White paper

Polycarbodiimides as classification-free and easy to use crosslinkers for water-based coatings

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Polycarbodiimides (CDI) selectively react with carboxylic acid (–COOH) groups in polymer chains. This type of crosslinking reaction results in a classic 3D polymer-crosslinker network. Compared to polyisocyanates, polycarbodiimides are much less sensitive to presence of water and able to achieve long pot lives. Due to the high reactivity, curing with CDI type crosslinkers can be done under room temperature or typical oven conditions used for drying of applied coatings. In addition to standard CDI crosslinker chemistry, on offer is also a range of dual reactivity CDI crosslinkers. A second type of reactive groups is attached to the polycarbodiimide in this range. Upon curing, this crosslinker not only reacts with the –COOH groups in the polymer chains, but also two of the reactive groups attached to the separate CDI molecules can couple to form an even denser network structure. Building further on the success of these polycarbodiimide crosslinkers, VOC-free polycarbodiimides, in aqueous delivery form, were introduced, which give extreme long pot lives.

1. Introduction

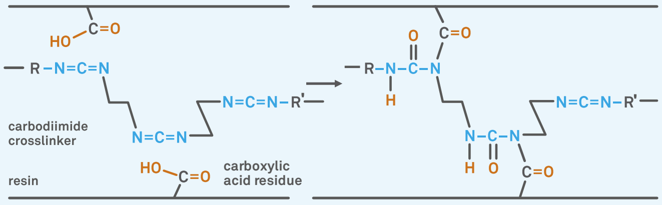
Crosslinking is widely practiced in nearly all the coating industries in order to improve the performance of the coating. These improvements include wear, abrasion and chemical resistances and toughness[1]. The improved performance originates from the formation of a continuous three-dimensional network, which may be formed by the crosslinker alone, or by reaction of the crosslinker with the binder[2].

Crosslinkers, with their reactive groups, can be harmful, irritant, sensibilizing or even toxic to humans or to the natural environment depending on the type of reactive groups, the molecular weight and the ease of penetrating living cells. Polycarbodiimides (CDI) do contain the carbodiimide reactive group, sometimes combined with other functional reactive groups. However, importantly, CDI are not harmful, irritant, sensibilizing nor toxic, as has been determined in toxicological studies[3]. Hence, CDI products do not carry a classification unless another harmful component is present, such as a solvent. As a consequence, CDIs are a safe and sustainable crosslinker choice. For clarification, in this article, polycarbodiimides (CDI) are considered to be oligomers or polymers containing on average two or more carbodiimide groups, and not polymers derived from carbodiimide monomers[4].

Crosslinking, especially network formation, has the potential to reduce elongation and to increase tensile strength, thus polymer hardness. One must therefore take care not to overdo crosslinking when dealing with flexible substrates. A high level of crosslinking may be acceptable for hard coatings on rigid substrates, but low levels may be best for soft coatings on extensible, flexible substrates such as rubber and leather. An important crosslinking system for aqueous resins involves the use of water-dispersible oligomeric polyisocyanates. The polymeric binders in such aqueous coatings are either polyurethane dispersions, acrylic resins or a combination of both. In general, the use of such polyisocyanate crosslinkers is not based on a reaction with functional groups in the coating, however they form an interpenetrating network upon the reaction with water. Main drawbacks of polyisocyanate crosslinkers are their sensibility to moisture and their limited pot life. Aziridines are another type of crosslinker and for a long time they were the reference standard for property development, however their use is decreasing due to concerns about their toxicity and handling.

The usage of CDIs in coatings based on aqueous resins is growing since new types are available which are very advantageous. These are the stable water-based CDIs and the newest developed VOC-free types. They are extremely easy to use and exhibit a much longer useful pot life than isocyanates could achieve. In addition, “multifunctional” water-dispersible CDIs are available that display a very high crosslinking performance.

The chemistry of polycarbodiimide crosslinking involves mainly the reaction of carboxylic acid residues (–COOH) in acrylic resins or in polyurethane dispersions with carbodiimide (–N=C=N–) groups of the crosslinker. After the formation of an unstable intermediate a stable N-acylurea is formed as shown in graph 1[5-8]. Since the CDI contains several –N=C=N– groups, one CDI molecule can react with carboxylic acid residues on different polymer chains tying them together forming a three-dimensional network. Reaction of carboxylic acid with carbodiimide can be quite fast under ambient or mild thermal curing conditions.



Graph 1: *Reaction of carboxylic acid residue from a resin with a polycarbodiimide crosslinker*

Solvent-based CDIs exist for many years and solvent-based CDIs that can be dispersed in water exist almost as long. They can be readily used as crosslinker in aqueous polyurethane dispersions or polyacrylate dispersions. A special family are the so-called multifunctional polycarbodiimides. These solvent-based CDIs contain additional functional groups which have a reactivity towards functional groups in the resin or towards corresponding groups, i.e. by self-condensation or self-addition. This results in an increased crosslinking capacity, since both the carbodiimide and the additional reactive functional group contribute to the crosslinking[9]. Such type of multifunctional CDI is now also available cosolvent-free, which is an important improvement over the older types of multifunctional CDIs[10].

Recently, stable aqueous CDIs have become available[11-13]. In essence, this is remarkable since a carbodiimide can react with water to form a urea. Some product and recipe parameters have to be selected wisely to be able to obtain stable aqueous CDIs. This selection ultimately influences the stability of the aqueous CDI, its pot life in aqueous resins and its reactivity as crosslinker. Hence, multiple types of aqueous CDIs are available in the market. Main advantages of such CDIs supplied in water are:

- Their ease of use is exceptionally good because they can be readily mixed into aqueous systems.
- They can be manufactured with zero VOC.
- They are non-harmful, non-toxic and nonirritant.
- They provide a pot life that is long to very long (up to several weeks), depending on the type of CDI and on the type of other components in the formulation.

In a typical aqueous latex resin, having no hydroxyl or other isocyanate-reactive groups, the amount of polyisocyanate crosslinker has no relation to the functional groups of the resin. On the contrary, CDI crosslinkers function by reacting with carboxylic groups of the resin. Hence, there exists a stoichiometric relation between the amount of CDI crosslinker to be used and the amount of carboxylic groups in the resin. However, it appears that for an optimal performance a higher or a lower level than the stoichiometric amount can be required. Running a dosage ladder will determine the optimum crosslinker level. In many applications typical use levels are often below stoichiometric.

2. Materials and Methods

Several polycarbodiimide crosslinkers were tested:

- Picassian® XL-701, a multifunctional solvent-based CDI (50% solids);
- Picassian® XL-702, a hydrophilic aqueous CDI (40% solids);
- Picassian® XL-725, a VOC-free multifunctional CDI (100% solids);
- Picassian® XL-732, a hydrophobic aqueous CDI (40% solids).

Various polyurethanes were used in testing the polycarbodiimides:

- Picassian® AC-188, a water-based acrylic resin from Stahl Polymers;
- Picassian® PU-488, a water-based, anionic dispersion of an aliphatic polyester urethane (40% solids) from Stahl Polymers;
- Picassian® PU-687, a water-based, anionic dispersion of an aliphatic polyester urethane (35% solids) from Stahl Polymers;
- RU-13-134, a water-based, anionic dispersion of an aliphatic polyester urethane (40% solids) from Stahl Europe;
- RU-13-734, a water-based, anionic dispersion of an aliphatic polyester/polyether urethane (40% solids) from Stahl Europe.
- RU-3901, a water-based, anionic dispersion of an aliphatic polyether urethane (40% solids) from Stahl Europe.

Mixtures of polycarbodiimides and resins were applied on wooden panels and dried for 2 min at 80°C. Testing was performed after 48 h. Solvent resistance tests were done according to DIN 12720 with an evaluation of the surface after the test with a scale running from 5 (best) to 0 (worst). Dry resin films were made with 1%, 3%, 5% and 10% XL-702 and without crosslinker. A portion of these films were soaked in water for 24 h and the weight increase was measured. The results were calculated into a reduction of water uptake by comparing results of the crosslinked films with the water uptake of the non-crosslinked film.

Various polycarbodiimide crosslinkers were evaluated on leather in a typical automotive top coat system. The top coat was sprayed twice in 26.9 g/m2 (2.5 g/ft2) on leather that was already base coated, and this base coat contained 3% XL-702 as crosslinker. The leather pieces were cured for 5 min at 70°C in an oven. Testing was performed after 24 h. The test methods were: Bally flexes using 100,000 bends; Cold (Bally) flexes at -18°C using 15,000 bends; and a wet rubs test, in which leather pieces were tested on the Veslic rub machine for 1,000 cycles with a felt that was soaked in distilled water, using a weight of 500 g on samples with 10% extension. Evaluation was done using a scale running from 5 (best) to 0 (worst).

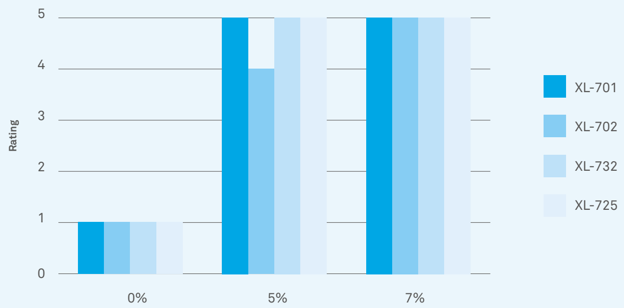
Pot life of a formulated coating mixture with crosslinkers was determined by applying the aged formula after certain time intervals, curing the coating in a normal manner and performing subsequently the solvent resistance test according to DIN 12720 as described above.

3. Results and Discussion

The performance of polycarbodiimide crosslinkers was evaluated in various resins or coating mixtures, in thin films made from these mixtures or on various substrates, like wood or leather.

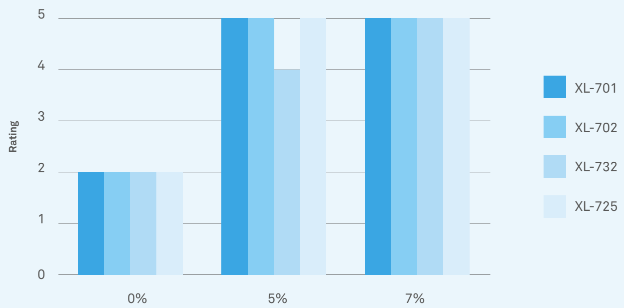
Tests on wooden panels

The ethanol resistances of coatings made from non-crosslinked and crosslinked polyurethane dispersion PU-488 on wooden panels as substrate are shown in graph 2. All four polycarbodiimide crosslinkers showed a large increase in the ethanol resistance, with XL-702 yielding a score of 4 when added in a 5% amount, and all other scores were the maximum of 5. When the mixture contained 7% of one of the four polycarbodiimides, the ethanol resistance was excellent for all four types of polycarbodiimides.



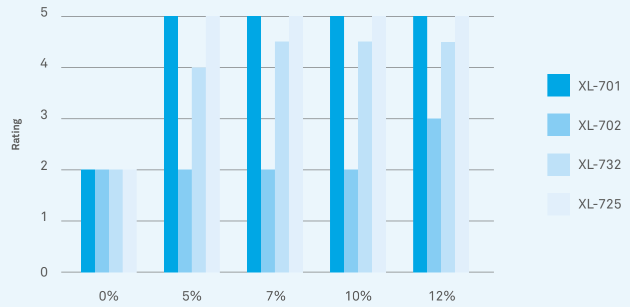
***Graph 2:** Ethanol resistance (50% ethanol, 1h), according to DIN12720 using PU-488 as resin*

The acetone resistances of the same coatings were similar to the ethanol resistances. The hydrophobic aqueous polycarbodiimide XL-732 yielded a score of 4 when applied in a concentration of 5%, and resulted in a score of 5 when applied in a 7% concentration. The three other types of polycarbodiimides resulted into scores of 5 when applied in 5% or 7% concentration (graph 3).



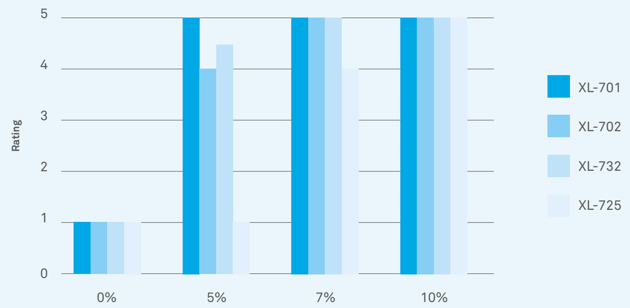
***Graph 3:** Acetone resistance (2 min), according to DIN12720 using PU-488 as resin*

However, evaluation of the same specimens for ammonia resistance yielded a significantly different picture. It turned out that the aqueous hydrophilic CDI (XL-702) hardly in increased the resistance against ammonia, whereas the other three CDIs did yield an increase in ammonia resistance (graph 4). The multifunctional polycarbodiimides XL-701 and XL-725 performed best in this test, even at relatively low concentrations, which demonstrates their higher crosslink-forming capacity.



***Graph 4:** Ammonia resistance (10%, 1 h), according to DIN12720 using PU-488 as resin*

The fact that the multifunctional polycarbodiimides gave the best performance in the evaluations depicted before does not mean that they always present the best choice for each combination of resin and crosslinker. This is demonstrated by the results depicted in graph 5. The ethanol resistance of another aliphatic polyurethane resin (PU-687) crosslinked with the four types of polycarbodiimides was now lowest with one of the "multifunctional" polycarbodiimides. Only at higher concentrations this combination resulted in a score of 5 as well.



***Graph 5:** Ethanol resistance (50% ethanol, 1h), according to DIN12720 using PU-687 as resin*

The comparison of results as depicted in graphs 2 - 5 leads to the observation that not all resins yield good results with all types of polycarbodiimide crosslinkers. A prediction of chemical resistances based on molecular weight or acid number is not feasible. But the acid number of a resin can be taken into account when predicting an optimum amount of a specific polycarbodiimide crosslinker for that specific resin, since the reaction mechanism favours a one-to-one ratio between carbodiimide groups and carboxylic groups to be the optimum.

However, the acid number of a resin is not always available and in addition, diffusion and mobility constraints during curing may lead to a different ratio than theoretically calculated that gives the optimal crosslinking performance. Therefore, it is important to run a dosage ladder to ascertain the optimum ratio between resin and polycarbodiimide crosslinker. Such a dosage ladder has been determined for the acrylic resin AC-188 in combination with the zero-VOC multifunctional polycarbodiimide XL-725.

Crosslinker amounts running from 0% to 5% were used and chemical resistances and König pendulum hardness were determined as function of the crosslinker amounts (table 1). From the data, the conclusion can be drawn that an amount of 2% of XL-725 is the optimum amount for crosslinking the acrylic resin AC-188. At this amount the König hardness is indicating that the coating is harder at this ratio and also the highest score for chemical resistances against ethanol, ammonia, acetone and hand cream were obtained at this ratio. It can also be observed in the data that increasing the amount of crosslinker beyond the optimum amount results in a decrease in properties, which is most notable in the ethanol and ammonia resistances and the König pendulum hardness test.

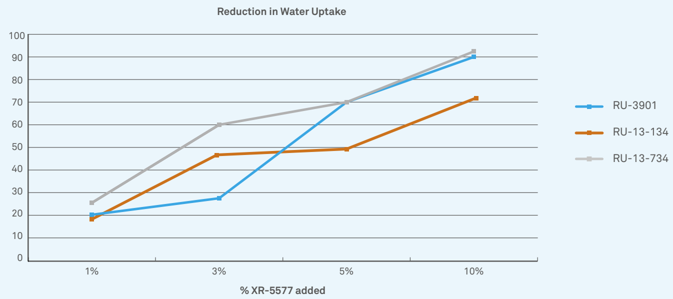
	50% ethanol (16 h)*	10% ammonia (1 h)*	Acetone (16 h)*	Hand cream (16 h @ 50°C)*	Pendulum hardness (sec)
AC-188, no XL	4-5	3	4	5	88
AC-188 + 1% XL-725	4-5	3	5	5	103
AC-188 + 2% XL-725	5	5	5	5	147
AC-188 + 3% XL-725	5	3	5	5	119
AC-188 + 4% XL-725	3-4	2	5	5	70
AC-188 + 5% XL-725	4	2	5	5	64

*Rating on a 1 to 5 scale: 1 is worst and 5 is best

Table 1: *Results from dosage ladder determination for combination of acrylic resin AC-188 and zero-VOC 'multifunctional' polycarbodiimide crosslinker XL-725*

Tests in polyurethane films

The water uptake of films made from three types of water-based polyurethanes crosslinked with XL-702 was measured as function of the amount of crosslinker. The results show that even a small amount of XL-702 reduces the water uptake already by about 20% (graph 6). Higher amounts of XL- 702 lead to higher reductions in water uptake, with up to 90% of reduction of the water uptake when 10% of XL-702 has been added. The water uptake was measured after 24 h of soaking in water.



Graph 6: *Reduction in water uptake as function of the percentage of XL-702 added, shown for three different types of polyurethane films*

Tests on leather

The capabilities of various polycarbodiimide crosslinkers were evaluated on leather in a typical automotive top coat system using an isocyanate crosslinker as reference. The reference isocyanate crosslinker (XL-728) was added in a typical amount of 10%, whereas most of the polycarbodiimides were added in a 5% amount compared to the total top coat formulation. Only XL-725 was added in a smaller dosage to compensate for its higher solids content. The leather pieces were subjected to various tests. The results are collected in table 2.

	No XR	XL-728	XL-702	XL-732	XL-701	XL-725
Dosage (% of total top coat):	0	10	5	5	5	3
Wet Rubs 1000	4	5	4	5	5	5
Sweat rubs 300	3	5	4	4/5 - 5	5	5
Flex 100,000	1	5	5	5	4	5
Cold -18°C Flex 15,000	1	5	5	5	4	5

*Rating on a 1 to 5 scale: 1 is worst and 5 is best

Table 2: *Evaluation results* *of various crosslinkers in a typical automotive top coat on leather*

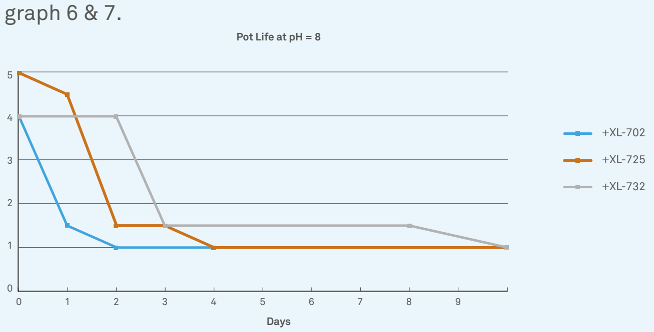
When no crosslinker was added, a fair rating was obtained in the wet rubs and the sweat rubs tests, however the results obtained in the flex test and the cold flex test were very poor. Clearly, the addition of a crosslinker improves the performance significantly. All CDI crosslinkers tested gave a good to satisfactory outcome in the 100,000 flex tests and the cold flex tests, since only the leather with XL-701 showed some minor damage after 100,000 flexes. Probably, the crosslinking was somewhat too strong here due to the multifunctionality of the XL-701, as described in the introduction. Both "multifunctional" polycarbodiimides (XL-701 and XL-725) gave an excellent performance in the wet rub and the sweat rub tests. The aqueous polycarbodiimide XL-702 showed some minor damage after the wet rub and the sweat rub tests (all rating 4).The other aqueous product XL-732 yielded a better outcome in the wet rub and the sweat rub tests (5 or 4.5 - 5 rating). Only the reference isocyanate crosslinker scored a 5 in all tests, whereas each particular polycarbodiimide scored some 5 ratings, however not one scored a 5 rating in all tests.

The results demonstrate that both aqueous and "multifunctional" polycarbodiimide crosslinkers are able to boost the performance of the coating on leather, making them a feasible alternative for a polyisocyanate crosslinker. Although the CDIs did not score the highest ratings in all the tests, they have other advantages over an isocyanate crosslinker such as a friendlier classification, greater ease of use and a much longer pot life. One should consider all these properties while selecting which crosslinker to employ in leather finishing.

Pot life

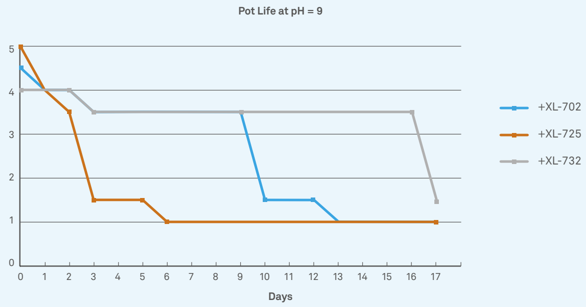
The pot life of a coating application mixture is an important parameter, since a short pot life is difficult to work with and will likely result in more waste due to incomplete consumption of the coating mixture. In the case of polycarbodiimides, in combination with aqueous resins, one has to be aware that polycarbodiimides react with carboxylic groups (–COOH). However, usually amines are employed to neutralize the carboxylic acid groups so that above a pH of 9 almost all carboxylic acid groups are inactivated since they have been transformed into an inactive carboxylate anion ($–COO^-$). As a consequence, above a pH of 9, the amine effectively blocks the reaction between the carbodiimide groups and the carboxylic acid groups of the resin. Upon drying the amine evaporates, releasing the carboxylic acid groups, decreasing the pH and activating the carboxylic acid groups again for a reaction with the carbodiimide groups.

However, the carbodiimide groups themselves hydrolyse below a pH of about 11. The polycarbodiimide crosslinkers are stable as provided, including the aqueous versions, but they will start to hydrolyse when they have been added to the resin. A high pH of the mixture of resin and polycarbodiimide thus limits the rate of hydrolysis and prevents the carboxylic groups from being formed. The effect of the pH on the pot life of a mixture of resin and polycarbodiimide crosslinker has been studied for the aqueous polyurethane PU-488 and three types of CDIs. The mixtures were prepared and set at a pH value of either 8.1 or 9.0 and the ethanol resistance of dried films was determined as a function of the age of the resin/polycarbodiimide mixture at the moment that the films were made from the aged mixture. The results are depicted in graph 6 & 7.



Graph 7: *Ethanol resistance (50% ethanol, 1h), according to DIN12720 using PU-488 as resin, as a function of the age of the mixture resin & polycarbodiimide crosslinker with pH at 8.1; Rating on a 1 to 5 scale: 1 is worst and 5 is best*

At a pH of 8.1 the pot life of the mixture of PU-488 with the three polycarbodiimides varied between a few hours and three days, with the hydrophobic aqueous polycarbodiimide XL-732 displaying the longest pot life of three days. However, at a pH of 9.0 the pot lives were much longer. At pH 9.0 the pot lives varied between two days for the multifunctional 100% solids polycarbodiimide XL-725 to 16 days for the hydrophobic aqueous polycarbodiimide XL-732. This demonstrates that the pH is a very important parameter for the pot life duration of mixtures of an aqueous resin and polycarbodiimides. Furthermore, it is exemplified that the aqueous polycarbodiimides XL-702 and XL-732 are themselves more resistant to hydrolysis due to their chemical composition, which is reflected in a long pot life when the pH of the coating mixture is high enough. The actual pot life that can be obtained with the aqueous CDI crosslinkers in a coating mixture is also dependent on temperature (lower temperatures are better) and the resin types that are contained in the mixture.



Graph 8: *Ethanol resistance (50% ethanol, 1h), according to DIN12720 using PU-488 as resin, as a function of the age of the mixture resin & polycarbodiimide crosslinker with pH at 9.0; Rating on a 1 to 5 scale: 1 is worst and 5 is best*

4. Conclusions

Polycarbodiimide crosslinkers are an excellent alternative to the more hazardous isocyanate and aziridine crosslinkers for crosslinking aqueous coatings, because they provide good chemical resistances and physical properties to coatings made from aqueous resins like polyurethanes or polyacrylics. Polycarbodiimides themselves have no classification and they can be readily mixed into the aqueous resins mixtures, especially the aqueous polycarbodiimides. Curing of the coatings can be done at ambient or low thermal conditions. Many types of polycarbodiimide crosslinkers do not contain VOC, which helps to reduce the overall VOC content of the complete coating mixture. It is advisable to perform a ladder study to determine the optimum ratio between the resin and the polycarbodiimide crosslinker, to achieve the desired properties of the cured coating. Pot lives of mixtures of aqueous polycarbodiimides and aqueous resins may be very long, up to multiple days, when the pH of the mixture of crosslinker and resin is 9.0 or higher.

These advantages make polycarbodiimides a safe and sustainable choice as crosslinker for aqueous polyurethane or polyacrylate coating systems. They are thus a very suitable building block for eco-friendly coating mixtures.

5. Acknowledgements

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