8 – 1.0 dry grams/ft^2
- Dry 5 minutes at 185°F
- For anti-soiling tests: topcoat spray application 1x - coverage 0.4 - 0.6 dry grams/ft^2
- Dry 5 minutes at 185°F

Tack – A side-by-side direct comparison, subjective.

Gloss – Measured at 60° with a BYK Gardner Micro-Tri-Gloss gloss meter (part# 5420)

TABLE V
Topcoat Formulations

	Single Binder	Dual Binder
	Weight in grams	
Water	145	165
Flow Agent	10	10
Pigment	---	30
Binder	400	200
Binder Free Dulling Agent	250	---
Polyester Bound Dulling Agent	---	400
Silicone Feel Agent	70	70
Post Added Thickener	25	25
80% Polyisocyanate	100	100
Total	1000	1000
Total Topcoat Solids	30.0%	30.0%
Zahn cup #2 Viscosity	25 +/- 2 seconds	

ΔL (Jetness) – 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. The ΔL value references 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. ΔL is the measured difference between the test sample and the control or reference sample.

TABLE VI
Single Binder Application Properties

Topcoat ID	A	B	C	D
Sole Binder	General Purpose Acrylic Fail Control	New Acrylic #1	New Acrylic #2	Polyester PUD Pass Control
	Tack			
Tack Ambient*	1.5	1.0	1.0	1.0
Tack Warm*	2.0	1.5	1.5	1.0
	Appearance			
60^o Gloss	1.6	1.7	1.4	1.5
ΔL (Jetness)	-0.41	0.02	0.26	Reference
	Flexibility			
Bally Ambient 100,000 cycles	Pass	Pass	Pass	Pass
Bally -10^{o}C 30,000 cycles	Pass	Fail	Fail	Pass
	Rub Fastness			
Dry Rubs (Burnish)	3.0	2.0	2.0	2.0
Wet Rubs	3.0	1.0	1.0	1.0
Alkaline Sweat Rubs	3.0	1.0	1.0	1.0
	Wear			
Gakushin***	1X	7.5X	3X	3X

*Tack rating 1 = good, very little to no tack, 5 = poor, film sticks to self face-to-face
**Rub rating 1 = good, very little change, 5 = poor, most change
***Gakushin rating 1X = cycles required to wear through the coating, 2X = twice as many cycles as 1X, Higher cycles means higher wear

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

Bally Flexibility - The finished samples were subjected 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^{o}C) conditions a Low Temperature Flexometer (Giuliani model G6FN) was used.

Rub Fastness – Measured with a Satra Footware Technology Center Model STM 421. An 11.5 X 3.5 cm swatch cut from the finished crust was rubbed with a 1.5cm^2 felt pad for 2000 cycles with a 1kg load. Variations of the test require that the pad be either dry, saturated with deionized water, or saturated with an Alkaline Sweat Solution. Alkaline Sweat solution consists of 0.5g L-Histidine hydrocholoride monohydrate, 5.0g Sodium chloride, 5.0g Sodium phosphate dibasic dodecahydrate, in 1 liter (by volume) of deionized water, neutralized to a pH of 8.0 with 0.1M Sodium hydroxide.

Wear support – The Gakushin wear test was run on a Schap Model 200255 equipped with No. 6 duck cloth, 1kg total head weight, and a 30 cycles/min stroke rate.

Wear Support - Taber abrasion test run on Model 5150 Abrader equipped with either an H-18 or CS-10 wheels depending on the respective test requirement. 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.

Flexibility: Cold Impact test involves mounting a leather sample in a metal template and placing it in a -40^o C freezer for 3.5 hours to equilibrate. The sample is then subjected to the impact of 800 gram cylindrical weight dropped from a distance of 150mm. After impact, the sample is evaluated for cracks in the finish.

Anti-Soiling - Measured using a Martindale 2000 Abrasion Tester in dynamic abrasion mode, fitted with either standard soiling cloths EMPA 104 or 128/1, 1000 cycles, 12 kPa pressure

Color - Delta E 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^o observer conditions.

TABLE VII
Mixed Binder Application Properties

Topcoat ID	E	F	G	H
Binder	**New Acrylic #2**	**New Acrylic #3**	**New Acrylic #4**	**Polyether/carbonate PUD Pass Control**
	Tack			
Tack Ambient*	1.5	1.5	1.5	1.0
	Appearance			
60° Gloss	1.0	1.2	1.2	1.3
ΔL (Jetness)	-0.42	-0.21	-0.15	Reference
	Flexibility			
Bally -10°C 30,000 cycles	Pass with trace micro cracks	Pass with trace micro cracks	Pass	Pass
Cold Impact	Fail	Pass	Pass	Pass
	Rub Fastness			
Wet Rubs	1.0	1.0	1.0	1.0
Alkaline Sweat Rubs	1.0	1.0	1.0	1.0
	Wear			
Gakushin***	1.0X	1.0X	1.0X	1.0X
Taber H-18	Pass	Pass	Pass	Pass
Taber CS-10	Pass	Pass	Pass	Pass

*Tack rating 1 = good, very little to no tack, 5 = poor, film sticks to self face-to-face
**Rub rating 1 = good, very little change, 5 = poor, most change
***Gakushin rating 1X = cycles required to wear through the coating, 2X = twice as many cycles as 1X, Higher cycles means higher wear

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

RESULTS AND DISCUSSION

The performance topcoat application properties for the single binder comparison (Table VI) includes a fail control which contains a general purpose acrylic binder, two coatings which contain experimental acrylic binders, and a pass control which contains a high performance polyester PUD binder. This comparison can be made because the final gloss is adjusted by means of a binder free dulling agent. The purpose of the experiment is to position the two experimental binders between known reference standards in pure binder systems. Use of a binder-containing (bound) dulling agent would have resulted in a mixed binder system. The experimental acrylic binders generally perform much better than the fail control and for some properties, such as wear, match or even exceed the pass control. It is important to note that these tests were run a number of times to assure that the values captured were statistically relevant. The one property of concern is the cold bally flex, which can be passed by both standards but not by either experimental. Cold flex failure was not anticipated because the Tg of the experimental binders is only a few degrees higher than the controls.

The performance topcoat application properties for the mixed binder comparison (Table VII) include three experimental acrylic binders and a pass control containing a high performance polyether/carbonate urethane dispersion. In this experimental, by design, 50% of the binder solids in each topcoat comes from a high performance PUD-containing dulling agent. The absolute performance is, therefore, based on the contribution of both the binder (variable) and the binder from the bound dulling agent (constant). The application properties found for the topcoat systems compared suggest

TABLE VIII
Anti-soiling Application Properties

Topcoat ID	I	J	K	L
Binder	**No Anti-soiling topcoat**	**Acrylic Pass Control**	**New Acrylic #3**	**New Acrylic #4**
	Appearance			
60° Gloss	2.2	2.3	2.4	2.4
	Flexibility			
Bally Ambient 100,000 cycles	Pass	Pass	Pass	Pass
	Anti-Soiling EMPA 104			
Delta E*	6.78	1.96	2.09	1.77
	Anti-Soiling EMPA 128/1			
Delta E*	9.86	4.49	3.65	3.23

* Delta E measured using the corresponding fully finished, but untested topcoat as the reference.
The lower the value, the less soiling occurred.

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

that New Acrylic #2 is still slightly deficient in cold flex and fails cold impact but is otherwise a good performer. New Acrylic #3 is slightly better in that both cold properties are met although the cold flex is a borderline pass. New Acrylic #4 is a better performer overall and matches or surpasses the pass control comparative for all properties measured.

The anti-soiling topcoat application properties (table VIII) compare two new acrylic binders to an existing commercial acrylic binder. In order to provide a fail control, the performance topcoated upholstery article used for this anti-soiling comparison was included without any anti-soiling overspray. The pass control significantly improves soiling resistance and the topcoats based on the two new acrylic binders perform similarly or demonstrate an incremental improvement (as in the case of New Acrylic #4). As noted earlier, the primary driver for this work is advancement in the performance topcoat, however, it is important to maintain anti-soiling performance to optimize commercial utility.

CONCLUSION

Dow Leather Solutions has developed a new class of high performance acrylic binders designed for automotive performance topcoats that approach application properties typically attributed to PUD binders. This allows for elevated acrylic binder use levels which in-turn enables the end-user to better leverage attributes ascribed to acrylic polymers such as thermal, hydrolytic, and UV resistance to degradation. Additionally, it was found that this new acrylic binder class offers consistent to slightly improved anti-soiling properties.

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