

UTOMOTIVE LEATHERS – EVALUATING THE PERFORMANCES LIMITS (PART II)

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Abstract

Leather used in car interiors is sold as a premium product. Consumers perceive leather as a durable and natural product and to support this image original equipment manufacture (OEMs) manufacturers have set demanding performance profiles defined by mechanical wear, protection from the elements, low emissions and sustainable manufacture. High wear and protection can only be achieved with a polymeric coating and poor performance of coated leather becomes visible if polymer coat is wearing off or cracks over time. Therefore ageing property is seen as a representative key performance parameter and was determined by checking how flexible and strong a polymer coating remains after leather has been exposed to light, heat and humidity for a given time. In a first approach different type of crusts (wet blue ,wet white) were prepared and finished with a standard polyurethane coating. It turns out that the selection of the right fatliquors and tanning agents as well as the presence of vegetable tannins play an important role. On top of this the effective use of protective chemicals like anti-oxidants is needed for the production of crust to reach high aged flexing performances. In this work the polymer coating (matrix) was optimized without the impact of leather which means testing of the various polymer films with and without coating additives (pigments, fillers, waxes, feel agents etc.). Testing has been carried out through the analysis of the strain and stress curves of the polymer films before and after exposure to heat, light and hydrolysis. Parameters like polymer type, application technology, and impact of additives were investigated and tested after ageing when applied on chrome automotive leather. Results show that not only the right selection of polymers is critical but also the way the coat is being applied. Additives in coatings like dulling agents, feel agents, waxes and fillers obviously play an important role and cannot be easily dispensed although their presence in

many cases would weaken the integrity of the polymer matrix and consequently reduce physical and chemical fastness properties. As to application, special emphasis is given to the transfer coating technology which potentially reduce the number of application steps, allow higher curing temperature and decrease the amount of additives while maintaining the aesthetic and haptic properties.

Keywords: durable, natural, polymeric coating, polyurethane coating.

1.INTRODUCTION

Consumers consider automotive upholstery leather as a premium product, in particular they perceive car interior leather as a natural material which has to satisfy important aesthetic properties such as colour and surface touch but also be resistance to high mechanical wear and chemical during its lifetime. In order to support this concept, original equipment manufacturers (OEMs) set demanding performance profiles defined by mechanical properties, protection from the elements, low emission and sustainable manufacture.

Leather performances are generally evaluated after production, although a real judgement of quality can only be made after many year of service. Long term durability can be predicted by several methods like extended ageing tests. A very challenging test set up is to expose leather to several cycles of light at given heat and humidity (e.g. FAKRA test according to UNI ISO 105 B06-1) and after such exposure test the mechanical properties like flexibility of the coating.

In our previous work ¹, we focused our attention on testing the performance of different types of crust, alone and finished with a standard polyurethane basecoat. The chrome and chrome-free crust sample were subjected to various test cycles according to ISO 105 B06-1 and then evaluated in terms of flexes, dimensional changes, softness and mechanical properties. The results showed that selection of

the right fat-liquors and tanning agents as well as the presence of vegetable tannins and appropriate antioxidants play a key role in achieving best performances. In a second part of our work the interesting results achieved, directed our attention to the optimization of the finishing coating.

Finishing is the final step of leather processing and plays a pivotal role for achieving the final performance of automotive leather. Depending on the quality of the crust (as to defects) and the requirements set by OEM, the thickness and aspect of the finishing coat will vary from semi-aniline with lowest add-on quantity to corrected, embossed leather having the highest coating add-on.

From a chemical aspect, a typical automotive finishing coat consist mainly of polyurethane dispersion (PUDs) and acrylic emulsions, which are formulated by addition of pigments, organic and inorganic dulling agents and various other additives for feel, flow and rheological control. Those additives together with cross-linkers and the application procedure can greatly impact the performance of the final polymeric coating with major concern after ageing.

Polyurethane dispersions (PUDs) represent a large family of polymers and due to their excellent properties find a wide application in leather finishing. They are obtained from the reaction of a diisocyanate and a polyol. With the availability of different diisocyanates and polyols many tailor-made solutions are possible. Automotive upholstery leathers are generally finished by the use of PUDs based on aliphatic diisocyanate which, as widely reported, can support a long-term stability.^{2,3}

On the other hand chemist resorts to a wide range of polyols which affect systematically the ageing behaviour of the final PUDs. Polyester polyols do not suffer severe degradation when they are exposed to UV-radiation, but heat and humidity can promote the hydrolytic cleavage of the ester group and lead to a loss of physical properties (hydrothermal aging).^{4,5} Polyether polyols show a better resistance to hydrothermal aging however they are susceptible to photo-oxidation phenomena which promote the cleavage of ether linkages resulting in a weakening of strength of the coating.⁶

Finally polycarbonate based polyols show the best resistance to both, UV and hydrothermal ageing, however their high costs prevent from a wide use in leather finishing.⁶

In this context, the co-use of acrylic binders offers interesting alternatives. It is not only the lower cost which make them interesting, but also their high resistance to light and hydrolysis whereas they are more thermoplastic and print retention when embossed is not as high as PUDs.

In the first part of this study the polymer coating (matrix) was optimized without the impact of leather which means testing of the various polymer films with and without coating additives (pigments, fillers, waxes, feel agents etc.). Testing has been carried out through the analysis of the strain and stress curves of the polymer films before and after exposure to heat, light and hydrolysis. In a second part of the work various polymer blends were applied on automotive crust leather which were then aged according to DIN EN ISO 105 B06-1 and tested for cracks in the finishing coat after a defined number of flexes. In a final optimization stage the impact of application was studied with an emphasis on transfer coating as an alternative to the more traditional spray and roller coat application.

In transfer coating the finishing coats (base and adhesion coat) are applied to a release (transfer) paper which has the desired surface texture (matt, gloss and embossed). Each coat is dried after application and the final polymer film is then transferred (laminated) via the carrier paper onto leather by applying heat and some pressure. Transfer coating technology reduces the number of application steps, allows higher curing temperatures and potentially reduces the amount of additives while maintaining the aesthetic and haptic properties.

2.1 Materials and Methods

2.1.1 Film resin preparation

Films of various polymers and polymer combinations (PUDs and acrylics) were prepared by casting a defined amount of resin dispersion on a levelled petri dish and allowing them to dry at room temperature. The residual volatile matter was removed by drying for 12 hours in a static oven at 50 °C.

2.1.2 Leather preparation and finishing

Applicative tests have been carried out on commercial full grain automotive crust leather. The finishing procedure consists of three basic steps, first the polymer base coat was applied on release paper (film thickness 130 µm) and dried; then an adhesion coat was laminated to

the base coat layer. The film coat on paper was then immediately laminated via a calender at a temperature of 100 °C to the leather substrate. The final top coat has been applied in two spray applications (total wet add-on of 5 g/ft²) and then dried for 2 minutes at 90 °C. Test pieces were allowed to rest for 5 days at room temperature before subjected to ageing test.

2.2 Accelerated ageing test

2.2.1 Ultraviolet (light) exposure – (xenon test)

Two specimens of leather (40 x 100 mm) were exposed to UV-irradiation using a Xenotest Alpha Light Exposure (Atlas Corporation) in accordance with ISO 105-B06-1. The exposure energy rate was 60 W/m² and chamber temperature was set to 65 °C at 30% of relative humidity, for a total radiant energy of 22000 KJ.

2.2.2 Hydrolysis test (exposure to humidity in climatic chamber)

Two specimens of leather (40 x 150 mm) were placed in a climate test chamber model WK3-180/40 (Weiss Technik) at a temperature of 70 °C and 90% of relative humidity for a total exposure of 400 hours. At the end of the tests the samples were removed from the chamber and allowed to equilibrate at 23 °C and 50% of humidity for 24 hours before further testing was executed.

2.2.3 Heat ageing test (exposure to heat in oven)

Two specimens of leather (40 x 150 mm) were placed in a ventilated oven model at a temperature of 100 °C for a total exposure of 400 hours. At the end of the tests the samples were removed from the chamber and allowed to equilibrate at 23 °C and 50% of humidity for 24 hours before further testing was executed.

2.2.4 Bally flexibility

Leather samples were cut into 45x70 mm pieces and mount on a Bally flexometer (Bally Matric 2182). Flexing tests have been carried out according to ISO 5402-1, each specimen was tested against 100000 flex cycles and examined after every 10000 flexes. Intensity of cracks was evaluated in a good light using, the following definitions were used to describe the final result:

- Cracks: Visible with naked eye.
- Fine crack: Visible with 6X magnifier.

- Micro cracks: Visible with 25X microscope.

2.2.5 Determination of gloss

Gloss has been measured with a BYK Gardner Micro Tri Gloss 20/60/85°, the measurement was carried out at 60° and the results were reported as an average of 5 different measures.

2.2.6 Strain and stress measurement

Strain and stress curve as well as modulus at 100% of elongation of polymer films were evaluated with a tensile strength machine (Instron Model 3343). From each sample at least five test specimens were tested. Table 1 shows dimension of the test specimen.

Table 1. Dimension in millimetre of the test specimen.

	L	L3	L2	b1	b	T
Measure (mm)	110	50	30	25	10	0.5 ± 0.05

Tensile strength measurements were recorded at a crosshead speed of 100 mm/min, with a maximum load capacity of 500 N; this method was used to determine the tensile strength at 100% of elongation with an experimental error lower than 1.5%.

3 Results and discussion

3.1 Effect of pigment on mechanical properties of polymer films

The number of parameters which influence physical properties of polymer film made from waterborne polyurethane and acrylic emulsion such as molecular weight, chemical nature and particle size distribution, introduce a considerable experimental uncertainty, leading to potential misunderstanding about the impact of difference variable on the polymer performances. In leather coating, this complexity is also increased by the use of different auxiliaries such as pigments, silica and dulling agents which increase the number of parameters involved in coating optimization.

In order to decrease the complexity, in the early stage of this project four different polymers, two polyurethane dispersions (PUD) and two acrylic resins (ACR) have been pre-selected by evaluating their physical and chemical properties as shown in table 2. The polymers exhibit high elongation and a rather low elastic modulus suited for their use in base

coats. Polyester based PUD's in this case were not selected although there are interesting products available on the market which satisfy most important physical requirements (included hydrolysis resistance).

Table 2. Physical properties of pure polymer.

Designation	Chemistry	Modulus 100% (MPa)	Elongation (%)	SHORE A (°)
PUD 1*	Polyether	5.7	450	96
PUD 2*	Polyether/ Polycarbonate	1.7	1000	74
ACR 1*	Polyacrilate	0.8	900	50
ACR 2*	Polyacrilate	1.6	750	62

Since pigments are the largest formulation component having an impact on physical properties of polymer films each of these polymers have been formulated with addition of 15% of inorganic black pigment. According to Fig. 1 all polymers under investigation show a significant increase in modulus (100% of elongation) when mixed with black pigment. The relative percentage increase is highest with acrylic binders (by average 22%). The pigment addition into polymer matrix lead to a composite material which maintains its elastic behaviour (no plastic deformation was observed) but shows higher stiffness. More force is required to stretch the film to the same elongation. Interesting is the behaviour of PUD 2, in which case pigment addition lead to a 9% increase of modulus at 100%, which is the lowest change among the polymers tested. These preliminary results point out that the effect of the pigment on physical properties of polymer matrix is not negligible leading to a systematic increase of stiffness which cannot be predicted with an 'a priori' model. Since pigments are fundamental in any leather coating all further work is done with pigmented films.

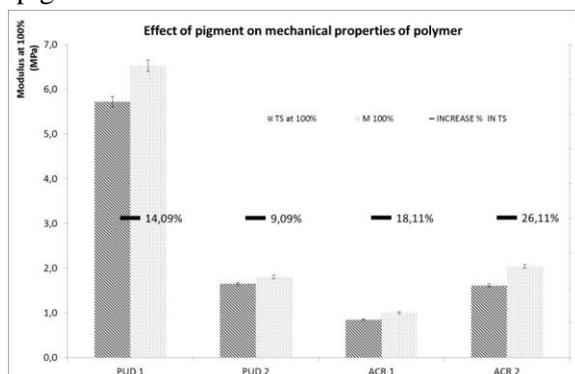


Fig. 1. Modulus at 100% of elongation of the polymer under investigation and the increase

percent of the same due to the use of 15% black pigment.

3.2 Effect of additives on mechanical properties of polymer films

To further investigate the impact of pigments and additives on elastomeric properties of polymer films, two blends were designed (see table 3). Both blends are formulated with the pre-selected polymers as listed in table 2 whereas basecoat 1 is representative for a typical basecoat and pol-mix just contains the polymers and pigment but no further additives.

Table 3. Composition of blends under investigation.

Component	Basecoat 1 (%)	Pol-mix (%)
PUD 2	30	60
ACR 1	20	40
PARAFFIN WAX*	10	/
SILICONE	2	/
SILICA DISPERSION*	20	/
WATER	18	/
BLACK PIGMENT*	15	15

Films of basecoat 1 and pol-mix were tested via the strain and stress curves for their physical performances (Fig.3). The addition of 30% of additives lead to a 45% increase of modulus at 100% of elongation, moving from 1.8 MPa of the polymers mixture to 3.3 MPa for the 'formulated' basecoat. This result shows how the addition of additive changes completely the behaviour of the polymer matrix, the material (polymer film) becomes stiffer. The 'additive-loaded' film breaks at around 134% of elongation while the 'additive-free' blend achieves 300% of elongation without any failure (break point could not be detected due to instrumental limits).

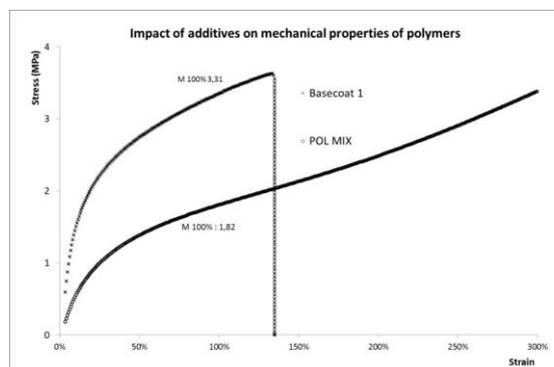


Fig. 3. Stress and strain curve of pol-mix and basecoat 1.

The influence of additives like waxes, feel additives and fillers is also visible in the behaviour of the material after exposure to light by the evaluation of the strain and stress curve in the low strain region (0-10 % elongation). In this region the material shows an ideal elastic deformation (Young Modulus). Both materials, before and after ageing maintain a linear elastic behaviour (Fig.4) however they show curves with different slopes. After aging basecoat 1 suffers a significant degradation by losing more than 25% of its initial modulus compared to the ‘additive-free ’blend (pol-mix) which also shows degradation but to a much lesser extent (appr.10%).

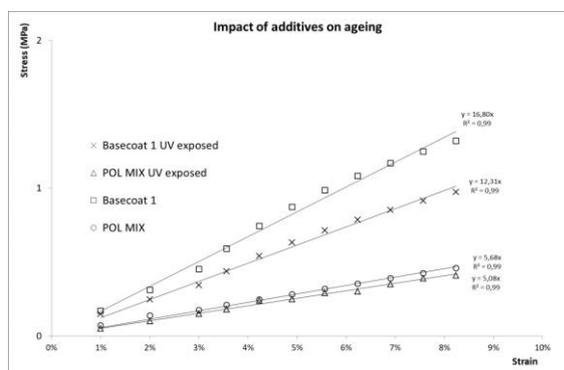


Fig. 4. Impact of light exposure (ISO 105B06-1) on Young Modulus.

3.3 Optimization of polymer matrix

The further optimization of the polymer films was carried by measuring the modulus of the films made with preselected polymers (see table 2) after exposure to light, heat and humidity.

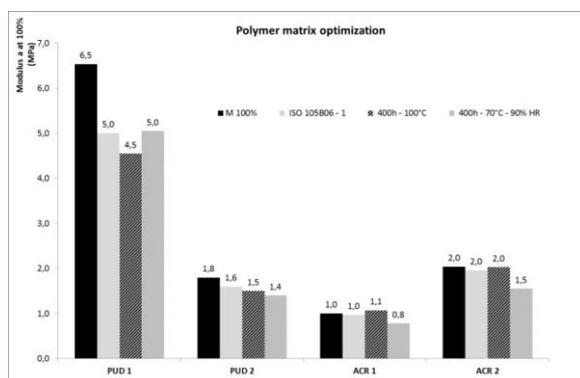


Fig. 5. Evaluation of modulus at 100% of various polymers after exposure to different ageing conditions.

The analysis of the data obtained after light exposure (ISO 105 B06-1) as shown in Fig.5

indicate a clear trend: the acrylic polymers almost maintain their mechanical properties with an average loss in modulus of only 3.3%, whereas PUDs show a significant decrease particularly PUD 1 losing 23% of its original value moving from 6.5 MPa to 5.0 MPa. Interesting is the behaviour of PUD 2, which shows a performance between PUD 1 and acrylic polymers by losing only 11% of its original modulus at 100%. The results obtained from heat ageing test (400 hrs, 100 °C) confirm above trend: acrylic emulsions maintain the same elastic moduli while PUD 1 and PUD 2 respectively lose 30% and 17% of their initial value. Results obtained after the hydrolysis test show how regardless of their chemical nature, the polymers when exposed for 400 hrs to 70 °C and 90% humidity show an average decrease of 22% in tensile strength value.

Based on these results the PUDs alone show inferior performances with regards to light and heat exposure than acrylic resins, with the exception of the hydrolysis test in which both resins suffered a loss of strength and elasticity. PUD 2, a polyether/polycarbonate polyurethane dispersion, shows a better overall behaviour than PUD 1 a polyether based PUD. In particular the good resistance to both UV-exposure and heat exposure could offer advantages when used as soft binder component. From this point of view the right ratio between PUD 2 and acrylic resins seems to offer the best solution to achieve an optimal cost/performance ratio. Therefore the idea for the next step of optimization was to improve PUD/acrylic blend while reducing the amount of additives via a different application approach.

3.4 Transfer coating technology as an innovative approach to high performance automotive leather

The results achieved by the stress testing of the film are an important part of the optimization but need to be fine-tuned when applied on crust leather. Already in part 1 of our studies it became evident that type of crust leathers has a significant impact on aging of the polymer coating. Particularly the flexing behaviour when tested after aging (checking for visible cracks in coating) of the finished crust leather gives a quite realistic view of real world conditions and how to best evaluate the performance limits of automotive leather.

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Therefore, three different blends of PUD 2 and ACR 1 with pigments only (see table 4) were applied on a chrome tanned automotive crust via paper transfer coating technology following the process as outlined in materials and methods (see paragraph 2.1.2).

Table 4. Composition of the polymer blends used in transfer coating of automotive crust leather.

Component	MIX 1 (%)	MIX 2 (%)	MIX 3 (%)
PUD 2	50	80	20
ACR 1	50	20	80
BLACK PIGMENT	15	15	15

Coated leather were first subjected to accelerated ageing according to ISO 105 B06-1 conditions, then flexed for a defined number of times and finally checked for cracks in the coating (see table 5). The best performance for flexing after aging is achieved by mixing equal parts of ACR 1 and PUD 2 (MIX 1). The increase of polyurethane dispersion PUD 2 (MIX 2) leads to a drop of the performances after ageing (fine cracks). This result is consistent with previous findings, which showed the good weathering behaviour of acrylics polymer films. Thus the addition of ACR 1 to PUD 2 seems to provide a synergistic effect, improving the performance of the coating. Reversing the ratio towards acrylic (MIX 3) leads to a basecoat which cannot withstand 100k flexes before aging, a basic requirement in automotive leather upholstery.

Table 5. Flexing performances of the blends. Tests were performed according to ISO 5402-1.

Name	100k	10k Dry Flexes
	Dry Flexes	3x ISO 105B06-1
MIX 1	NO CRACKS	NO CRACKS
MIX 2	NO CRACKS	FINE CRACKS
MIX 3	MICRO CRACKS	/

This outcome is not unexpected and can be explained by refers to the 100% modulus of the polymeric films made from the three blends. As shown in Fig.6, MIX 3 has the lowest elastic modulus, which is the main cause why the coating fails to pass 100k flexes even before ageing. Also the performance of MIX 1 and MIX 2 can be explained by the analysis of the tensile strength properties of the polymer films: after one cycle of ISO 105B06-1, MIX 1 shows a 9% decrease of the modulus at 100% while MIX 2 loses more than 20% of its original value showing the worst ageing performances.

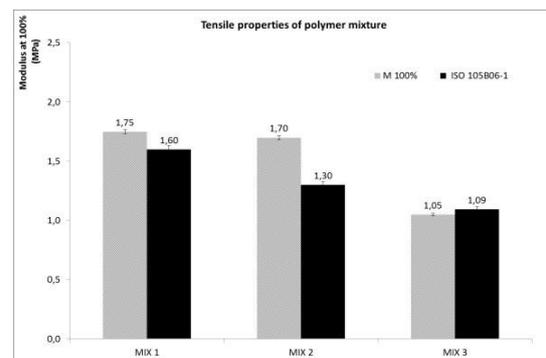


Fig. 6. Modulus (MPa) at 100% elongation of polymer blends films before and after one cycle of ISO 105B06-1.

In order to see potential benefits provided by transfer coating technology, a comparison with a classical finishing approach has been done. One piece of automotive leather was coated with basecoat 1 (see composition in table 3) via roller-coating for total dry add on of 3.8 g/ft². In parallel, another specimen of same crust leather was coated with MIX 1 (only pigments no further additives) through transfer paper coating technology (see experimental part). The two pieces were dried and stored overnight; then a dull organic top coat, which composition is reported in table 6, has been sprayed two times with a total wet add on 5 g/ft². The final leathers were stored five days at room temperature before being subjected to the aging tests.

Table 6. Composition of the dull top coat

Component	(%)
ORGANIC DULL PU	70
PERFORMANCE SILICONE	8
WATER	17
ISOCYANATE CROSS LINKER	5

As shown in table 7 there is no significant difference in gloss between the two applications after exposure to heat and hydrolysis, although no silica dulling agent was used in basecoat of transfer coating application (TC). However there is a significant increase of gloss on both samples after they were exposed to three cycles (ISO 105B06-1). This loss of opacity is due to the degradation of the dull PUD particles and can be reduced by the co-use of suitable silica duller and optionally the use of antioxidants and UV stabilizers.

Table 7. Test results of final articles (TC = transfer coating of ‘additive-free’ basecoat; STD = roll coating application of basecoat 1; same total dry add on and finished with dull top coat by spraying).

Property	TC	STD
Gloss 60°	0.6	0.7
Gloss 60° after 3x ISO 105B06-1	2.5	2.1
Gloss 60° 400h 100°C	0.5	0.6
Gloss 60° 40h 70°C 90% HR	0.5	0.6
100k Dry Flexes	No Cracks	No Cracks
10k Flexes 3X ISO 105B06-1	No Cracks	Fine Cracks
100k Flexes 400h 100°C	No Cracks	No Cracks
100k Flexes 40h 70°C 90% HR	No Cracks	Fine Cracks
Dry Adhesion (N/cm)	12.0	7.2
Taber (CS 10)2000 cycles (10X Magnification)	Repolish-No Damage	Repolish-No Damage

With regards to flexing after aging the use of transfer coating offers clear advantages. According to table 7, the specimen of leather coated with the standard basecoat and standard application does not pass 10k flexes after three cycles of ISO 105B06-1 and at the same time it fails the hydrolysis test, showing cracks already at 60k flexes. With transfer paper coating technology, however the stringent flexing requirements after aging can be passed. This is mainly due to the reduction of additives and use of suitable papers along with selected polyurethane and acrylic polymers used in an optimized ratio.

4 Conclusions

The aim of this study was to examine the performance limits of automotive leather with regards to the flexibility of polymer coatings on automotive crust after being subjected to various aging conditions. In the first part of the work the impact of pigments and additives was shown via the analysis of the strain and stress curves of polymer films. As a matter of fact pigments like carbon black t and additives like fillers, dulling agents, waxes and feel additives increase modulus

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at 100% and thus the stiffness of the polymer coating. The comparison between a basecoat with typical coating additives and a ‘additive-free’ polymer blend show that auxiliaries not only increase the stiffness of the coating but after light exposure lead to a loss of the elastic modulus.

The coating polymer matrix consisting of selected PUDs and acrylic emulsions was further optimized with regards to resistance to heat, light and hydrolysis by testing the 100% modulus. Acrylic emulsions show the best fastness performances while PUDs provide strength to the polymer matrix. The final coating optimization has been achieved through the application of a polymer blend based on equal parts of a specific acrylic and polyurethane dispersions by using transfer coating technology. This technology allows reduction of coating additives (mainly dulling agents like silica) via use of a matte transfer papers. The results show that the critical step is not only the right selection of polymer but also the way the coat is being applied, from this point of view a significant improvement is offered by transfer coating technology which avoids the use of additives while maintaining aesthetic and haptic properties.

Trade Name

Designation	Trade Name
PUD 1	RODA©PUR MB
PUD 2	RODA©PUR 65
ACR 1	RODA©CRYL 5416
ACR 2	RODA©CRYL 2130