Acid and Scratch Resistant Coatings for Melamine Based OEM Applications

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Summary: Increasing the mar resistance of OEM clear coats has been one of the main R&D priorities of paint manufacturers over the last years. Reaching a good mar resistance level without compromising other coating properties such as acid resistance proves to be a major challenge. We investigated the use of branched glycidyl esters in melamine based OEM acrylic formulations. Our results show that systems based on this type of esters lead to good overall coating properties as well as a good balance between acid and scratch resistance.

Key-words: scratch and mar resistance, etch resistance, OEM, acrylic clear coats

Introduction

In the automotive industry increasing attention is given to the ability of coatings to retain their new car appearance by resistance to damage caused by weathering (e.g. acid rain) but also by resistance to chemical and physical damage such as scratches. There is a particular interest for OEM coatings providing both acid and scratch resistance as a combination of these properties is difficult to obtain.

It is well known that the acid etch resistance of polyacrylic-melamine (also called TSA-systems) is poorer than that of PolyUrethane Resin (PUR) coatings. The cause of this weakness is the hydrolytic degradation of the crosslinkages between the melamine resin and the polyacrylate [1]. The incorporation of Cardura® E10P, the glycidyl ester of Versatic® acid, is a way to minimise this problem [2]. This monomer imparts good acid resistance to coatings via steric protection of the crosslinks against hydrolytic degradation.

In order to obtain good mar resistance, a low glass transition temperature (T_g) of the coating is desirable [3]. As the incorporation of Cardura E10P in acrylics via the adduct with acrylic acid

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contributes to a low T_g, we decided to study if the incorporation of Cardura E10P into acrylic resins would allow the design of melamine based clear coats with good acid as well as mar resistance. The structure performance study into these systems including the development of a simple and reliable test method to measure mar resistance are the subject of this paper.

Cardura E10P chemistry

Cardura E10P (CE10P) is the glycidyl ester of Versatic acid, a low viscosity, heavily branched, saturated C10 acid (see Figure 1)..

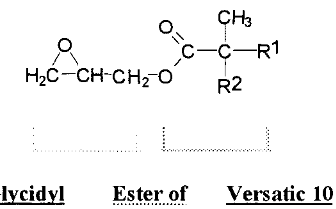


Figure 1. Structure of Cardura E10P

It can be easily incorporated into acrylic resins by conversion into a radical-polymerisable monomer with unsaturated acids such as (meth)acrylic acid. CE10P based acrylic resins can be prepared in different ways. The potential advantage of Cardura in processing is however only fully exploited, if both the radical polymerisation and the esterification of Cardura are executed in one single step. The reaction between the epoxy group of the glycidyl ester and the acid group of (meth)acrylic acid takes place very rapidly under the reaction conditions used for the radical polymerisation of acrylic monomers. This allows Cardura-based acrylic resin production in a single step during which acrylic acid reacts with the epoxy group of the glycidyl ester and simultaneously polymerises with the other acrylic monomers. Upon esterification a hydroxyl group is generated, which can be used in the crosslinking process (Figure 2).

It has been demonstrated that the presence of a solvent can often be completely avoided by putting Cardura in the initial reactor charge, gradually esterifying the epoxy group with acrylic acid during the radical polymerisation. This is possible because of the low viscosity of Cardura-based acrylic resins at high solids contents and at the usual synthesis temperature. However, if desired, a wide variety of solvents can be used with Cardura.[4].

The performance benefits of the incorporation of Cardura, such as high solvent compatibility and low viscosity of paints as well as the impressive acid resistance and outdoor durability can be understood by taking a closer look at one of the possible resin intermediates, the acrylic monomer ACE (Figure 2).

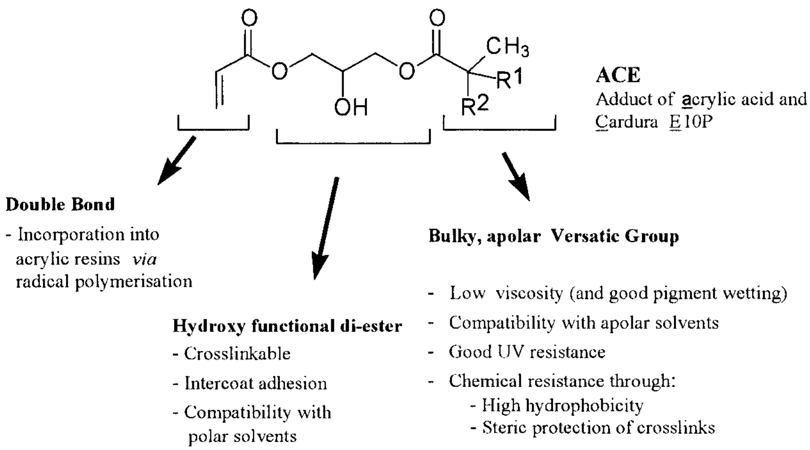


Figure 2. Structure and properties of the ACE adduct

The ACE monomer has a di-ester structure, which compatibilises the resin with polar and apolar paint components. The Versatic entity provides a high hydrophobicity and low viscosity due to the tertiary aliphatic structure. The low surface tension of the adduct also ensures a very good adhesion even on low surface energy substrates which are difficult to coat (e.g. plastics). In addition, a large T_g-region as well as changing co-polymerisation reactivity can be obtained by choosing different unsaturated acids to form the adduct. A comparison with T_g's of different acrylic monomers is given in Figure 3.

On December 14th 2001, Resolution Performance Products successfully started a new plant for the production of Cardura E10P. Cardura E10P is the same product as Cardura E10 except that it is produced at a higher level of purity. The higher purity finds expression in a higher Epoxy Group Content (EGC) and lower product colour

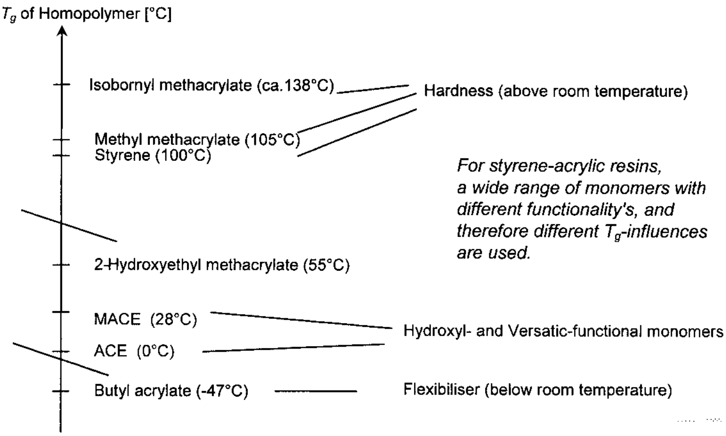


Figure 3. Glass transition temperature of the different acrylics

Scope of the study

The study carried out was limited to acrylic OEM clear coat finishes as, especially for these systems, acid etch and mar resistance are important performance features.

Resin composition

To study the effect of the incorporation of Cardura in polyacrylic-melamine systems, a range of acrylics resins with Cardura content between 0 and 40 wt% was made.

The hydroxy equivalent weight, which affects crosslink density and hence performance, was kept constant for all the resins at 425 g/mol. This corresponds with 4 wt% OH in the resin composition and an OH number of 132 mg KOH/g which is the recommended concentration to obtain good mar resistance [5][6]. The T_g of the various resins was varied between 0 and 25 °C. The different resin compositions are given in Table 1.

Table 1. Acrylic resin composition

Name:	Resin A	Resin B	Resin C	Resin D	Resin E	Resin F	Resin X
CE10P concentration [wt%]	20	20	20	20	20	40	0
Theoretical Fox T_g [°C]	24	15	15	15	0	0	15.8
Acrylic acid [wt%]	6	6	6	6	6	12.01	0.70
Hydroxy ethyl acrylate [wt%]	17.64	17.64	17.64	0	17.64	7.97	0
Hydroxy ethyl methacrylate [wt%]	0	0	0	19.8	0	0	31
Styrene [wt%]	30	30	30	27.8	26.7	18.45	30
Methyl methacrylate [wt%]	13.66	7.56	7.56	0	0	0	0
Butyl acrylate [wt%]	12.7	18.8	18.8	26.4	29.66	21.57	38.3

The resins were all prepared in the same way, i.e. at 140°C with 1.5 wt% di-tert. amyl peroxide (DTAP) as initiator. During the post cooking phase an extra 1 wt% initiator was added. This initiator was chosen over DTBP because we observed earlier that acrylic resins initiated with DTBP showed lower mar resistance than DTAP based ones. The reason for this is probably the broader molecular weight distribution obtained with the resins prepared with DTBP, as a result of the initiator ability to abstract hydrogen atoms and to form carbon-carbon crosslinks [7].

For the resins prepared with Cardura, the initial reactor charge consisted of the whole Cardura quantity together with 25 wt% of xylene. In the case of Cardura free resin formulation, only the solvent (xylene) was present as initial reactor charge. At the end of the reaction, the acrylic resins were cooled down and diluted with butyl acetate till a solids content of 60 wt%.

All resins had a similar low colour of about 20 Pt/Co and a low acid value of 4-6 mg KOH/g. The viscosity reducing effect of the incorporation of Cardura E10P becomes clear when comparing resins with similar Mw (Table 2).

Table 2. Viscosity cutting power of CE10P

	Resin X	Resin D	Resin F
CE10P content [%]	0	20	40
Mw [g/mole]	14400	11440	11300
Viscosity [mPa.s] at 22°C, 60 wt% solids	5330	1960	500

Clear coat formulation

Scratch resistance in 1K clear coat systems depends a lot on the melamine type. In our study Cymel 1158 (ex. Cytec Industries), a partially alkylated (butylated) high NH melamine resin with a low monomer content was chosen to cure the resins and to compare their coating performance. This product is recommended by Cytec Industries as a good crosslinker to obtain good overall coating properties. In addition, its low monomer content minimises the risk of self condensation which has a negative effect on coating performance [3]. Furthermore, this crosslinker has a high reactivity and consequently does not require the presence of an additional strong catalyst during curing. The carboxylic groups along the backbone of the acrylic resin are sufficient to catalyse the crosslinking reaction.

All the acrylic resins were cured with Cymel 1158 with a resin/crosslinker weight ratio of 70:30. This ratio was found to be the optimum in a small study carried out separately. The wet coatings were applied onto black base coated standard Q-panels with a wire-wrapped barcoater. After drying at room temperature for 15 minutes they were cured at 140°C for 30 minutes. The dry film thickness varied between 30 and 35 µm.

As reference system for the evaluation, a standard commercial acrylic resin, free of Cardura was included in the study (resin Y). It was cured in the same way as the experimental systems, not using any additives.

Mar resistance test method

There are 2 kinds of scratches, the fractured, irregular ones involving particle loss, and the smooth regular ones involving only elastic and plastic deformation. Mar resistance can be described as the ability of a coating to withstand permanent deformation against surface abrasions or scratches. The scratches of automotive top coats are mostly caused by car washing, and not necessarily by the nylon bristles but more by the dirt grit particles present on the coating : it is these scratches which reduce the gloss of the coating.. Most of these visible scratches belong to the category of the fractured scratches and therefore, we wanted to use a method which would simulate these damages. The literature places a lot of focus on methods to characterise the damage. These methods, which cover indentation methods, scanning electron microscopy and nano-scratch measurements, are rather complex and difficult to link to eye perception.

Therefore a simpler method which simulates car wash damage (combination of ASTM D2486 adapted with some recommendations given in reference [6]) was applied and fine-tuned. This method is based on gloss and ΔL* measurements.

Standard Q-panels were coated with a commercially available black waterborne base coat. Black was chosen as dark colours shows larger ΔL* values than light colours [8]. The clear coats were applied on the base coat as described above. Then, the panels were put for 4 days at 23°C before evaluation. The coatings were not evaluated directly after cure as it was found in an earlier study on two different acrylic resins, with different T_g and composition that the gloss after abrasion was influenced by the time the coatings were allowed to "rest" after cure.

As shown in Figure 4, highest gloss levels were obtained with coatings which were evaluated 4 days after cure. After 10 days there was no significant change anymore.

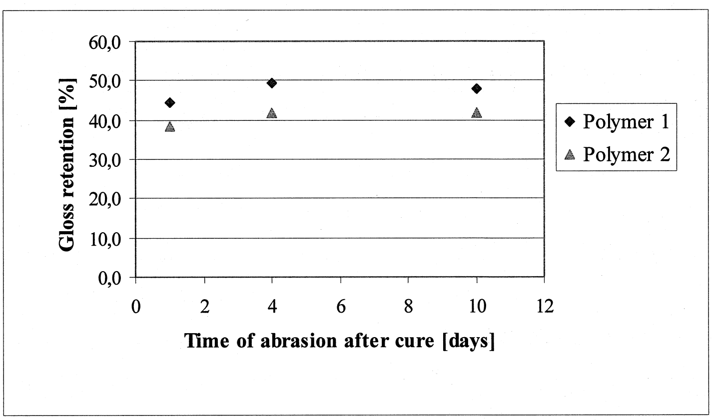


Figure 4. Experiment on determining full cure for melamine based coatings

After 4 days storage at 23°C, the panels were rinsed with water and carefully dried. The panels then were mounted on a glass plate in a wet scrub tester (Braive instruments). Subsequently 5 ml of an abrasive slurry, consisting of 6 wt% sand (Minex 4), 5 wt% of isopropanol and 89 wt% of deionized water was placed on the panel. The abrasive slurry was mixed 10 minutes before use. Before use the nylon bristle brush (meeting the requirements as specified in ASTM 2486) was rinsed with water and then, the panels were scrubbed. Some extra weight was put on top of the brush so that the the total weight on the coating was 438g.

During the scrub test the brush was moved 10 times back- and forwards over the panel with a stroke frequency of 37 cycles per minute. The panel then was removed, rinsed with deionised water and carefully dried with soft paper. The damage was assessed by measuring the 20°gloss retention and also the ΔL*. Figure 5 shows that, there is a clear linear relation between ΔL* and the 20° gloss.

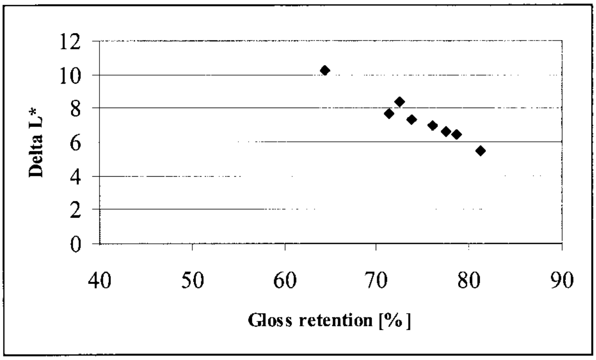


Figure 5. Relation between 20° gloss retention and ΔL* of the clear coats after abrasion

To determine the reliability of the test method, the level of variation in the mar resistance test was determined using the principle of the minimum discernible difference.

Determination of the minimum discernible difference in the wet scrub mar resistance test

For determination of the minimum discernible difference (MDD) in the wet scrub mar resistance test, the clear coat based on polymer 2 was applied onto 5 test panels which were subsequently subjected to the wet scrub mar resistance test as described above. Table 3 shows the results together with the calculated standard deviations. To allow a comparison of the test results, the MDD was calculated. For a single observation, the MDD is 4.52%. This means that if one panel per system would be evaluated, the results of two different systems would only be significantly different if their gloss retention differed more than 4.52%. Reducing the MDD is possible by increasing the number of test panels (n). For example if the number of test panels is increased to 4, the MDD decreases to 2.26%. This was considered as an acceptable level of variation and therefore always 4 clear coats were applied and tested for each system.

Table 3. Detection of the minimum discernible difference (MDD) in the wet brush test

WET SCRUB

Polymer 1	Average gloss before abrasion [%]	Average gloss after abrasion [%]	Average gloss retention [%]
Panel 1	89.1	40.8	45.8
Panel 2	89.6	38.0	42.4
Panel 3	89.3	38.1	42.6
Panel 4	89	38.7	43.5
Panel 5	89.4	37.2	41.6
Average:	**89.3**	**38.6**	**43.2**
Pooled standard deviation:	**0.24**	**1.36**	**1.61**
Standard error of average: (standard deviation/ sqrt(n))	**0.10**	**0.68**	**0.81**
95% conf interval based on s:	**0.18**	**1.87**	**2.06**
MDD for a single observation:	**0.67**	**3.81**	**4.52**
MDD for an average of 4 observations:	**0.33**	**1.91**	**2.26**

The recovery of our polyacrylic-melamine systems was measured to see if mainly fractured scratches were generated. This was done by remeasuring the gloss retention after one week storage at 23°C after abrasion and comparing the difference between the two gloss values obtained. The recovery was in general very small which demonstrates that almost all scratches were fractured. This is in line with other studies that showed that fractured scratches do not recover [1]. This shows that our test method is indeed adapted for measuring the permanent deformation caused by mar resistance. Another difference between fractured and plastic scratches is that fractured scratches are visible, independent of the incident light and observation direction [9]. Also this was the case for our test panels.

Determination of crosslink density and glass transition temperature T_g

From literature it is known that mar and acid etch resistance of coatings are influenced by their crosslink density and T_g and therefore a study into these parameters was done using dynamic mechanical analysis (DMA). The crosslink density is based on the tensile storage modulus, E' in the rubbery plateau region above T_g and is defined as ν_e, i.e. the number of moles of elastically effective network chains per cubic centimetre of film. T_g was determined using the temperature at which E" is maximum. The free coating films were obtained by applying the clear coats on release paper from which they could easily be removed after cure. This technique is well documented in literature [10].

Discussion of results

The performance of Cardura E10P based acrylics

Melamine based coatings are primarily crosslinked via ether linkages, which are prone to hydrolysis upon exposure to acid rain.

Typical factors that improve the acid resistance of a coating are a high coating T_g, high crosslink density and high hydrophobicity as they minimise water absorption of the film. Also the incorporation of bulky hydrophobic groups is known to increase the acid resistance as such structures shield vulnerable linkages from acid attack.

In this context it can easily be understood that the incorporation of Cardura into the resin imparts improved acid resistance. To obtain the right acid resistance with Cardura free acrylic coatings, the coating T_g must be high. When using Cardura, this is no longer mandatory.

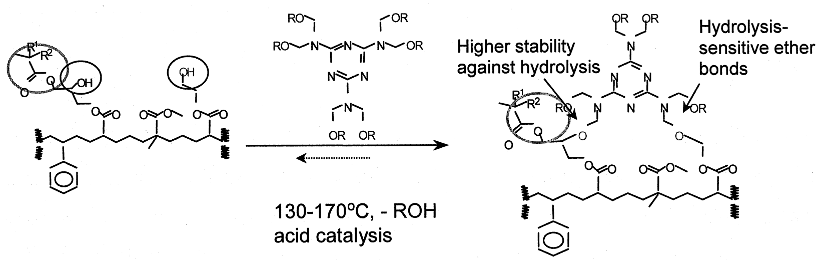


Figure 6. Protection of melamine ether bounds by the Versatile bulky group of CE10P

Mar resistance depends on a number of factors such as chemical composition of the resin, choice of crosslinker, crosslink density, additives, processing procedures but also coating T_g.

The possibility to decrease the coating T_g when using Cardura, without jeopardising acid resistance, is a real advantage as it might allow the design of coatings with good scratch and acid resistance.

To confirm this assumption concerning these anticipated benefits of incorporating Cardura, a range of acrylics all containing 20% Cardura E10P but with having varying theoretical Fox T_g's (in order to obtain different coating T_g's) were prepared. To obtain these differences in coating T_g's, the concentrations of BA and MMA in the resins were slightly varied. For resins D and E, also the styrene concentration was adjusted.

Within this series of resins, the crosslink density was almost the same (see Table 4).

Table 4. Crosslink density of the 20% CE10P made acrylic resins

Name :	Resin A	Resin B	Resin C	Resin D	Resin E
Cardura E10P concentration [wt%]	20	20	20	20	20
Crosslink density (mole/m^3)	1260	1310	1200	1300	1310

Figure 7 clearly shows the linear relation between the gloss retention and the coating T_g at constant crosslink density : the lower the coating T_g, the higher the gloss retention. The best scratch resistance, i.e. a gloss retention of 81%, is obtained with resin E, which has the lowest coating T_g. This is in line with previous results of the open literature publication [5]. The recovery of the coatings was also measured, but was not considered to be significant. More details on the overall coating characteristics of this resin E are given later.

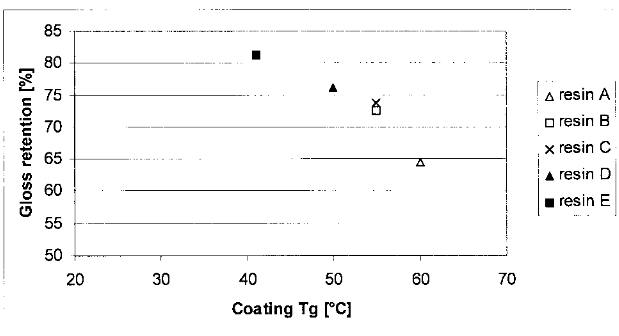
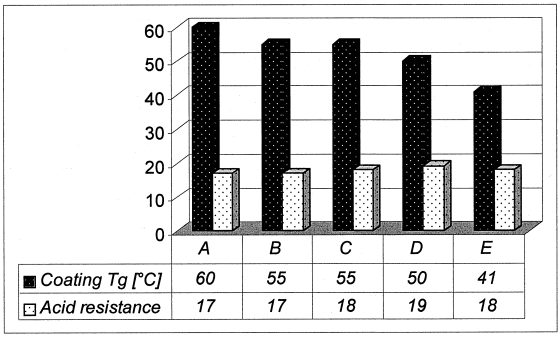


Figure 7. Gloss retention versus coating T_g for a series of 20% Cardura E10P containing resins

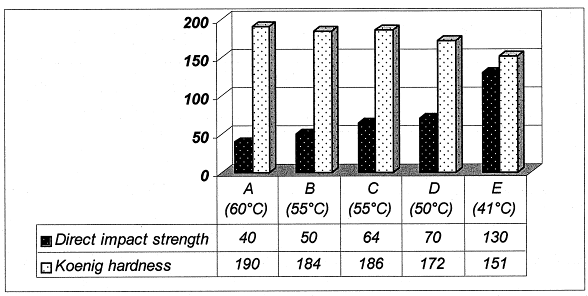
On the other hand, acid resistance normally decreases with decreasing coating T_g. However, Figure 8 clearly shows a stable performance in acid resistance, whatever the coating T_g. This is linked to the incorporation of 20% of Cardura E10P.



	A	B	C	D	E
Coating Tg [°C]	60	55	55	50	41
Acid resistance	17	17	18	19	18

Figure 8. Acid resistance versus coating T_g for a series of 20% Cardura E10P containing resins

Figure 9 shows that, as expected, the coating hardness of the systems containing 20% CE10P increases with increasing coating T_g whilst lowering the coating T_g improves the flexibility of the coating. Ideally coatings should have both high hardness and high flexibility or at least a good balance between both. This balance is best with the resin E.



	A (60°C)	B (55°C)	C (55°C)	D (50°C)	E (41°C)
Direct impact strength	40	50	64	70	130
Koenig hardness	190	184	186	172	151

Figure 9. Hardness and flexibility for the 20% Cardura E10P containing clear coats with different coating T_g

The results discussed above concerned resins with a fixed Cardura content of 20 wt%. In the next step the effect of varying Cardura content on coating performance was studied. Therefore, 4 experimental acrylic resins, with 0%, 20% and 40 wt% Cardura were evaluated. A standard commercial resin for OEM automotive applications, which contained no Cardura (resin Y), was also used as benchmark.

Table 5. Coating characteristics of acrylic resins with different Cardura concentrations.

	Resin X	Resin Y	Resin E	Resin F
Cardura E10P concentration [%]	0	0	20	40
Final AV of the resin [mg KOH/g]	5.5	9.7	4.7	4.1
Crosslink density [mole/m^3]	1850	1630	1310	940
Coating T_g (by DMA) [°C]	64	44	41	30
Surface tension	34	38	<34	<34
Gloss retention [%]	78.7	71.4	81.3	77.5
Recovery [%]	2.8	5.5	2.7	1.7
Acid resistance [0= poor,-30= excellent]	10	3	18	22

Several remarks concerning the resins and coating properties listed in Table 5, can be made. Firstly, the obtained crosslink densities are somewhat different. This can most likely be explained by the differences in final acid value of the resins which plays a role on the crosslinking as the butoxymethyl melamine that is used, is catalysed by acid. Secondly, it is clear from the table that not only the crosslink density is important for obtaining a good mar resistance (expressed as gloss retention). The positive contribution of increasing the Cardura content at low T_g is clearly demonstrated. The two coatings based on the 0% CE10P resins are higher in crosslink density than those containing Cardura, but despite this higher crosslink density, their gloss retention after the scrub test is not as good as that of the resin E. This confirms that scratch resistance is not only influenced by the crosslink density, but by a combination of different parameters including the resin composition.

The analysis of the acid resistance results show the positive influence of incorporating CE10P in the resin: resins E and F clearly outperform the benchmarks in that respect. Resin E can be considered as an optimum if a good balance of acid and scratch is needed.

For commercial application in automotive OEM, coatings should in general impart not only a good acid and/or mar resistance, but also good mechanical properties. Spider charts are a way of simultaneously illustrating the various coating performance attributes relative to the assumed best achievable or desired level. The overall performance of the systems increases with increasing surface of spider chart.

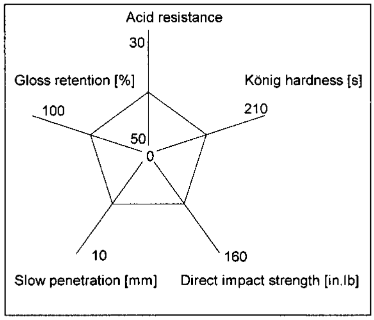


Figure 10. Legend of the spider chart on coating properties

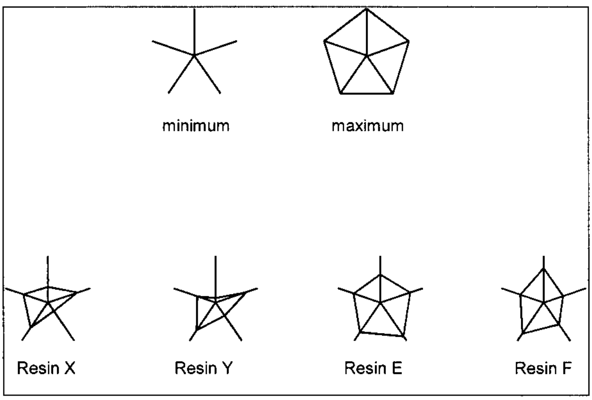


Figure 11. Spider chart on coating properties

Figure 11 shows the overall coating performance as a function of the Cardura content of the base acrylic resins. It clearly demonstrates that resin E imparts the best performance and provides unique properties, i.e. a combination of very good acid and mar resistance together with very good mechanical properties. This system outperforms the commercial benchmark as well as the Cardura free resin X.

Conclusions

As a first step of this study, we developed a simple and reliable method for testing the mar resistance of coatings. This method allowed us to assess the importance of incorporating Cardura E10P in OEM melamine-based systems. Our results show that Cardura is an excellent building block for the design of high quality resins as it allows to get coatings with a very good acid and mar resistance in combination with very good mechanical properties.

Acknowledgements

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References

[1] U. Meier-Westhues, U. Biskup, Ph. Yeske and M. Bock: "Polyurethane clearcoats with optimized resistance to scratching and chemicals", *Praxis-Forum meeting of the "Automobilkreis Spezial"*, Bad Nauheim (February 1999).

[2] RPP: "Cardura E10P based acrylic polymers for high quality first finish automotive clear coats", *Product Bulletin, CM 4.2.1.*

[3] B.V. Gregorovich and I. Hazan: "Environmental etch performance and scratch and mar of automotive clearcoats", *Progress in Organic Coatings, 24* (1994) 131-146.

[4] RPP: "Solvent selection for acrylic polymers", *Product Bulletin, CM 4.1.1.*

[5] Peter Betz and Angelika Bartelt: "Scratch resistant clear coats: development of new testing methods for improved coatings", *Progress in Organic Coatings, 22* (1993) 27-37.

[6] J.L. Courter and E.A. Kamenetzky: "Micro- and nano- indentation and scratching for evaluating the mar resistance of automotive coatings", *PAINTINDIA* (1999) 115-128.

[7] V. R. Kamath and J. D. Sargent Jr.: "Production of high solids acrylic coating resins with t-Amyl peroxides: A new way to meet VOC requirements", *PAINTINDIA* (1991).

[8] K. Shibato, S. Beseche and S. Sato: "Studies on acid etch- and scratch resistance of clearcoats for automotive industry", *4th Asia-Pacific Conference* paper 4.

[9] V. Jardret, B. N. Lucas and W. Oliver: "Scratch durability of automotive clear coatings: A quantitative, reliable and robust methodology", *Journal of Coatings Technology* (August 2000) Vol.72.

[10] L. Hill, K. Kozlowski: "Crosslink Density of high solids MF-cured coatings", *Journal of Coatings Technology*, 59 (751), 63-71 (1987).