Macromol. Symp. ***187****, 281–292 (2002)*

New Low Viscous Polyisocyanates for VOC Compliant Systems

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Summary: Since 1961, aliphatic polyisocyanates based on HDI-biurets are used as light stable hardeners for 2-K polyurethane coatings. The market introduction of the HDI-isocyanurates or simply 'trimers' in the early 1980's was driven by their lower viscosity and their better monomer stability. The most recent development in HDI-polyisocyanate research are the iminooxadiazinediones (asymmetric trimers). In this paper, a new product based on that technology with a very low viscosity (700 mPas@23°C) and a NCO-functionality of more than 3 is presented. Because of its low viscosity, this hardener can be easily incorporated into aqueous systems and is the solution for high and full solids coatings as well.

Keywords: aliphatic polyisocyanates, iminooxadiazinediones, asymmetric trimers, High Solids coatings, Waterborne 2K PUR coatings

Introduction

Since 1961, aliphatic polyisocyanates based on HDI-biurets are used as light stable hardeners for 2-K polyurethane coatings. The market introduction of the HDI-isocyanurates or simply 'trimers' in the early 1980's was driven by their lower viscosity and their better monomer stability.

The most recent development in HDI-polyisocyanate research are the iminooxadiazinediones (asymmetric trimers). In this paper, a new product based on that technology with a very low viscosity (700 mPas@23°C) and a NCO-functionality of more than 3 is presented. Because of its low viscosity, this hardener can be easily incorporated into aqueous systems and is the solution for high and full solids coatings as well.

Today, 2-K polyurethane systems based on aliphatic polyisocyanates are the standard of the coatings industry for high quality applications such as automotive OEM, car refinish, plastics, furniture, commercial vehicle coatings, and general industrial applications [1].

However, after the discovery of polyurethanes in 1937 [2], the first polyurethane coatings have been made of aromatic hardeners such as TDI-adducts (Brand name 'Desmodur L', where L stands for 'Lack' German for: laquer, varnish, paint) and Polymer-MDI. They are, due to their low price and high reactivity, still the choice for a variety of applications especially for wood coatings and flooring (Fig. 1).

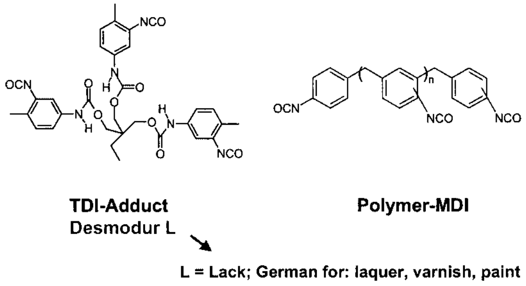

Figure 1

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Unfortunately, high reactivity corresponds to a short potlife: in the case of aromatic polyisocyanates this potlife time can be in the range of only a few minutes. Additionally, and perhaps even worse, the light stabilty of coatings derived from aromatic isocyanates is limited.

This lead to the introduction of aliphatic polyisocyanate hardeners (Brand name 'Demodur N' where N stands for 'Nicht vergilbend'; German for “non yellowing“) some forty years ago[3].

The first example was a biuret type, which could be made by the reaction of hexamethylene diisocyanate (HDI) with water, subsequent loss of carbon dioxide and addition of another molecule of HDI to the intermediate urea (Fig. 2).

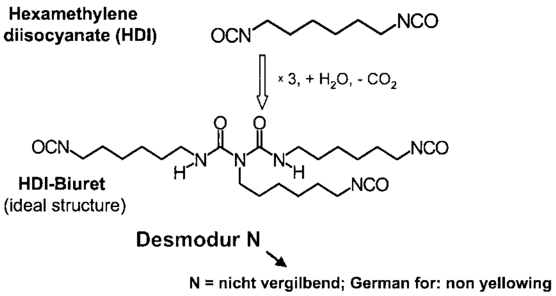
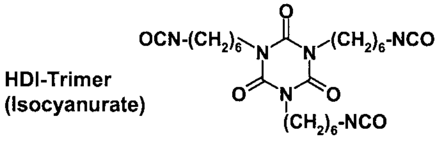


Figure 2

These hardeners quickly became the standard for aircraft and automotive refinish applications as they provide for several hours of potlife, not mentioning the excellent durability of the final coating.

Later on, the biuret-type of Desmodur N hardeners experienced support - and competition - by HDI-isocyanurates or simply 'trimers' [4]. Their advantages over the biurets are a better monomer stability, and a somewhat lower viscosity as well (Fig. 3). Both effects can be attributed to the absence of N-H-fragments in the isocyanurate‘s backbone rendering the structure essentially inert towards reverse reaction (monomer formation) and intermolecular hydrogen bonding, respectively, the latter beeing one reason for a higher viscosity of biurets versus trimers.



=> lower viscosity
better monomer stability
vs. HDI-Biuret

Figure 3

The well established term 'trimer', however, only incompletely reflects the true nature of a polyisocyanate hardener. An HDI-isocyanurate, being undoubtedly the first stable product derived from the interaction of three HDI molecules under the influence of a so called trimerization catalyst, contains three NCO groups which are essentially as reactive to further 'trimerization' as those of the starting monomer. This leads to the subsequent formation of higher molecular weight species, such as pentamers (containing four free NCO groups), heptamers (containing five free NCO groups), and so on. This reaction array is depicted in Figure 4 beside a gel chromatogram of a typical commercial 'HDI-trimer' based hardener. Therefore, commercial 'trimer' based hardeners are more than NCO-trifunctional.

In addition, technical resins usually contain to some extend a number of species with structures like uretdiones, ureas, urethanes, and allophanates - to name the most common - that are different from the naming type; “isocyanurate“ in the above mentioned case. They certainly do have some influence on hardener properties like NCO-content and -functionality (*vide infra*).

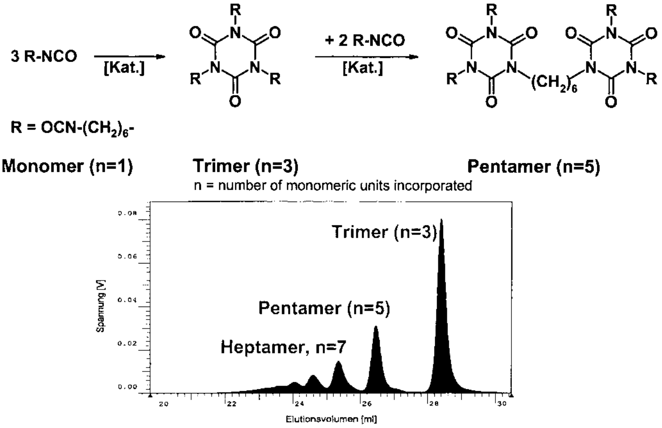


Figure 4

These different, homologue isocyanurates exhibit different physical and chemical behavior. The lower the content of higher molecular weight oligomers in a given product, the lower the viscosity of that individual hardener, and the closer the NCO-functionality is to three.

This way, special hardeners for high solids coatings can be produced containing about 70 % of the real trimer, here often referred to as the 'ideal structure'. These hardeners are very low viscosity, even in the absence of solvents (Table 1).

On the other hand, products containing a larger fraction of higher molecular weight species with a higher NCO-functionality provide for faster drying films. Of course, these hardeners, are less well suited for the formulation of high solids coatings due to their higher viscosity (Table 1).

Table 1. Influence of oligomer distribution on viscosity and drytime

HDI-Trimer	Viscosity @ 23°C [mPas]	NCO-functionality	Drytime	oligomer distribution		
				n=3	n=5	n>5
high viscous	15,000	~ 4.0	++	~ 30 %	~ 20 %	~ 50 %
Standard	3,500	~ 3.5	+	~ 50 %	~ 20 %	~ 30 %
low viscous	1,200	~ 3.1	o	~ 70 %	~ 15 %	~ 15 %

Results

1. Polyisocyanates for High Solids

The search for VOC compliant solutions focuses on a number of different technologies, such as powder coatings, UV, waterborne and high solids, depending on the application. The interest in high solids systems holds especially true for clear coats in the automotive refinish sector.

The majority of the developments in recent years have been aimed at low viscous polyols, as well as reactive diluents. The goal was to minimize the content of volatile organic compounds in the formulated paint to less than 420 g/l (for high solids) or even 250 g/l (for very high solids). Another option to achieve that is lowering the vicosity of the polyisocyanate hardener.

This can be done, as has already been outlined above, by using HDI-isocyanurate hardeners with a low content of higher molecular weight oligomers, or by employing HDI-uretdiones and/or allophanates. Both type of products exhibit considerably lower viscosities compared to isocyanurates (Fig. 5).

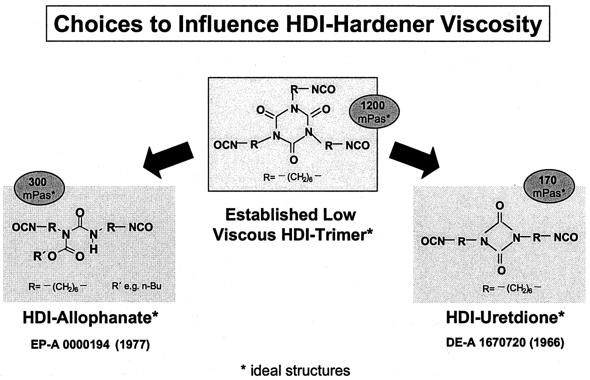


Figure 5

Contrary to isocyanurates with functionalities greater than three (*vide infra*), uretdiones and mono-alcohol based allophanates are, independently of molecular weight, only NCO-difunctional. This leads to a lower crosslink density of the cured film resulting in inferior performance. As a rule, uretdione, as well as allophanate, based polyisocyanates are only used as reactive diluents in combination with isocyanurate or biuret based hardeners.

2. Low Viscous Asymmetric Trimers

At the end of the last century, the hithereto almost unknown iminooxadiazinediones - isomers of the well known isocyanurates - have been investigated in more detail[5].

Structurally they differ from the latter only in one detail: one NCO-group is incorporated into the six membered ring by opening the C=O double bond, instead of the usually occuring C=N bond scission. This detail renders the structure, in contrast to the flat and centrosymmetric isocyanurate ring, completely asymmetric, and thus leads us to name them asymmetric trimers ("AST" for short, see Fig. 6).

In the course of our investigations, it has been discovered that HDI-ASTs are an almost ever present companion of their symmetrical counterparts. Their amount in the established products, however, is quite low and can only be increased significantly by employing a new type of catalyst [5].

ASTs exhibit almost no difference in terms of reactivity, stability, and technological properties of cured films, compared to isocyanurate based hardeners.

The color of the products is at present some 10 to 20 APHA units higher than that of the established trimers, but a lot of improvement in that matter has been achieved over the last couple of years.

Moreover, the dilution stability, as well as the resistance of the hardener towards moisture, is considerably better than those of the classical trimers.

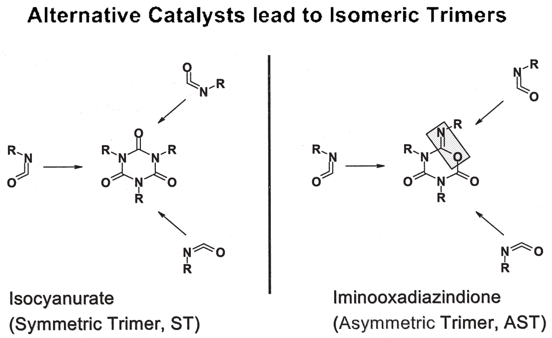


Figure 6

Finally, the main advantage of HDI-ASTs is their dramatically lower viscosity over isocyanurates of comparable molecular weight. Therefore, ASTs are a promising approach to achieving lower viscosity, while maintaining at least NCO trifunctional hardeners, avoiding the use of difunctional products like uretdiones or allophanates (Fig. 7, Table 2).

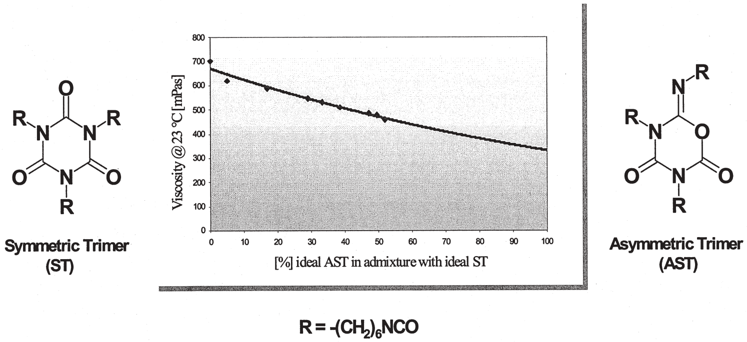


Figure 7

Table 2. Properties of various HDI-based hardeners

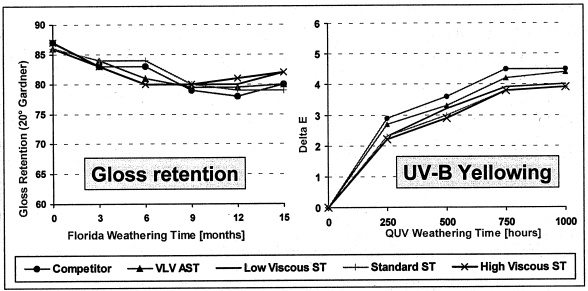
HDI-hardener	Viscosity @ 23°C [mPas]	NCO-functionality	NCO [%]	TSCA Status	Colour [APHA]	
					spec.	typical
Standard Symmetric Trimer (ST)	3,000	3.5	21.8	approved	<40	<15
Low Viscous Symmetric Trimer (LV ST)	1,200	3.1	23.0	approved	<40	<15
Very Low Viscous Asymmetric Trimer (VLV AST)	700	3.1	23.8	approved	<40	20 - 30
Allophanate	300	2.5	20.0	SNUR	<50	<30
Uretdione	170	2.5	21.8	approved	<80	<30

This paper will focus on a very low viscous HDI-AST that has recently been introduced to the market, from here on referred to as VLV AST. At a value of 700 mPas at 23°C, the viscosity of that new product equals the viscosity of the ideal HDI-isocyanurate. One has to keep in mind that the latter could only be isolated by rather cumbersome separation technique, like molecular distillation or extraction, and therefore would be very expensive to manufacture on a large scale[6].

The VLV AST enables the formulator to further decrease the VOC content in solvent borne high solids applications (see Chapter 4), while also showing utility in aqueous polyurethane systems due to its low viscosity, allowing it to be incorporated very easily (see Chapter 5).

3. Low Viscous Asymmetric Trimers in High Solids Applications

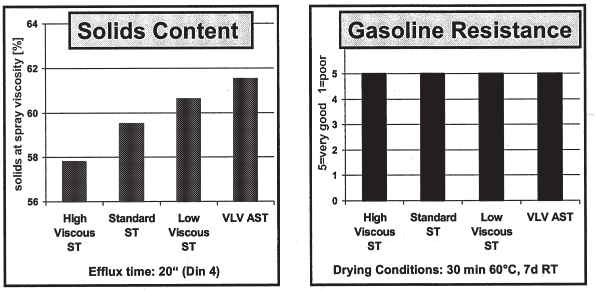
The VLV AST has been tested in automotive refinish clearcoats in comparison to other, established HDI-trimers, all in combination with a high solids polyacrylate. No difference in mechanical (i.e., hardness and elasticity) or optical properties can be observed among these clearcoats. The results of weathering studies are identical as well (Fig. 8).



High Solid Clear Coat based on High Solid Polyacrylate containing 0,03% DBTL on Solids and 3% Tinuvin 292/1130 (1:2)

Figure 8

As can be seen from Fig. 9, employing the VLV AST in even an already optimized system, the solids content can be further increased by 1 to 3 % without sacrificing the properties of the cured film.



Refinish Clear Coats based on High Solids Polyacrylate Containing 0,03% DBTL on Solids; NCO/OH= 1:1;

Figure 9

Due to the somewhat lower molecular weight of the VLV AST compared to conventional HDI-trimer hardeners at equal catalyst levels, the potlife of the formulation is increased. Additionally, the chemical, as well as physical drying of the paint, is slower (Fig. 10). This can be compensated by higher catalyst levels.

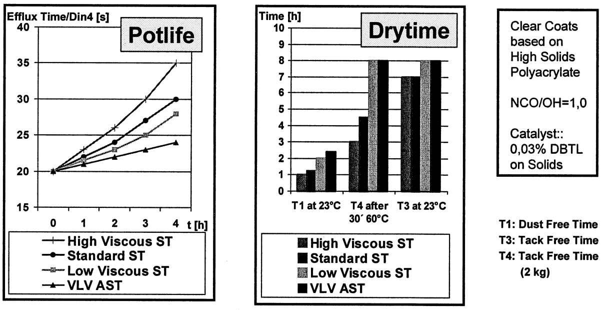


Figure 10

In order to answer the question of whether the NCO groups of an AST really are as reactive as those of an isocyanurate, 2-K high solids clear coats have been monitored for NCO decrease by IR spectroscopy while curing at room temperature (without forced drying) (Fig. 11).

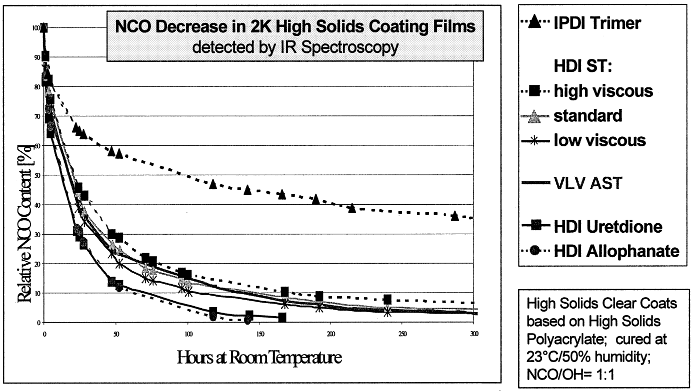
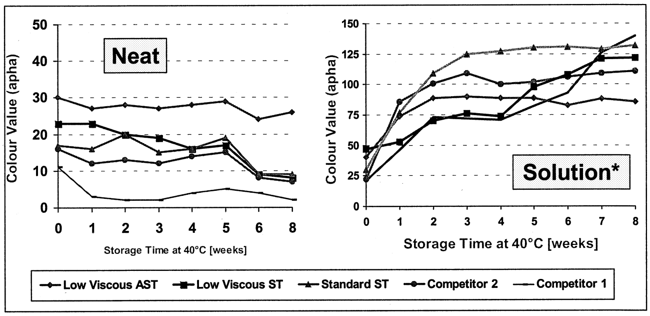


Figure 11

On one hand, Figure 11 clearly demonstrates the considerably lower reactivity of IPDI-based trimers over HDI-based products, which can be attributed to the presence of secondary NCO groups, as well as to a higher T_g of that system. On the other hand, a somewhat faster cure response has been detected for the low functionality derivatives, uretdione and allophanate, over the trimers. Among them, only negligible differences are observed, no matter if the polyisocyanates backbone is an isocyanurate or an AST.

As has been outlined above, the initial color of the VLV AST is slightly higher than that of the established products. This is, in our opinion, essentially due to the somewhat limited experience one has today manufacturing this new type of product. In addition, one has to take into account the shorter production periods, as the demand for these products is naturally not yet at the level of the established resins. However, the color stability of the VLV AST, no matter if a neat hardener, or a catalyzed, diluted solution is investigated, shows good comparisons to other hardeners (Fig. 12).



*: 60% Hardener in Butyl Acetate/Solvent Naphtha 100
+ 0,03% DBTL on Solids

Figure 12

The viscosity stability of the VLV AST is equal to, or exceeds, that of established products (Table 3).

Table 3. Viscosity increase of non-catalyzed, neat hardeners upon storage at 40°C

	Viscosity [mPas] at 23°C			Viscosity increase [%]
	Initial	after 4 weeks at 40°C	after 8 weeks at 40°C	
Standard ST	3000	3100	3270	11
Competitor 1	1330	1330	1420	7
Low Viscous ST	1200	1200	1300	8
Competitor 2	990	1100	1180	19
VLV AST	650	680	705	8

The VLV AST has also successfully been used for VOC reduction in 2-K PUR OEM applications, without deteriorating the technological properties of the clearcoats such as gloss, scratch and solvent resistance.

4. Low Viscous Asymmetric Trimers for Waterborne Applications

Waterborne systems, beside high solids, represent an interesting approach to coatings with a dramatically decreased solvent content, fulfilling today already the requirements of future VOC-legislation. Meanwhile, waterborne systems have been developed for even high end applications.

Besides a proper choice of the polyol, the suitability of the corresponding polyisocyanate hardener is crucial for the performance of the whole system.

In order to make the incorporation of the hardener into the aqueous phase easier, specially designed, water-emulsifiable aliphatic polyisocyanates have been developed. However, these products carry their hydrophilicity into the cured film, which results in a somewhat limited water and chemical resistance and deteriorates the corrosion protection properties.

These hydrophilically modified polyisocyanates are usually made of HDI- or IPDI-trimers that have been made water-dispersible by the internal or external incorporation of small amounts of hydrophilizing agents. The term "internal" stands for NCO-reactive agents, e.g. ROH-started polyethylene glycols (R = lower alkyl) which may form a urethane group upon reaction with the mother hardener (Fig. 13, top) or, more elegantly, are further converted to an allophanate (Fig. 13, bottom). The term "external", on the contrary, stands for additives which do not react with the isocyanate groups of the hardener [7].

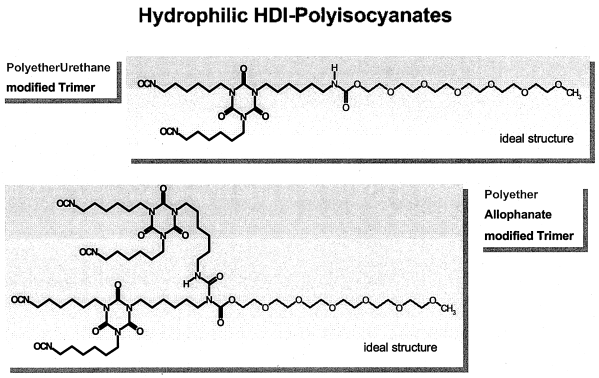


Figure 13

If the hardener has to be emulsified manually, e.g. by simple stirring with a mixing stick, hydrophilized products are indispensable. However, in many applications mechanical mixing devices like stirrer, dissolver, or even jet-stream-dispersers may be used, making the use of mixtures of hydrophilically modified and conventional hardeners possible.

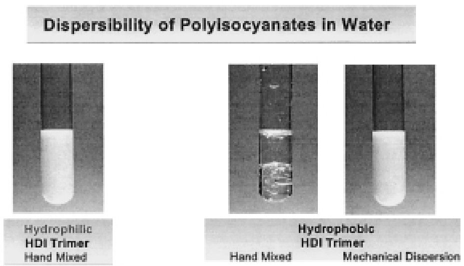


Figure 14

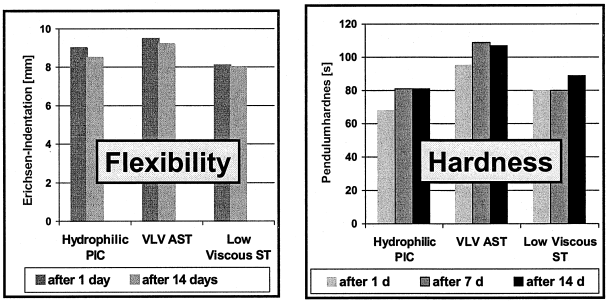
In some instances, the use of hydrophilically modified crosslinkers can be completely avoided (Fig. 14). Especially in the latter case, the viscosity of the hydrophobic hardener is important for good mixing results. This can be achieved by the use of solvents, but they, in turn, have a negative impact on the VOC level of the mixture. Therefore, low viscous polyisocyanates are being favored. Uretdiones and allophanates are being used in certain applications already, but the above mentioned lower NCO-functionality results here also in a lower crosslink density of the final film. The VLV AST represents an interesting alternative for waterborne applications, combining the advantages of low viscosity with a high NCO-functionality.

4.1 Waterborne 2-K Industrial Topcoat

The use of hydrophobic polyisocyanates in waterborne applications, although providing for durable, chemically resistant coatings, has drawbacks in terms of gloss and other optical properties.

Due to its low viscosity, the VLV AST provides for a much better balance of chemical and optical film properties, no matter if used in combination with a hydrophilized hardener employing manual mixing, or as a single hardener and mechanical mixing with a dissolver as is exemplified in Figure 15 with an air-drying, 2-K PUR industrial topcoat.

The hardness of the film made from VLV AST exceeds that of those made from hydrophilic hardeners (softening effect of the polyether tails) and with a low viscous, hydrophobic conventional trimer (film inhomogenity due to poorer mixing), respectively (Fig. 15, right). The flexibility of all three films, however, is comparable (Fig. 15, left).



Waterborne White Top Coat based on Polyacrylate Secondary Emulsion
Mechanical Mixing of the Hardener (Dissolver, 2000 rpm)
NCO/OH= 1:1,5; 53% Solids (VOC: 140 g/l) Curing Conditions: 23°C/50% Humidity; 35 µ on Steel

Figure 15

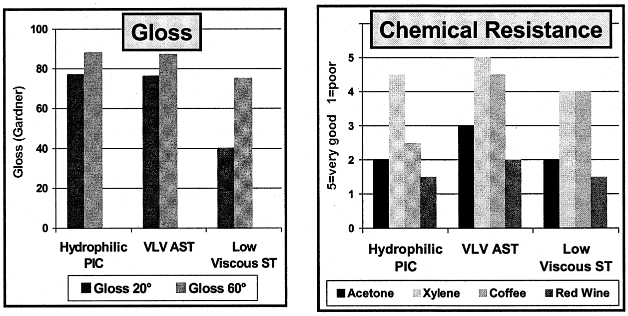


Figure 16

As expected, the gloss is highest for the hydrophilic hardener, but the VLV AST almost matches that result (Fig. 16, left). On the other hand, the stability of the coatings to typical household chemicals is best in the case of VLV AST (fig. 16, right).

The same picture is obtained after storage in water. Adhesion and gloss retention both reach maximum levels when films are derived from the VLV AST (Fig. 17).

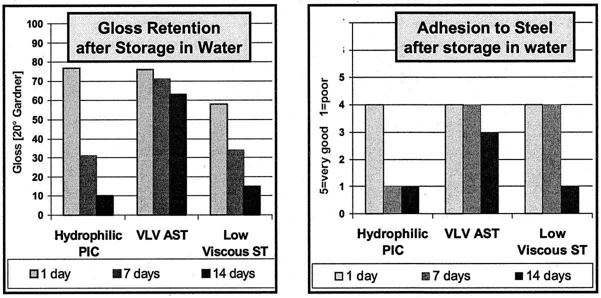


Figure 17

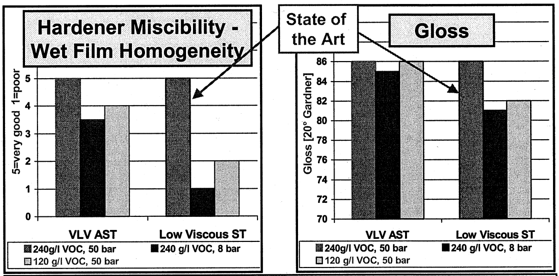
4.2 Waterborne 2-K PUR Automotive OEM Clearcoat

Conventional, solvent borne 2-K PUR coatings are standardly used for top quality OEM clearcoats today, combining an outstanding quality level of the coating in terms of weather and chemical resistance with excellent optical properties.

The development of waterborne systems with equally good properties is challenging, especially since the typical hydrophilized hardeners cannot be used for OEM applications due to their negative impact on the weatherability of the coating.

Meanwhile, waterborne 2-K clearcoats that equal the high quality level of the well established conventional 2-K solvent borne coatings are at the edge of a broad market introduction. These new systems are based on a combination of polyacrylate or polyurethane dispersions, respectively, which are crosslinked with a low viscous, hydrophobic hardener. The components are mixed prior to application using a jet stream disperser working at 50 bar (~ 725 psi) and contain 240 g/l VOC or less.

Applying the new VLV AST as a hardener in that kind of formulation allows for an even further VOC-reduction (from 240 to 120 g/l) and/or makes it possible to reduce the pressure of the disperser to 20 bar (~ 290 psi). At that pressure, even conventional gear pumps may be employed as they are used today in the recirculation lines at the automotive OEM sites.

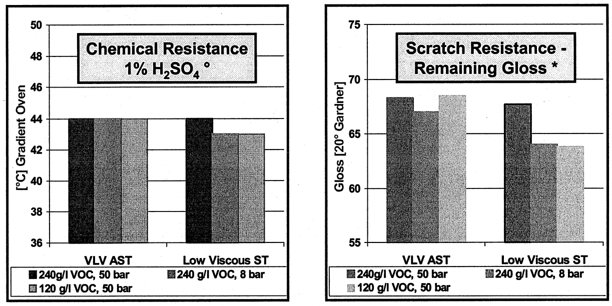


Waterborne Clear Coat based on a Combination of PAC and PUR Dispersion
NCO/OH= 1:1,5; 48-50% Solids; **VOC: 240 g/l or** 120 g/l
Curing Conditions: 10 min@40°C/30 min@130°C; 40 µ on Base Coat
Application: **50 bar: ,DSD-Wagnerpump‘**; 8 bar: gear pump

Figure 18

When using VLV AST instead of conventional low viscous isocyanurate based trimers, even at lower pressure, or at lower co-solvent content respectively, the miscibility of the components is improved, thus leading to a better homogeneity of the wet film and providing for higher gloss of the cured coating (Fig. 18).

When using VLV AST as a hardener at either lower VOC or lower pressure, no deteriorations in terms of chemical or scratch resistance are observed (Fig. 19), compared to conventional trimer based coatings.



° Comparable with NaOH, Pancreatine, Brake Fluid   * after 10 car wash cycles

Figure 19

Conclusion

A new isocyanate hardener for 2-K polyurethane coatings based on HDI iminooxadiazinediones (asymmetric trimers, AST) has been developed. This product, herein referred to as VLV AST, combines the advantages of a very low viscosity (700 mPas/23°C) with a high NCO-functionality (≥ 3), thus making it an ideal candidate for promising future developments in the coatings industry aimed at low VOC or 'high solids' in the conventional, solventborne sector, and for waterborne applications as well.

The VLV AST is an interesting alternative to established hardeners in many applications such as: automotive OEM, car refinish, coatings for commercial vehicles, plastics, furniture, and general industrial applications up to thick film flooring and corrosion resistance.

The VOC content of high solids systems can be further reduced without sacrificing the mechanical, optical, or chemical properties of the coating.

Waterborne coatings benefit from the low viscosity of the VLV AST, leading to a better mixing behavior compared to other hydrophobic, non-hydrophilized hardeners. Depending on the mixing technique (manually, mechanically, or jet-stream-dispersed) the amount of hydrophilic hardener in the formulation can be diminished or removed entirely. That, in turn, leads to a significantly improved mechanical, optical, and chemical performance of the coating.

Acknowledgement

The authors are grateful to H. Brümmer, U. Freudenberg, T. Klimmasch, M. Mechtel, H. Neyers, R. Reyer, and N. Yuva who contributed to the success of the work discussed in that paper, to R. Halpaap and W. Hovestadt for many helpful discussions, and to S. Grace for language polishing.

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