

OH-functional resins

Acrylates or polyesters for low VOC 2K-PUR coatings?

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For car refinishing and industrial finishing, two new OH-polyester resins have been developed, which can be used as sole binders or as cobinders for 2K low VOC PUR lacquers. The films show good drying properties, high film hardness and good chemical resistance. VOC values are below 420 g/l for clear and pigmented coatings and weatherabilities of these systems are often better than those of corresponding acrylic polyol systems.

The EU solvent regulation (1999/13/EG) and DEKO regulation (2004/42/EG) demand that industrial or handicraft varnishers use only compliant varnishes or lacquers. Thus, for car refinishing the following maximum emissions are valid from 1.1.2007.

- Primer surfacer: max. 540 g/l (wet on wet), otherwise: 250 g/l
- Base coat, clear coat or pigmented top coatings: max. 420 g/l

In addition, the EU-commission will discuss in 2008, whether a further reduction of emission limits is possible and necessary.

Higher solid content will have to be achieved by 2007

Today, "medium solids" 2K clear or pigmented top coats for car refinishing, or pigmented coatings for high performance industrial applications are based on medium viscous OH-functional acrylic resins (OH number: 100 to 160 mg KOH/g solids resin). Such coatings show an excellent gloss, good drying (dust free: ca 15 min.,

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tack free: ca 3 hours), good resistance against weathering and a good chemical resistance (e.g. against gasoline, diesel, motor oil). They are formulated with approx. 55 w/w% solids (21 s, cup 4 mm, 23°C), corresponding to ca. 455 g/l emission. In 2007, however, about 59 w/w% will be required to fulfill the regulations (420 g/l).

Acrylics: Low Mw reduces VOC, but affects performance

Molecular weights will then have to be reduced drastically, because the solid content of the lacquer is inversely proportional to the molecular weights of both the polyisocyanate and the polyol components.

For acrylic resins, this can easily be achieved by higher initiator concentrations, higher polymerization temperatures or by the use of special initiators, which result in narrow molecular weight distributions. Although such OH-acrylic resins show the required higher solid content, they also tend to show very long dust and tack free times, because these systems are governed by the strong reduction of the glass transition temperature below a critical molecular weight. Therefore, "high solids" acrylic resins normally have a lower styrene content and special monomers



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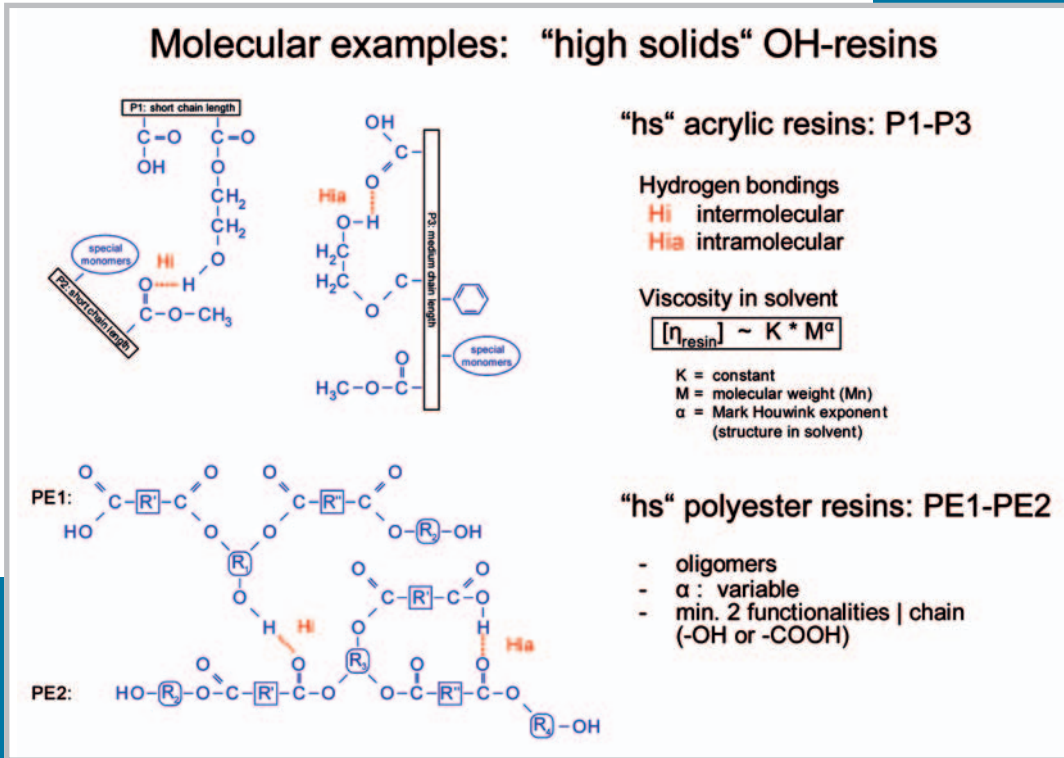


Figure 1: Comparison of the molecular structure of "high solids" acrylic and polyester polyols

are incorporated to achieve a good physical drying and viscosity reduction at the same time. However, the main disadvantages of these acrylic resins are still present: The degree of functionality (i.e. the number of OH-groups/chain) is lower and so is the polyurethane network density, often resulting in a reduced chemical resistance and weatherability. If, on the other hand, the OH-functionality is increased, this results in more hydrogen bonds and a viscosity increase (Figure 1), ultimately leading to "higher VOC lacquers".

Acrylic resin end groups are vulnerable to UV light

In addition, the polyurethane network with medium solids acrylic resins contains about 100 chain ends/cm³, whereas about 1000 chain ends/cm³ are present in the high solids acrylic products. More chain ends imply a more likely deterioration of the coatings by UV-light in outdoor applications.

High solids polyesters with OH- and acid functionality

A new concept is represented by condensation products, i.e. low molecular weight

polyesters, without aromatic structural units, which have at least two functionalities at the chain ends: an OH-group for isocyanate hardening and a COOH-group for catalytic effects.

Table 1: Properties of the new OH-functional polyester resins

| | WP 6756 | WP 6741 |
|--|---------------|---------------|
| Solid content in butyl acetate (%) | 78 | 80 |
| OH-number (mg KOH/g) | ca 185 | ca 135 |
| Acid-number (mg KOH/g) | ca 22 | ca 18 |
| Viscosity (delivery form, 20°C, mPa s) | 20000 - 50000 | 10000 - 20000 |
| Density (20°C, g/cm ³) | ca 1,1 | ca 1,1 |

Table 2: Performance of the OH-functional polyesters in a white 2K top coat test formulation, without catalysts

| | WP 6756 | WP 6741 |
|------------------------------|------------|---------|
| VOC content(at 20s cup-4 mm) | 390 g/l | 360 g/l |
| Approximate Pot life | 5 h | 6 h |
| Dry film thickness | 50 - 55 µm | |
| König pendulum hardness | 170 s | 140 s |
| Gloss (20°) | 86 | 84 |

For the synthesis of such low molecular weight polyesters, normally a large excess of OH-functional building units is used, allowing to reach OH-numbers above 200 mg KOH/g. Also, to reach a short reaction time, COOH-numbers higher than 30 mg KOH/g are usually required. But in contrast to this, such short reaction times were achieved with acid numbers below 30 mg KOH/g as well, using special or branched raw materials and a proper production technique, yielding polyester resins, which, upon cure with low molecular weight polyisocyanates, form a network with good drying properties and good weatherabilities.

In this respect, new polyester products, for the first time showing moderate OH-functionalities, have recently been introduced. Table 1 summarises their properties.

Solvent choice is important

For the formulation of 2K coatings with a reduced solvent content containing these low molecular polyesters, it is important to use appropriate solvents. Butyl acetate was chosen as an excellent solvent to deliver the polyester resins, because of its evaporation rate and viscosity reducing effect, and because it has a better odour than ketones - although ketones (e.g. MEK) show a larger effect in viscosity and density reduction. For the formulation of high performance low VOC lacquers, however, small amounts of further solvents (e.g. methoxy propyl acetate, xylene, solvent naphtha A or butyl (di)glycol acetate) are required not only to adjust the viscosity and density, but also to achieve good levelling and degassing.

OH-polyesters improve drying time and weather resistance

Both new polyester resins, were tested in a white 2K top coat formulation. To crosslink the polyester resins, a low viscous aliphatic polyisocyanate trimer was used. The first test formulation did not contain any catalyst, its performance is shown in Table 2. In further trials, depending on the reactivity of the polyols, different catalysts were considered. Figure 2 shows the effect of some of these catalysts on the coatings hardness and pot life in a white 2K-top coat based on WP 6741.

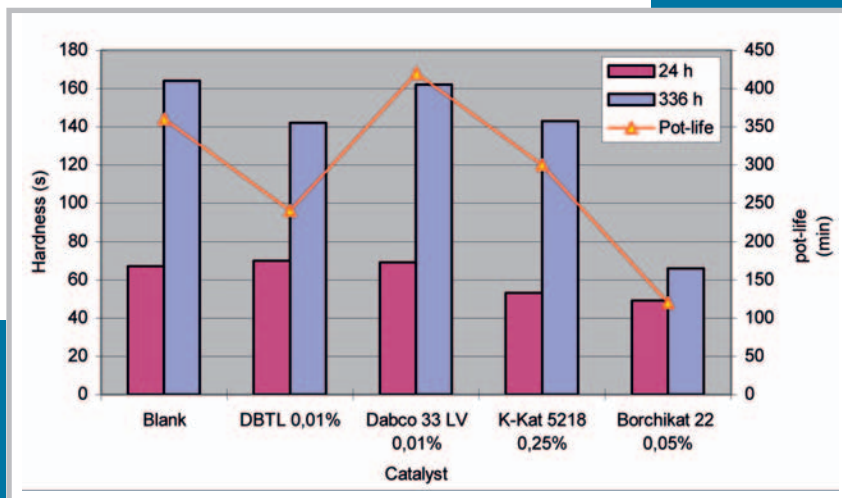


Figure 2: Effect of different catalysts on the performance of a white 2K-top coat formulation based on OH-polyester WP 6741

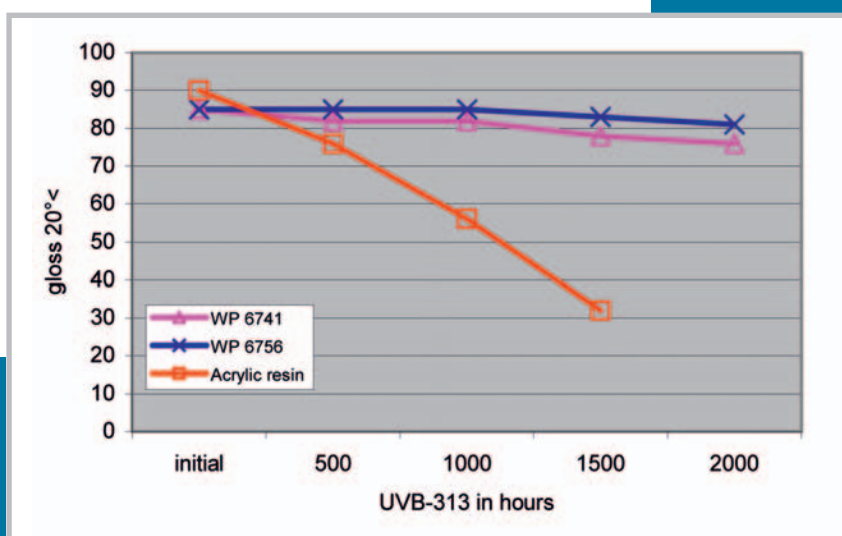


Figure 3: QUV accelerated weathering test of 2K white top coats based on high solids acrylic and polyester polyols

Another very important property is the stability of the coatings during atmospheric exposure. Especially in case of cars, busses, trucks, agriculture and construction machinery the long lasting gloss is very important. Here, the low VOC-polyesters have a decisive advantage, compared with a low VOC-acrylic polyol. Thus, Figure 3 shows the UV-light stability of 3 top coats containing typical quantities of HALS and hydroxyphenylbenzotriazole.

In conclusion, low VOC acrylic or polyester resins for 2K PUR coatings certainly both have their advantages and disadvantages. The new polyesters, however, can improve formulations in terms of VOC-reduction, drying time and weather resistance. It is therefore interesting to use these polyesters alone or in combination with low VOC acrylic resins to achieve an optimum performance for such coatings.