



Soft, Matting Polymeric Particle Technology for use in Leather Finishing Processes

E. Nungesser, T. Kermis, C.J. Chung, J. Hoefler and E. LaFleur

¹The Dow Chemical Company¹, 727 Norristown Road, Spring House, PA 19044, Phone (215) 619-5494, Fax (215) 619-1622, Email: TKermis@dow.com

Abstract

A new class of very soft matting polymeric particles can be used in leather finishes to create low gloss finishes with high optical clarity, soft-touch and high physical performance including burnish resistance, soiling resistance and UV/Hydrolysis stability.

Leather finishes are a key part of creating an aesthetically appealing article. Appearance and “hand” characteristics can create a good experience for the consumer whether it be upholstery, shoe or garment items. Creating this favorable impression requires the development of impactful technologies for leather finishing. Much of the leather produced exhibits low surface gloss, and all of the leather produced requires a nice feel. The demand for improvements in article richness and robustness continues to drive the development of even higher performing matting technologies.

We will describe a new matting polymer approach to achieving aesthetic richness and high physical performance in leather finishes.

Introduction

Polymers that are used for leather finishes are highly engineered materials. A significant amount of processing goes into a leather article and the final product is very dependent on the quality of the raw materials used in the finish. High quality polymers are required at every step of the process from impregnation, to embossing and finally top coating. Colloidally stable, heat resistant, physically tough yet soft polymers are intricately designed to specifically perform during each of these processing steps.

Once applied to leather, unlike any other coating application, finishing polymers are required to deliver the rare combination of abrasion resistance, temperature, moisture and light stability, and high flexibility across a broad temperature range. They need to achieve these requirements at low film thickness, and they need to be aesthetically pleasing.

As the expectations on performance and aesthetics continue to rise, new materials must continually be developed to enable leather consumers to have a good experience with the leather articles they purchase, as well as to maintain the premium status on leather products. To the consumer, performance is assumed but the appeal of the article rests in how it feels and looks, and these are critical considerations in the purchasing decision.

Fashion trends continually change but at any period of time many leather articles require a matt or low luster appearance. A low luster finish provides two very important visual aspects to the article; the appearance of good surface coverage and an overall impression of surface uniformity.

¹ Dow Leather Solutions, a global leader in developing novel acrylic, polyurethane and silicone chemistries for the leather industry, has developed a patented polymer technology that is designed to be added to high performing basecoat and topcoat finishes to provide a low surface luster, visually appealing color clarity and an exquisite soft-touch to a leather article.



Aqueous based polymeric matting beads which are uniform, smooth and soft will provide opportunities for differentiated formulations that can enable low luster finishes with high color clarity and a soft-touch feel.

Experimental

Experiments conducted on polymers

Refractive index: Index of refraction of film forming polymer dispersions were determined by applying a very thin coating of dispersion to the cover glass of a digital refractometer (ABBE mark II, Model 10480, AO Scientific Instruments). The dispersion was allowed to dry for at least 16-24 hours prior to measuring the refractive index.

Compression determination: The compression factor of polymeric beads was determined using a micro-compression instrument (Model MCTM-500PC, Shimadzu Corporation). For this determination at least 5 individual particles were assessed.

Experiments conducted on leather

Commercial quality corrected grain leather was used as the substrate for all studies. We spray applied approximately 3-4 dry grams of basecoat per square foot of crust. The Basecoat formulations are presented in Table III and were prepared in a 1 liter container. The paint components were mixed using a tongue depressor. The basecoats were dried in a 180°F oven for 2-3 minutes and further dried at ambient conditions overnight.

After completely drying, the base-coated leather was smooth rolled at 180°F. A pigment-free, clear topcoat was applied to the smooth basecoat. The topcoat formulations are presented in Table IV and were prepared in a 1 liter container. The paint components were mixed using a tongue depressor and filtered through a 200 mesh screen. The topcoat was sprayed over the basecoat 1x 2.5gram wet. The total dry amount of topcoat applied was 0.5 dry grams per square foot of leather. After each application of topcoat, the leather was dried in a 180°F oven for 2-3 minutes and after the total amount of topcoat was applied the leather was further dried at ambient conditions overnight.

The following methods were used for assessing appearance and physical properties after the topcoat was completely cured.

Gloss (Tables III and IV): Surface gloss was measured on all substrates using a gloss meter (BYK Gardner USA Micro-TRI-gloss meter catalogue number 4520).

Color (Table IV): Color of the finished leather was measured using a spectrophotometer (Xrite USA model Xrite8400, XriteColor Master CM-2). Reflectance data was captured using the spectral component included mode and under D65/10° observer conditions.

Wet rub Fastness (Table IV): Wet rub fastness was conducted using a rub fastness tester (Satra Footware Technology Center model STM421). An 11.5cm x 3.5cm swatch was removed from the finished crust. To determine the finish fastness of the top-coated leather, a 1.5cm x 1.5cm felt rubbing pad was saturated with water and placed on the equipment rubbing head (total weight of rubbing head was 1Kg). To complete the testing, the leather swatch was inserted into the rub fastness tester and stretched an additional 10%, the water saturated felt pad was applied to the finished surface and 300 rubbing cycles were completed. The finish was visually evaluated for damage and the felt pad used for the test was visually evaluated for pigment transfer by comparing it to a control felt pad (un-used felt pad). The color difference between the felt pads was assessed using a grayscale chart.



Bally Flex (Table IV): A 4cm x 6.7cm swatch of the finished crust was attached to a Bally flexometer (Otto Specht, Stuttgart, Germany Model 2397) and subjected to 100,000 flexing cycles at ambient temperature. After flexing, the leather was evaluated using a stereo scope (at 45x magnification) to assess damage to the finish (cracking or white crazing).

Finish feel (Table IV): A subjective assessment of the finished article was conducted by feeling the leather in multiple ways. To assess the touch (or hand) of the finished article, the leather surface was evaluated by rubbing the topcoat surface and measuring level of smoothness and softness provided in the topcoat. The top-coated article was also rubbed “surface to surface” to determine the level of “grip” of the topcoat.

Matting Technologies for Leather finishes

The benefits and detriments of inorganic silica to provide a low luster surface are well documented¹. Silica is a highly efficient matting agent that is used at relatively low levels in a coating. Typically, 1-3% by weight in a formulation is sufficient for matt finishes. Polymer bound or un-bound silica compacts are widely used in leather finishing to provide the surface luster required of the article. Poorly dispersed compacts or compacts in which silica has flocculated are prone to haze development, “flake back” and white specking. Silica containing finishes also burnish easily.

Though silica matting is still broadly used, within the last 10 years matting agents based on polymeric particles have been introduced for leather finishing^{2,3,4}. Though not as efficient at matting as inorganic silica, they provide a significant improvement over silica for haze optimization, reduced specking, color clarity and burnish resistance.

Polymeric matting agents are mostly spherical and because of their large particle size require complex manufacturing processes. As leather finishes typically have a dry coating thickness range of 30-50µm for basecoats and 3-15µm for topcoats. The useful particle size range of a polymeric matting particle is 3-15µm. Particles that are larger than the thickness of the coating make the finish, especially topcoats, feel raspy and gritty.

Figure 1 is a concise illustration on the application of polymeric matting agents in leather coating formulations. Figure 1a is a Scanning Electron Micrograph (SEM) of a uniform, smooth and soft novel acrylic based matting technology. Like all leather finishing formulations, this matting polymer can be blended with a film forming emulsion or dispersion for optimized physical performance. The formulation strategy (at least as a starting point) is to maintain polymer solids constant and replace film forming polymer solids with polymeric matting polymer solids until the desired performance balance is obtained. Finishing auxiliaries such as feel modifiers, flow control additives and thickeners are also added for product customization. Figure 1b is a SEM of a cross-section of a coating that contains by solid weight 60% acrylic matting particle and 40% film forming emulsion. This interesting and exquisite coating morphology leads to finishes that have exceptional aesthetics and high physical performance.

Physical and Chemical Requirements of Polymeric Matting Particles

When polymeric matting agents are used for leather coatings they cover a significant amount of surface area (see figure 1b). As such they must be stable to:

- Heat:
If the particle is overly thermoplastic heat exposure will cause the particle to flow and deform which leads to a reduction in surface roughness and an increase in surface gloss¹. Heat can also cause yellowing in some polymers that are not stable toward heat.

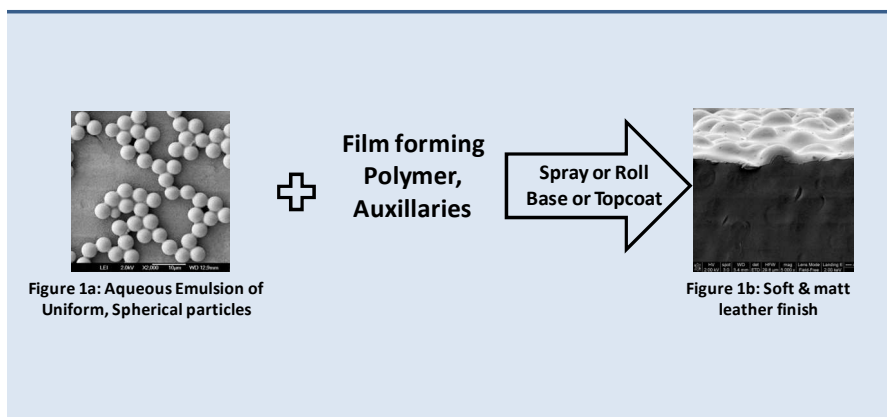


Figure 1: Illustration on the application of polymeric matting agents in leather coating formulations.

- **Light:**
It is especially important that matting polymers possess stability to the ultra-violet, high energy portion of the light spectrum (<400nm). In a coating, UV light causes free radical initiation which ultimately degrades the polymer leading to reduction of polymer molecular weight. Of course polymer molecular weight is very important in maintaining the physical and aesthetic performance of a coating. When a polymer is not stable toward UV light, the coating can yellow, whiten, become tacky and lose key physical performance attributes.
- **Moisture:**
Matting polymers should be resistant to moisture to reduce polymer swelling and hydrolytic degradation of the polymer. Polymer swelling causes film whitening and a loss of physical consistency in the coating, as hydrolytic degradation leads to irreversible damage to the polymer content of the film.

Stability to heat, light and moisture is specifically required in many automotive finishing specifications but it is a benefit to all leather applications.

Of all the polymers used for leather finishing, polymers based on acrylic technology provide the best performance for heat, light and moisture stability^{1,2,4}. Acrylic polymers are used in numerous applications that require stability to heat, light and moisture including exterior industrial and architectural applications⁵. Leather finishing polymers including basecoat and topcoat polymers that are used as film formers and matting agents should provide stability to these challenging conditions.

Aesthetics: Visual and Haptic Properties

When polymeric matting agents are used in leather finishes, they are used in high proportions in a formulation. To provide a matt surface (which is typically a 60° specular gloss of 1-3), the polymeric matting component content of a dried leather topcoat is usually 30-60% of the dried coating. This is due to the relatively low dulling efficiency as compared to silica matting agents. However, to obtain vibrant color clarity and excellent haptic properties in a finish, it is always better that the coating contain as much polymeric matting material as performance allows.

Control of spectral reflectance at the coating surface leads to gloss control of a leather article. Coating gloss is a function of the morphology created at the surface of the coating. Silica is highly efficient flattening material because it is an irregular structure and it creates a very rough surface morphology. Polymeric matting agents are mostly spherical in shape and do not provide rough surface



morphology like silica. Polymeric matting particles also protrude through the surface of a coating which leads to the scattering of spectral oriented light and lower gloss. The matting efficiency of spherical polymeric particles depend on the amount of matting polymer in the coating as well as the PS (and PS distribution) of the particles. More mass of matting material leads to lower surface luster and at comparable loadings, a larger particle leads to lower surface luster. Generally, a rougher surface promotes lower surface gloss. For coating surfaces, Scanning Probe Microscopy (SPM) is used to determine the roughness of a coating surface^{6,7}. To illustrate this, Figure 2 is a scanning probe microscopic analysis of the surface of three dry films (cast by drawdown). Figure 2a represents a drawdown of a neat acrylic emulsion film (-12.6°C T_g) which has a very smooth surface and an arithmetic mean surface roughness (Ra) of 6nm. As expected a film of this smoothness has a very high surface gloss (>100 at 60° and 85° spectral angles) and a bright appearance. As polymeric matting agent is blended with the emulsion there is an increase in the surface roughness and a decrease in the surface gloss. Figure 2b is a coating with a polymer solid ratio of 40% acrylic matting technology/60% film forming acrylic emulsion. This coating has a Ra surface roughness of 378nm and a 60°/85° surface gloss of 2.6/13.4, respectively, and this coating has the appearance of a moderate gloss finish. Figure 2c is a coating with a polymer solid ratio of 70% acrylic matting technology/30% film forming acrylic emulsion. This coating has a Ra surface roughness of 828nm and a 60°/85° surface gloss of 0.5/8.9, respectively, and this coating has the appearance of a very low gloss finish.

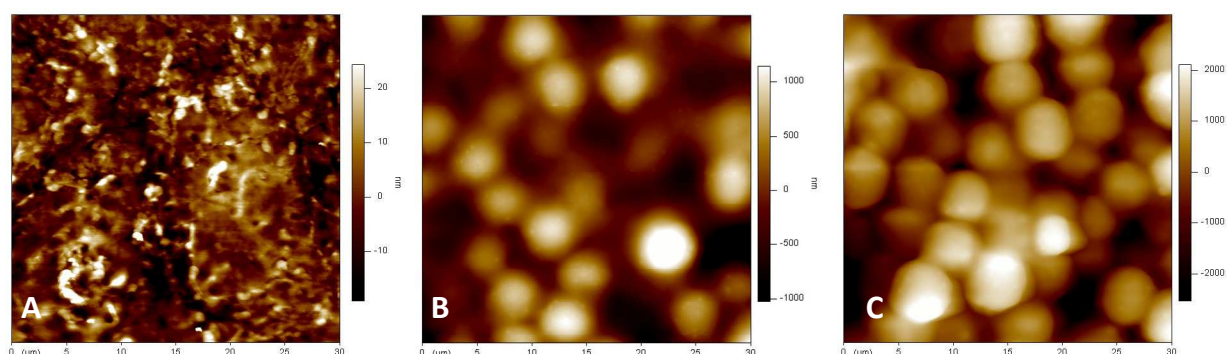


Figure 2: Scanning Probe Microscopic analysis of the surface of three dry films (cast by drawdown)

Table I: Ra surface roughness as determined by Scanning Probe Microscopy and surface gloss of dry coatings

	Neat binder film (T _g - 12.6°C) (A)	40%bead/60% binder (S/S) coating (B)	70%bead/30% binder (S/S) coating (C)
Surface gloss (60°/85°) 1.5mil bird applicator over Penaptec 1B chart (black portion)	>100/>100	2.6/13.4	0.5/8.9
Ra Surface roughness (nm)	6	378	828

For moderate to low surface luster (60°gloss of 1-30), polymeric matting agents can be used as the sole matting agent in a formulation (silica free formulation), and it is very typical for the overall polymer content to be 30-60% polymeric matting agent. In other cases when it is necessary, to balance matt appearance, color clarity and soft feel with high abrasion resistance, it is common to balance the formulation with a polymeric matting agent and a silica dispersion (bound or unbound)³.

After a coating has cured, polymeric matting agents are distributed throughout the entire coating. The particles are at the surface as well as buried inside the coating. For all topcoats, especially pigment-free topcoats, it is essential that the coating delivers contact color clarity so that the color designed



into a basecoat is visible and vibrant. To achieve coating clarity, it is essential for the refractive index of matting polymer to be very close to the refractive index of the other components of the coating including the film forming polymer. According to the Fresnel Equation:

$$R = (\eta_1 - \eta_2)^2 / (\eta_1 + \eta_2)^2$$

Differences in material refractive index cause internal reflection and scattering of visible light, which leads to a hazy appearance in the finish. Haze development is especially problematic when air voids due to poor pigment (silica) dispersions are introduced to the coating. Haze is especially a problem in pigment-free topcoats. Table II provides refractive index of leather finishing polymers.

Table II: Refractive Index of Typical polymers used in Leather finishing

	Glass Transition Temperature Measured by DSC (heating rate, 10°C/min)	Refractive index of neat polymer film
Air		1.0000
Topcoat Acrylic	-12.6°C	1.4729
Topcoat Acrylic	-43.0°C	1.4728
Topcoat PU	-51.5°C	1.5020
Acrylic Matting Technology	-39.5°C	~1.48

Optimization of the ratio of polymeric matting agent to film forming emulsion polymers for surface matting, color clarity, coverage and overall vibrant appearance can be applied to basecoat and topcoat formulations and examples can be found in Tables III and IV.

Table III: Basecoat Formulations containing New Acrylic Matting Polymer for Furniture Upholstery

Solids ratio of Matting polymer/film forming emulsion	Control (1)	15%/85%	25%/75%
Acrylic Matting Emulsion (32% solids)	-	8.2	13.7
Acrylic Basecoat Emulsion (Tg -10°C, 35% solids)	50.0	42.5	37.5
Softening Agent (25% solids)	10	10	10
Inorganic Dulling Agent (23% solids)	7	7	7
Black Pigment (23% solids)	12	12	12
Thickener	2	2	2
Water	19.0	18.3	17.8
Viscosity (FC4)	25-30'	25-30'	25-30'
(Spray base 2x 5grams Corrected grain)			
60° Gloss basecoat	2.6	1.7	1.4
Coverage appearance	=	+	++
(Spray top (Table IV 60/40) 1x 2.5 grams)			
60° Gloss topcoat	1.7	1.3	1.2
Jetness after topcoat	=	+	+



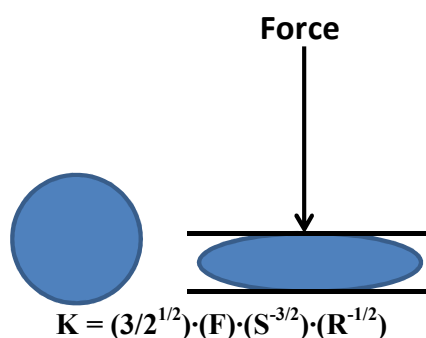
Table IV: Silica-Free Topcoat Formulations Containing New Acrylic Matting Polymer for Furniture Upholstery

Solid agent/film emulsion	ratio	matting forming	25%/75%	60%/40%	70%/30%
New Acrylic Matting Emulsion (32% solids)			17.4	41.6	48.8
Acrylic topcoat Emulsion (Tg -10°, 35% solids)			47.8	25.7	19.1
Thickener			1.8	1.8	1.8
Silicone Feel additive			1.9	1.9	1.9
Flow Additive			1.6	1.6	1.6
Water			29.5	27.4	26.8
Solids % of mixture			26%	26%	26%
Viscosity of Mixture			1000-2000cPs	1000-2000cPs	1000-2000 cPs
60° Gloss of mixtures (drawdown 3mil bird black penaptec 1B)			8	1	0.7
20% solids Spray tops from Topcoat mixtures (Basecoat: Table III control (1))					
Topcoat mixture			60	60	60
Water			32	32	32
Water dispersible iso-cyanate (50% solid)			8	8	8
Viscosity (FC4)			27-30'	27-30'	27-30'
Gloss over smooth finflexed black basecoat			2.0	0.7	0.5
L* value (basecoat L* = 23.5)			23.2	22.1	21.3
Bally Flex 100K RT			No white break or cracks	No white break or cracks	No white break or cracks
Wet Fastness (300 cycles/1Kg)			5	5	4-5
Feel of article after topcoat			Very nice, smooth, soft, no grip +	Very nice, smooth, soft, Velvety, no grip ++	Very nice, smooth, soft, Velvety, no grip ++

Matting Polymer Softness

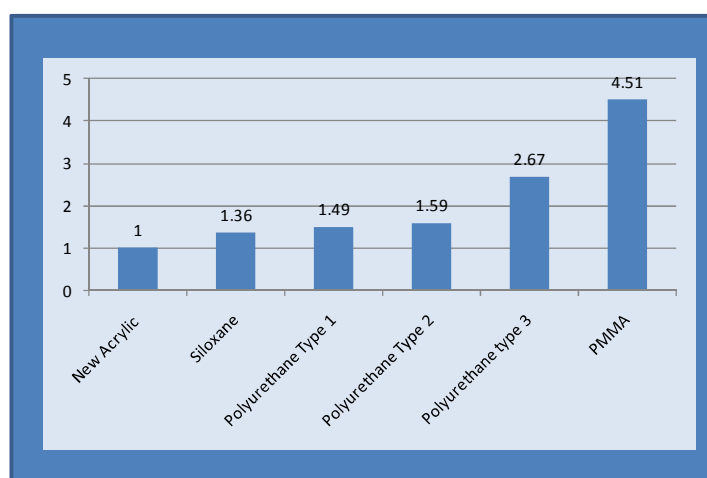
For most leather finishes, it is desirable to have a finish with a soft and gentle feel. Feel additives are used to deliver a specific feel such as “slippery”, “waxy” and “buttery” to a leather finish. Feel additives overcome the inherent feel of the film forming binders which in some cases can be hard or tacky. Use of polymeric matting agents dramatically changes this dynamic because they protrude far above the surface of the coated films and are somewhat compressible. Compressibility is a key factor in achieving a soft-touch or haptic feel. In addition to the new acrylic technology, which is based mostly on low Tg acrylate chemistry, there are a number of different chemistries available as matting agents including; polyurethane (PU), poly methylmethacrylate (PMMA) and siloxane. Assessment of polymer softness is usually conducted on films using a durometer, which measures the depth of indentation in a polymer film that is created by a force on a standard presser foot. The depth of penetration of the presser foot is dependent on the polymer hardness and the viscoelastic properties of

the polymer. A type “A” durometer is typically used to determine the hardness (Shore A) of leather finishing polymer films. Additionally, leather polymer film hardness is determined using an Instron tester. For this assessment, the modulus, which is the stress (pounds per square inch) at 100% elongation, or strain (called the M100), is used to compare polymer softness. Shore A and M100 are determined on cast polymer films (film forming polymers). To determine the hardness of polymer particles a micro-compressor is typically used^{8,9}. For this analysis, individual particles are isolated and a force is applied to the particle. The force needed to compress the particle a defined distance (Figure 3) is determined and is called the “K-Value”. Particle hardness is directly related to the force required to compress the particle. Graph 1 lists the relative K-values of matting polymers. The K-values of these polymers were determined after maximum compression of the particles (average of at least 5 measurements) and the values were normalized to the new acrylics polymer (to normalize the variability of the analysis). As Graph 1 shows, the hardest particle tested was a 5µm PMMA particle. PMMA particles are not commonly used in leather finishes because these particles harden leather finishes and reduce flexibility. Polyurethane particles are used as matting agents in leather finishes and provide many of the performance attributes we discussed in this report. As measured by micro-compression polyurethane particles are significantly harder than either Siloxane particles (siloxane particles are commonly used for cosmetic applications and light diffusing films) or the new acrylic matting polymer.



R=sample Radius
S=Displacement distance

Figure 3: Determination of Particle Hardness using Micro-Compression



Graph 1: Relative K-Value for Spherical Polymeric Particles



Conclusions

Surface morphology is an important consideration in controlling surface gloss and feel quality of leather. Novel materials provide formulators with additional options for differentiated products. Polymeric matting agents are tools for leather finishers to use to achieve a high level of aesthetic value and physical performance. When used in a well balanced formulation, polymeric matting agents provide a unique blend of low surface gloss, vibrant color clarity and soft-feel that can be used to upgrade leather articles.

References

- 1- Nungesser, E.; Hoefler, J., Journal of the American Leather Chemists Association (2005), 100(2), 54-60
- 2- Levy, J.; Bouchard, J., Journal of the American Leather Chemists Association (2002), 97(3), 114-121.
- 3- Nungesser, E.; Kar, A.; Yang, D.; and Hageman, B.; Novel Acrylic/Silica-Free Matting Technology for Furniture Leather Upholstery Topcoat Finishes Presented at the IULTCS XXIX Congress of the World Washington DC, 2007.
- 4- Hoefler, J.; Chung, C.J.; and LaFleur, E.; Novel Acrylic Particle Technology for High Performance leather Finishing Presented at the 2011 American Leather Chemist Association meeting, Red Wing, Minnesota.
- 5- Friel, J.M.; Acrylic Polymers as Coatings Binders, Paint and Coatings Testing Manual- Fourteenth Edition of the Gardner-Sward Handbook (1995), 39-52.
- 6- Germinario, L. T.; Beccaria, D.; Capra, A.; Bejko, I.; A closer look at low gloss powder coatings, European Coatings Journal (2003), (10), 25-26, 28, 31.
- 7- Gebhard, M. S.; Clark, M. B., Jr.; Willey, K. F.; Antrim, R. F.; Acholla, F. V.; Newman, J. B.; Weidemaier, K.; Assessment of various analytical techniques on naturally weathered paints as a predictor of long-term gloss retention for waterborne acrylic architectural paints, JCT Research (2006), 3(1), 15-27.
- 8- Kim, D. O.; Jin, J. H.; Mechanical property investigation of single polymer particles with the variation of molecular structure of crosslinking monomer, Journal of Applied Polymer Science (2007), 105(2), 783-789.
- 9- Kim, D. O.; Jin, J. H.; Investigation for surface morphology and mechanical property variations of single polymer particles, Journal of Applied Polymer Science (2007), 104(4), 2350-2360

Acknowledgments

The Authors would like to acknowledge the contributions of their Colleagues from The Dow Chemical Company: Mr. Bradley Hageman, Mrs. Kelly Klein, Mr. James McHugh, Mr. Patrick Patton and especially Dr. Rebecca Smith for providing unwavering support for this work. The authors would also like to acknowledge their colleagues from the Lanxess Corporation: Mr. Michael Franken and Mr. Jeorg Menrath.