New low-VOC acrylic polyol dispersions for two-component polyurethane coatings

J Billiani and W Wilfinger

Solutia Austria GmbH, A-8010 Graz, Leechgasse 21, Austria

Summaries

New low-VOC acrylic polyol dispersions for two-component polyurethane coatings

Two-pack water-borne polyurethane coatings are a relatively new technology which promises excellent performance properties combined with a low content of volatile organic compounds (VOCs). In this paper the effects of a polymer structure of acrylic polyol dispersions on film-formation and final coating properties (pot life, hardness, gloss) are investigated. Two kinds of water-borne acrylic polyols have been investigated. Both water-borne polyols show good results in applicability, hardness and chemical stability when elevated temperatures can be used. The polyol based on a single-step synthesis route is superior in pot life, hardness and chemical stability. The low paint VOC of 130g/l indicates that this polyol already fits demands of future VOC regulations.

De nouvelles dispersions de polyol acrylique à faible teneur en VOCs dans le domaine du polyuréthane deux composants (two-pack)

Les revêtements de polyuréthane à deux composants (two pack) hydrodiluables représentent une technologie qui est relativement nouvelle et qui promet d'excellentes propriétés dans le domaine de performance. Elles ont aussi une faible teneur en VOCs.

Dans cet article les effets des dispersions d'une structure polymérique de polyol acrylique sur la formation de feuils et sur les propriétés finales du revêtement (la durée de conservation en pot, la dureté, le brillant) sont étudiés. Deux types de polyols acryliques hydrodiluables ont été investigués. Les deux polyols hydrodiluables produisent de bons résultats dans les domaines de la facilité d'application, la dureté, la stabilité chimique quand des températures élevées peuvent être employées. Le polyol qui est basé sur une route de synthèse à une étape s'est montré supérieur en ce qui concerne la durée de conservation en pot, la dureté, et la stabilité chimique. La faible teneur en VOCs du revêtement (130g/l) indique que ce polyol répond déjà aux futures exigences des règlements concernant les VOCs.

Neue Lösungsmittelarme Acryl-Polyol Dispersionen für Zweikomponenten Polyurethane

Zweikomponenten Polyurethanlacke auf Wasserbasis sind eine relativ neue Technologie, die hervorragende Leistung mit einem geringen Lösungsmittelgehalt kombiniert. Diese Studie beschäftigt sich mit dem Effekt der Polymerstruktur von Acryl-Polyol Dispersionen auf Filmbildung und die Eigenschaften des Lackes, wie Haltbarkeit, Härte und Glanz. Zwei Arten von wasserlöslichen Acryl-Polyol Dispersionen wurden erforscht. Beide erzielten gute Ergebnisse in bezug auf Auftragbarkeit, Härte und Hitzebeständigkeit. Das Polyol, das mittels einer Einstufensynthese hergestellt wurde, zeigte bessere Haltbarkeit, Härte und Stabilität. Der geringe Lösungsmittelgehalt von 130 Gramm/Liter zeigt, daß dieses Polyol bereits für zukünftige Lösungsmittelgrenzwerte verwendbar ist.

For correspondence contact

J Billiani

Solutia Austria GmbH, A-8010 Graz, Leechgasse 21, Austria

Tel: +43 316 344 263 Email: Johann.Billiani@vianova-resins.de
Fax: +43 316 344 130 263

Copyright OCCA 2002

Introduction

Conventional two-component polyurethane-based (2K-PU) water-borne coatings have become increasingly popular over recent years, driven by market demands for higher-performance, formaldehyde-free, low-VOC thermoset water-based coatings. Nowadays legislation, restricting emissions and residues, is the major driving force for the development of low-polluting or even pollution-free coatings. VOC (volatile organic compound(s)) is the key phrase in the paint and/or binder industry, and is one of the driving engines for the development of new, environmentally compatible binders like high solids, aqueous or powder coating resins.

For the moment there is no uniform definition for VOCs. In the USA for example, VOCs are only those products which are photochemically active in the atmosphere. European guidelines however, define VOCs as those organic compounds which have a vapour pressure >1 Pa at 20°C. As with definitions, VOC regulation is also lacking uniformity. In the USA VOC regulations have existed for several years. In Europe only some countries (UK, Austria and Switzerland) have set up regulations. The other EU members are now following in converting the new solvent directive (1999/13/EC) into national law. The logical consequence is that environmentally compatible binders, for example high solids or water-bornes, will continue to grow in importance.

Background

Conventional two-component polyurethane systems (2K-PU) have been successfully used in various high performance applications. Typical examples are OEM (original equipment manufacturing) topcoats and clearcoats, automotive repair coatings (fillers, clear- and topcoats), industrial paints, furniture lacquers, plastic coatings, etc. The unique cross-linking chemistry, based on the reaction of OH-functional binders with polyisocyanate hardeners, results in high molecular-weight polyurethanes with excellent outdoor durability, outstanding chemical resistance and very good mechanical properties. The urethane linkage in the polymer backbone provides high resistance against chemicals (solvents as well as acids and bases), and the high density of hydrogen bonding results in the formation of a stable physical network which contributes to the good mechanical properties of the coating.

Among the various options for very low emission coatings, water-borne binders generally have a high potential for decreasing VOCs. In addition to the usual problems which generally result from the use of water as a solvent, 2K-PU cross-linking suffers from the undesired secondary reaction of the polyisocyanate hardener with water.

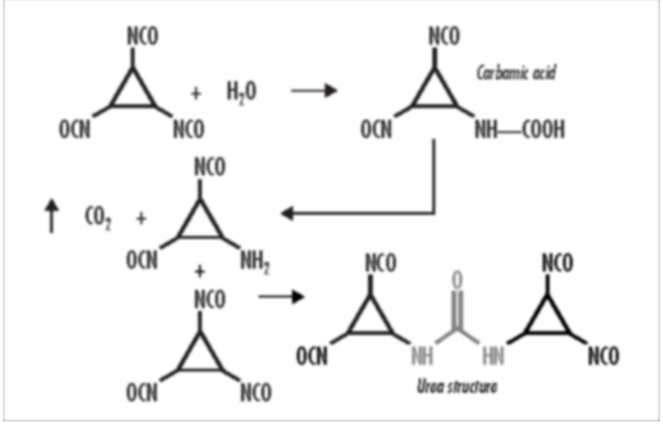
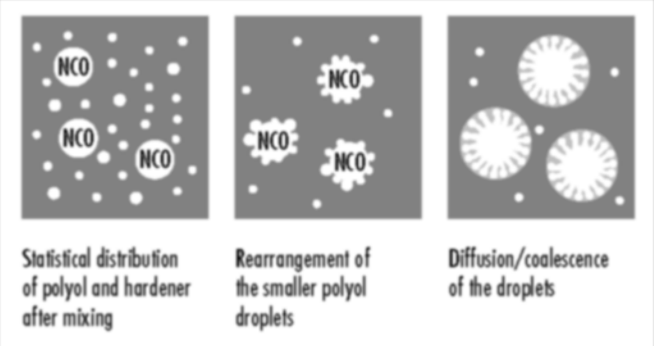


Figure 1: Reaction of polyisocyanate with water

This well known side reaction was responsible for the fact that the use of isocyanate hardeners in aqueous systems was unthinkable among experts until the beginning of the 1990s, when aqueous 2K-PU systems were introduced.[1] Fortunately it has been recognised that this side reaction is less critical than was previously thought.The reactivity of aliphatic isocyanates with water is much lower than with the hydroxyl groups of polymers.[2] When mixed with an aqueous resin emulsion, hydrophobic polyisocyanate hardeners tend to migrate preferably into the organic resin phase, due to their solubility characteristics. There the productive cross-linking reaction with hydroxyl groups of the resin is favoured.



Statistical distribution of polyol and hardener after mixing
Rearrangement of the smaller polyol droplets
Diffusion/coalescence of the droplets

Figure 2: Mixture of polyol dispersion and polyisocyanate hardener

The undesired secondary reaction with water, which leads to the by-products poly urea and carbon dioxide, takes place as well, but it will not impair the coating properties if only low amounts of these by-products are formed. After application, coalescence of the polymer droplets and evaporation of water is a fast process. In this final stage the reaction with water can be balanced sufficiently.

A major aspect in developing aqueous 2K-PU systems is to prevent the undesired secondary reactions with water and obtain the best cross-linking possible. Appropriate modification of the hardener component (hydrophilised polyisocyanates) has improved dispersibility of the hardener and ease of mixing, but extensive hydrophilic modification may cause drawbacks in hardness and chemical resistance. Sophisticated mixing equipment is another tool to overcome some of the problems,[3] but the use of this kind of machinery has not really been accepted in the paint industry. The polyol is a major component in aqueous 2K-PU systems. It should support dispersibility and quick incorporation of the polyisocyanate hardener. Optimisation of the polyol component is a powerful measure which can contribute much to the performance of the 2K-PU system. The aim of this work was to investigate the effects of the synthesis route of two water-borne acrylic polyols on their application properties in aqueous 2K-PU coatings.

Acrylic polyol synthesis

Water-borne acrylic polyols for cross-linking systems are low-to-medium molecular-weight polymers which are stabilised in the aqueous phase mainly electrostatically. Thus amine salts of pendant carboxylic groups have to be formed. With water-borne binders the tailoring of the rheological behaviour is one of the keys for good performance at the application stage. Rheology can be affected by various parameters. One of the most important is suitably tailored polymer segmentation. It has been proved that polymer structures with hydrophilic and hydrophobic segments that are separated, exhibit better rheology than where these functions are distributed statistically along the polymer backbone. Actually the authors use different synthesis routes to build polymers of segmented hydrophilic/hydrophobic structures.

Single-step synthesis

The single-step synthesis route is based on a special solution polymerisation technique, which additionally utilises the reaction between oxirane and acid groups to produce water-borne binders suitable for one and two-pack applications. After charging an oxirane-functional component, a monomer mixture containing carboxyl- and hydroxyl-functional monomers is fed into the reactor by constant feed rate and polymerised continuously. During the early stages of the polymerisation the carboxylic groups of the polymer are consumed by the oxirane component and ester linkages are formed.

Thus non-ionic, hydrophobic polymer segments are created during the first stages of polymerisation, preferably while ionic, hydrophilic polymer structures are built in the final reaction period, when all available oxirane functionality has been consumed. Finally the polymer is neutralised and emulsified by addition of water.

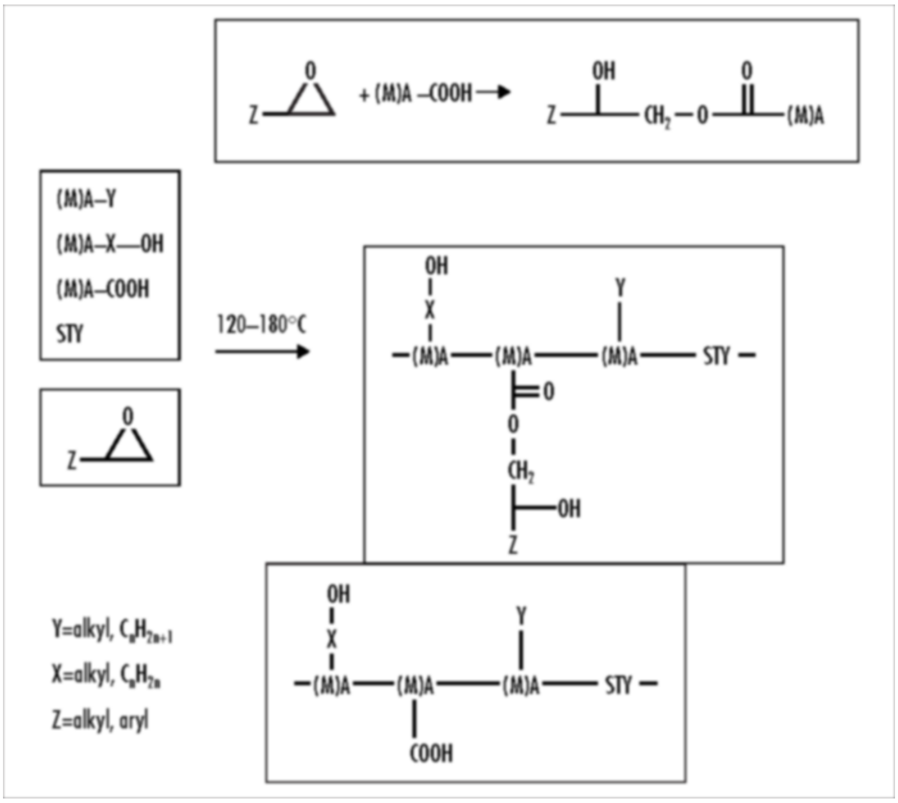


Figure 3: Single-step synthesis scheme

Multi- step synthesis

This synthesis route is subdivided into discrete steps. Carboxyl-functional (hydrophilic) and hydroxyl-functional (hydrophobic) acrylic intermediates are made separately by solution polymerisation techniques. After partial co-esterification of the two intermediates, a water-soluble polymer is formed which is consecutively emulsified by neutralisation of the mixture with amine (dimethyl ethanol amine, DMEA) and the addition of water. Polymers of this type have been used in thermosetting applications for years with very good success (VIACRYL™). For low temperature two-pack applications the surface properties, for example levelling of the existing one-pack-type polymers, was rather poor. Therefore the flow properties had to be improved, which was achieved mainly by lowering the molecular weight.

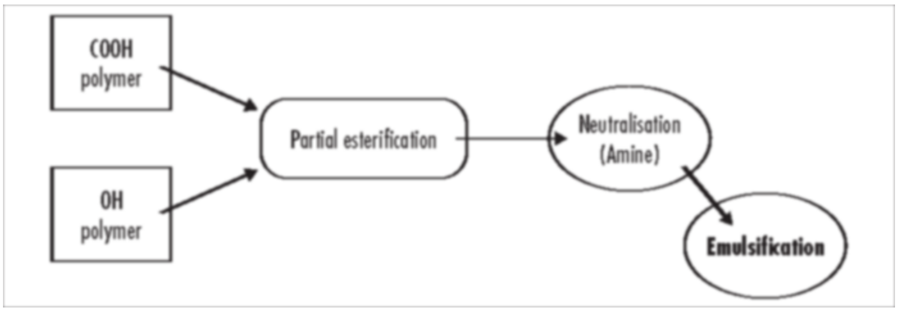


Figure 4: Multi-step synthesis scheme

In Table 1 the major characteristics of the two acrylic polyols are summarised.

Table 1: Characterisation of the acrylic polyol dispersions

	*Polyol *1*	*Polyol *2*
Synthesis route	single step	multi step
Solids (%); DIN ISO 3251	42	43
Acid value (mg/g); DIN ISO 3682	30	36
Hydroxyl value (mg/g); DIN 53240	130	110
Dynamic viscosity (mPa.s) DIN EN ISO 3219	2000	1500
Cosolvents (%)	4	12
VOC (g/l (lb/gal))	90 (0.8)	239 (2.0)
Particle size (nm)	120nm	180nm

Preparation of white paint

The polyol dispersions described in Table 1 were investigated in a simple white paint formulation. The polyols were cross-linked with commercially available polyisocyanate hardeners. A mixture of a hydrophobic isocyanurate- type hexamethylene diisocyanate (HDI) trimer containing 23% NCO and a hydrophilic-modified type with 17.4% NCO (ratio 4:6) was used at a NCO:OH ratio of 1.5. The pigment binder ratio was 0.8:1. No cross-linking catalyst was used. A white pigment paste was put down, and a polyol dispersion, additives and hardener (pre-mixed with solvents), were added in sequence by stirring. Final-

Table 2: Characteristics of white paint

	*Polyol *1*	*Polyol *2*
NCO:OH ratio	1.5	1.5
Pigment/Binder ratio	0.8/1	0.8/1
Viscosity DIN 53211, 23°C(s)	28	29
VOC (ready to use) (g/l)	129	244
VOC (ready to use) (lb/gal)	1.1	2.1
High solids – value (%)	91	82
Paint solids (%)	57	57

ly the paint was diluted with water and viscosity was adjusted to about 30 DINs (DIN 53211, 23°, 4mm). After ten minutes defoaming the paint was applied.

Results and Discussion

Cross-linking

Cross-linking very much depends on the drying temperature. Several industrial applications preferably use elevated temperatures, but in many cases (with heavy and bulky substrates) the reaction must take place at ambient temperature only. A serious, and in terms of practice, relevant evaluation must consider both cases. Therefore the following conditions were used for testing: one and seven days drying at ambient temperature (23°C), and forced drying at 60°C for 45 minutes followed by one and seven days drying at 23°C.

In hardness as well as solvent resistance, polyol 1 outperforms polyol 2. It is very significant that really good cross-linking is reached only under forced drying conditions (see Figures 5 and 6). At ambient temperatures only polyol 1 reaches a sufficient level. In both cases a significant part of the cross-linker capacity is hindered from reaction probably by chain mobility restrictions.

The rather low cross-linking level of polyol 2 at ambient temperature was surprising, because this kind of polyol performs well in one-pack thermosetting applications. The authors surmise that there are two possible explanations for this finding both of which are related to the synthesis route. During partial esterification of the two acrylic components a certain amount of carboxyl-functional intermediate remains unreacted in the mixture. This component probably does not participate in cross-linking, since it is bearing COOH groups only. It behaves like a plasticiser. Further partial esterification of the two acrylic intermediates leads to small amounts of pre-cross-linked microgel, which could probably be responsible for early freezing of the cross-linking reaction.

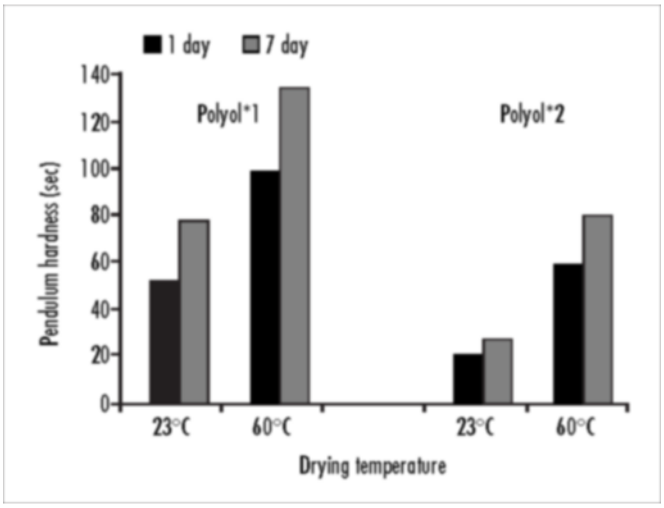


Figure 5: Dependence of hardness development on drying conditions (200µm wet film thickness application on glass plate)

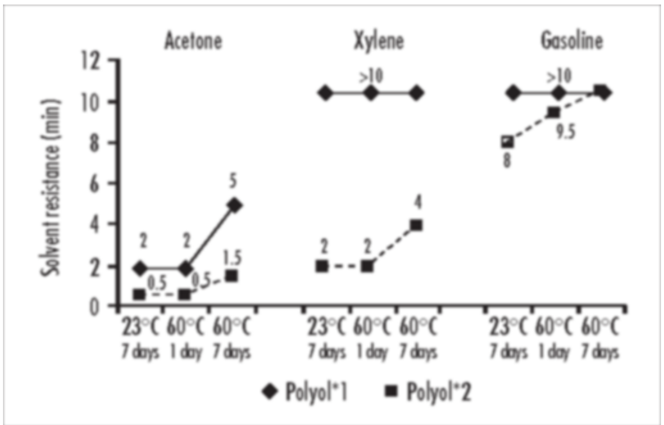


Figure 6: Chemical resistance of paint films under various hardening conditions (one day and seven days) (200µm wet film thickness application on glass plate)

Potlife

For evaluation of potlife the behaviour of the paint was monitored visually (gassing, viscosity change, coagulation). Unlike conventional 2K-PU systems, which exhibit a steady increase of viscosity, water-borne 2K-PU paints do not always have a reliable relationship between viscosity increase and potlife (see Table 3). Well stabilised aqueous paints can remain nearly unchanged in terms of viscosity and appearance, even though a large portion of the reactive groups of the hardener have already been consumed.

Table 3: Viscosity change during paint potlife (DINs, DIN 53211, 23°C, 4 mm)

	*Polyol *1*	*Polyol *2*
0 h	28	30
2 h	26	72
4 h	29	foam, gelled

Therefore the paints were applied additionally onto glass plates instantly after mixing with the hardeners, and at intervals of two and four hours (induction time) after paint preparation respectively. Pendulum hardness and gloss of the coating were measured after one and seven days drying at 23°C (see Figure 7).

These data, combined with the authors' visual observations, were used to estimate potlife. Polyol 1 shows significantly better potlife (four to five hours) than polyol 2 (maximum two hours). Paints based on polyol 2 become increasingly foamy when approaching the end of potlife, which indicates a higher amount of side reaction with water. This was not expected, because this kind of polymer is known to be an even better emulsifier for other (hydrophobic) partners than polyol 1. The lowering of pendulum hardness, which is observed in both systems with increasing induction time, clearly indicates that significant amounts of the isocyanate have reacted with the polyol and/or water in the pot already and hence are missing for the cross-linking reaction after film formation. This is seen in the

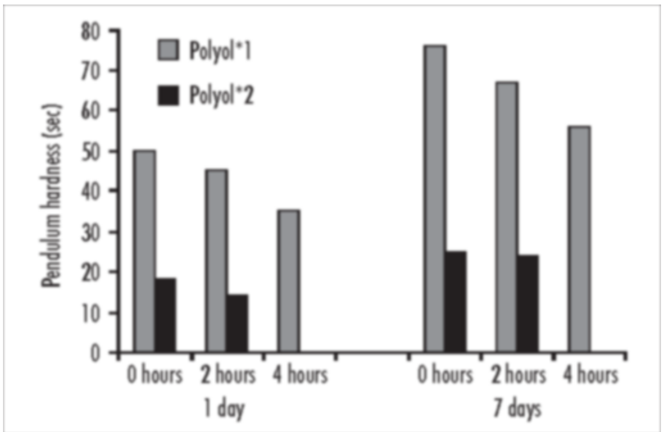


Figure 7: Effects of potlife on development of hardness (application on glass plate, 200µm wet film thickness)

ambient temperature results (see Figure 7) as well as at an elevated temperature. Fortunately the pre-cross-linked domains of the paint are small enough to cause no surface defects, because gloss remains more or less unchanged (see Table 4).

Table 4: Measurement of gloss with increasing induction time (% gloss at 20° angle; application on glass plate, 200µm wet film thickness; seven days dried at 23°C)

	*Polyol *1*	*Polyol *2*
0 h	74	78
2 h	74	78
4 h	70	—

Paint application

Application was characterised by spraying a thickness gradient on steel panels (30x20cm) with a series of holes of 0.5cm diameter arranged diagonally to evaluate sagging. The plates were inspected after drying for one day at ambient temperature.

Table 5: Spray application results

	*Polyol *1*	*Polyol *2*
Levelling (µm)	≥ 20	≥ 15
Pinholes (µm)	≥ 62	≥ 48
Sagging (µm)	≥ 66	≥ 44
Gloss 20°/60°	73/86	82/92
Scratch hardness (fingernail)[a]	0	4

a Arbitrary rank: 0 = no marks (best), 4 = scratched (worst)

Coalescence and levelling are very good in both systems. With polyol 2 significantly better gloss is obtained, but polyol 1 also shows good gloss and is superior in sagging and solvent popping (degassing). Scratch hardness behaves as expected from pendulum hardness results.

Table 6: Humidity cabinet test (144 hours treatment)

	*Polyol *1*	*Polyol *2*
Drying conditions: 7 days, 23°C		
Gloss 20°[a]	72/70/70	81/27/64
Degree of blistering, DIN 53209	m0/g0	m2/g3
Drying conditions: 45 min, 60°C followed by 7 days, 23°C		
Gloss 20°[a]	73/73/71	80/72/73
Degree of blistering, DIN 53209	m0/g0	m0/g0

a Initial result/immediately after test/after 16 hours regeneration

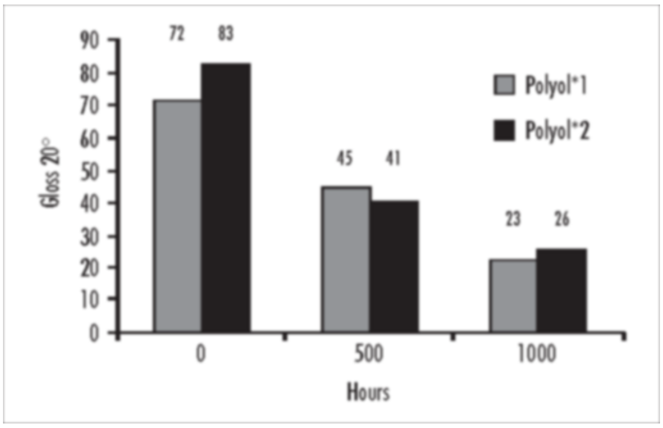


Figure 8: Weather resistance (144 hours treatment, accelerated weathering/UVCON)

Even under ambient dry conditions polyol 1 already shows good performance, whereas polyol 2 clearly fails. Obviously polyol 2 is cross-linked insufficiently under those conditions. After applying higher temperatures the performance level significantly improves.

Accelerated weathering results are good for both systems. Long-term exterior durability tests are still running. The preliminary results are very promising for both acrylics.

References

1. Mirgel V, 'New resin systems for high performance water-borne coatings, Proc 18th Int Conf of Organic Coatings Science and Technology, Athens, 6th to 10th July 1992
2. Hegedus C R, A G Gilinski and R J Haney, 'Film-formation mechanism of two-component water-borne polyurethane resins', *Journal of Coatings Technology*, **68**, 51–61, 1996
3. Hovestadt W, B Kliensiek and M Melchiors, Homogenes Vermischen von wässrigen 2k-Polyurethanlacken, *Farbe & Lack*, **106**, 40–4, 2000