

AN UPDATE ON CROSSLINKING OF LEATHER FINISHES WITH POLYCARBODIIMIDES

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ABSTRACT

Crosslinking is useful and effective at coaxing the highest performance out of both on-site-applied and industrially-applied coatings in fields as diverse as coating spacecraft and finishing leather. There has been an evolution in the nature of what is used to crosslink leather finishes as performance targets edge ever upward and tolerance for VOC (Volatile Organic Content) diminishes. This paper will cover some of the reasons polycarbodiimide crosslinkers failed to be competitive in our industry until recently. We will demonstrate that they do possess certain advantages, such as long potlife, and that they can, if properly used, compete on the basis of performance. Of special importance are new polycarbodiimide crosslinkers and technology which include all- aqueous polycarbodiimides free of VOC and higher-performance multifunctional polycarbodiimides. A striking discovery is that the chemistry of carbodiimide crosslinkers may not be as simple as previously thought, and in particular, stoichiometric predictions that assume traditional interpretations of carbodiimide chemistry have been found to be invalid. Various aspects of the chemistry, comparison of results obtained from free film testing, and results culled from extensive leather finish testing will be presented which demonstrate that polycarbodiimides appropriately employed can be effective, environmentally friendly, long-pot-life crosslinking agents.

INTRODUCTION

Crosslinking is widely practiced in nearly all of the coatings industries, be the end-use application as coatings for the exterior surfaces of cars and airplanes, high-wear interior wood flooring, or for flexible substrates such as paper, textiles, and leather. In all cases where crosslinking is employed, the object of its use may be stated generally to be to improve performance. The improvement desired and achievable through the means of crosslinking is usually one related to wear, resistance (to water, solvent, staining, etc.), of toughness, to improve mechanical film properties (hardness, toughness, resistance to abrasion) or to maintain integrity after repeated flexure. Crosslinking can be used in all the indicated fields of application to improve in one way or another the performance of solvent-borne and of aqueous coatings. In our leather industry, where now coatings are largely if not almost entirely water based -- only upon those will we focus -- the highest performance end-uses are in automotive. One would be hard-pressed to identify any leather used for automotive seating or steering wheel covers where the topcoat or, less likely, base as well as topcoat are not crosslinked.

In the leather industry, the most prevalent crosslinking system involves the use of water-dispersible oligomeric polyisocyanates. The polymeric binders in such aqueous coatings are either polyurethane dispersions in water, or acrylic latexes or the two

used in combination. Trailing distantly behind isocyanates as crosslinkers are water-dispersible polycarbodiimides, and trailing still further behind are an assortment of other crosslinking technologies, including polymers that are self-crosslinking.

This presentation will summarize the several and serial advances in the oligomeric polycarbodiimide realm that promise to elevate that chemistry to a place of prominence hoped for but never earned by offerings which began to appear in the marketplace as long as two decades ago, at about the same time, curiously, that water-dispersible oligomeric isocyanates burst upon the scene. We will review the chemistry of polycarbodiimides, including the surprising and important observation that though carbodiimides do react with carboxylic acids as all the literature sources stress to be the principal expected reaction, the traditional view of reaction with carboxylic acid being the only path freely available to carbodiimide for most ambient-curing aqueous coating chemistries is surely and sorely in error.

HISTORICAL

The targeted markets for water-dispersible oligomeric polyisocyanates and polycarbodiimides were different even though they arrived upon the coatings scene around the same time and both were intended for crosslinking of aqueous coatings. Water dispersible isocyanates came about as automotive upholstery finishing was mutating from domination by isocyanate-cured solvent-borne vinyls and vinyl-urethane systems in color- and topcoats, to all-aqueous finishes. The aqueous chemistries had to be crosslinked every bit as much as did the solvent-based chemistries they were destined to replace. It occurred to some bright chemist to make a water-dispersible isocyanate to cure the latex acrylics and aqueous polyurethane dispersions being tried, since isocyanates worked so well for the solvent-based solution chemistries. This is rather an amazing development when considering the context: the aqueous acrylics and PUD's that were being investigated had no obvious functionalities that could readily react with isocyanate, whereas the solvent polymers did, and any chemist would know that isocyanates react with water, so pot stability would be a problem. In fact, water-dispersible oligomeric polyisocyanates became a great success story.

The stimulus for water dispersible polycarbodiimides emerged from a quite different set of circumstances. Many industrial coatings applications that used aqueous carboxyl-functional acrylics as the main binders, and were cured with crosslinkers that required long and high temperature baking. Aziridine crosslinkers that cured at low-temperature and even ambient temperature was at the time gaining a foothold and had become the gold standard for property development under mild cure conditions. Aziridines struggled under the weight of concerns about toxicity, handling, and even performance plusses were being balanced off in some applications by concerns about yellowing. What better way, it seemed, than to cure carboxy polymers in water with a polycarbodiimide, and to do that, to make that polycarbodiimide water dispersible.

Polycarbodiimide crosslinkers for aqueous systems flopped, the reasons for which can be summarized as follows: the hoped for ability to replace polyaziridines simply wasn't there on performance grounds; use was mostly with hard acrylics where data suggests reactivity was simply too fast leading to a surface crosslink that may have interfered with film-formation and maybe because of fast reaction at the particle

surface afforded insufficient through-cure. The market failure was rationalized by speculation on technical reasons for it. Inability of polycarbodiimides to perform as low-temperature crosslinkers for aqueous acrylic systems were generalized to hard polyurethane dispersions, probably somewhat but not entirely valid, then further generalized to soft polyurethane dispersions, a generalization which is even less supported by experiment and experience.

OUTLINE

The situation concerning polycarbodiimides in leather finishing is changing. What has changed are the following: We now not only have water-dispersible polycarbodiimides but fully aqueous – zero VOC – polycarbodiimides. These have decent stability in water, and exhibit much longer useful potlife than isocyanates could achieve. Higher performance multifunctional water-dispersible polycarbodiimides exist and new ones are now coming off the drawing board. We are discovering the right way to make use of them for leather finishing, overcoming some issues, the most troubling of which can be summarized as consequences of overcrosslinking, for example, imperfect adhesion on recoat.

Today we start by reviewing what a polymer is and what crosslinking does. We will compare the chemistries involved in crosslinking of polyisocyanates and polycarbodiimides, and we will show you some exciting results regarding potlife, performance, and not least in importance, evidence that conventional chemical wisdom is wrong about carbodiimide chemistry as we use it for crosslinking. We find that carbodiimides do not necessarily cure only by reaction with carboxylic acid as journal and textbook references suggest. The huge surprise is that at least for use in our industry and maybe for all users, formulation to some particular stoichiometry of carbodiimide to carboxylic acid should not be the criterion for arriving at crosslinker dosage. Finally we will assemble some conclusions.

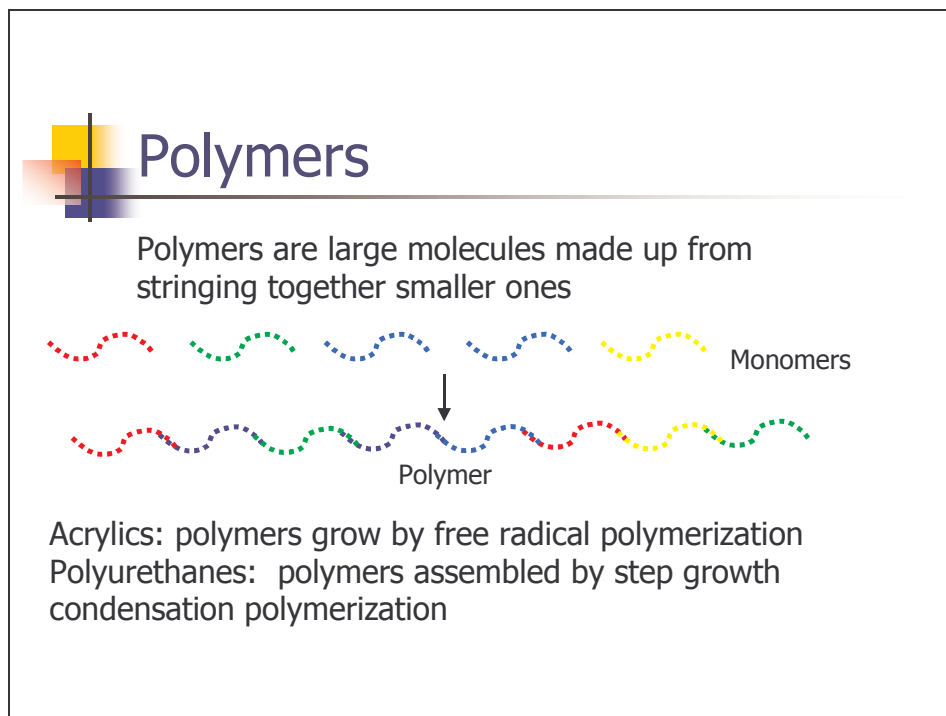



Fig.1 Schematic illustration of a poly-mer built up from mono-mers

Polymers (Fig. 1) are large molecules made up from smaller units and can be assembled in various ways. Poly-mers are made from mono-mers. Those polymers most used in the leather finishing arena are acrylic acid latexes and polyurethane aqueous dispersions, both of which have low levels of potentially reactive carboxylic acid functionalities. Acrylic latexes are assembled from acrylic and methacrylic acid and ester monomers by free radical polymerization, whereas polyurethane dispersions are made in an entirely different multi-step process from diisocyanates (usually di-, sometimes di- and tri-) reacted with polyols and usually with a dihydroxy carboxlic acid included as one of the polyols to impart dispersion stability, and finished of by being dispersed in water and chain extended to increase molecular weight.

We will not spend time on the polymerization specifics further except to state that both the acrylic monomer building blocks and those used to construct polyurethanes can give rise to varied and versatile polymers as dispersions in water that contain available carboxylic acid (-COOH) functional groups.



Concept of Entanglement

- Conventionally
 - Short chains easily disentangled
 - Long chains not, so longer chains are better
- Consider interchain interactions that can restrict mobility
- Result whether from long polymer chains or chain-to-chain interaction: the many intertwined, interacting chains give rise to mechanical properties
- Chain-to-chain interactions: can be polar interactions , hydrogen bonds, crystalline regions, hard & soft domains...




Fig. 2 – The concept of entanglement

Long polymer chains can entangle (Fig. 2) and interact and that is the origin of useful polymer properties. Analogies are sometimes better than rigorous science for visualizing in one's mind the consequences and performance benefits of entanglement, and the analogy of spaghetti is offered with apologies to our more sophisticated colleagues to explain entanglement, and even crosslinking.

Consider a plate of spaghetti (since we are in Italy) and the simple act of teasing out a single strand. Entanglement will make that difficult and a plate of freshly-made spaghetti has some considerable tensile strength owing to entanglement. Allow some of the starchy water to start to dry onto the strands, and the chains can be thought of as interacting, and it becomes more difficult to tease out a strand. Now allow the spaghetti to dry; the remaining starch glues the strands together tightly wherever

adjacent strands intersect – acting just like crosslinks in a polymer do, bonding adjacent chains – and the mass of spaghetti becomes stronger yet. When you finally stretch that mass to the breaking point, the mass will be less elongated at the point of breakage compared to doing the same thing before you allowed the starch to dry and bond adjacent strands.

So what do we expect from crosslinking? We expect to make short and medium and even long chains longer, enhancing entanglement; we expect to tie adjacent chains together, generating a network in three dimensions. That network can in principal create the fabled infinite molecule that will no longer dissolve or be swollen by solvent, and by inference be less susceptible to staining by organic color bodies.

Crosslinking, especially network formation, has the potential to reduce elongation and to increase tensile strength, thus polymer hardness, and we must therefore exercise care not to overdo crosslinking. For hard coatings on rigid substrates we can go all out with crosslinker; for soft coatings on extensible, flexible substrates such as leather, low levels may be best.

BACK TO CHEMISTRY

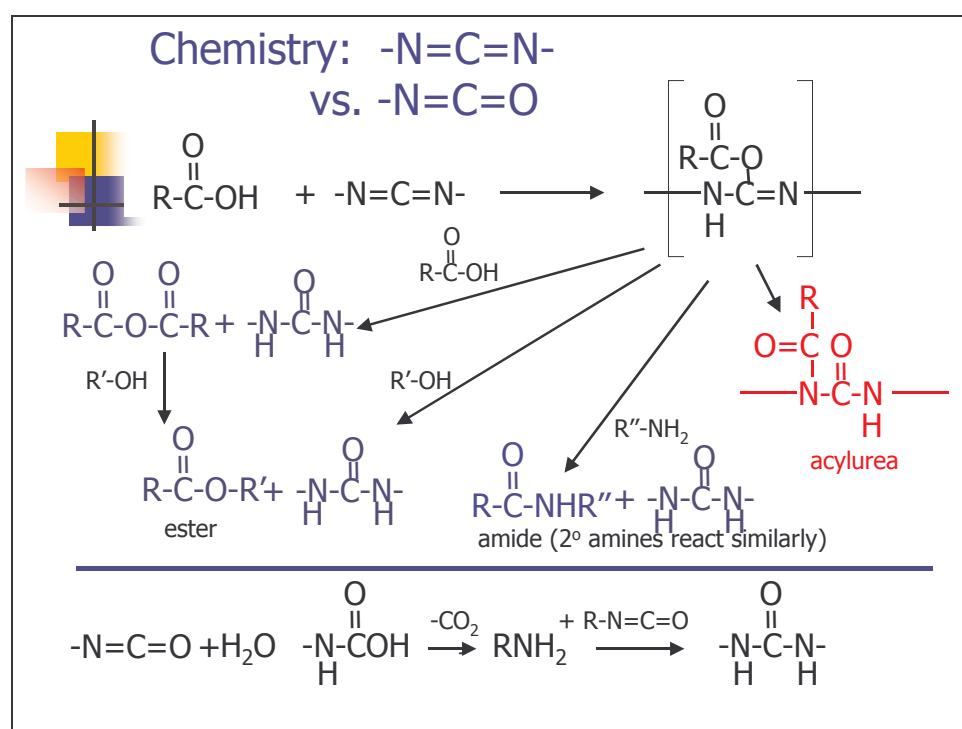


Fig. 3 – Some reactions of carbodiimides and isocyanates

The chemistry of polycarbodiimide crosslinking involves mainly the reaction of carboxylic acid ($-COOH$) groups in acrylic latexes or in polyurethane dispersions with carbodiimide ($-N=C=N-$). As shown in Fig. 3, an O-acyl urea is formed as an intermediate and it rearranges to an N-acyl urea. The O-acyl urea is a reactive species in its own right, and it can do many things as we illustrate here, though most of these do not apply because the functionalities indicated may not be present.

Since the polycarbodiimide contains several $-N=C=N-$ groups, one polycarbodiimide molecule can react with carboxyl groups on different polymer chains tying them together via the reaction, in other words, forming a crosslink.

Reaction of carboxylic acid with carbodiimide can be quite fast under ambient or mild thermal cure conditions, rendering that chemistry near ideal, on paper at least, though not entirely so in practice yet, for crosslinking aqueous leather finishes. Very surprising to us, we have not been able to confirm with model compounds that stronger acids react faster than weaker ones, but there is copious evidence that carboxylic acid groups, generally from acrylic or methacrylic acid co-monomer, react faster – sometimes much faster -- than the hindered carboxylic acid in a polyurethane dispersion made from 1,3-dimethylolpropionic acid as a building block

In most leather finishes, there is no significant amount of hydroxyl or other reactive functionality capable of reacting with isocyanate, a situation not so in most other fields where isocyanate crosslinkers are used. So the reaction when isocyanate crosslinkers are employed in leather finishing is probably one of simple moisture cure, but believed to occur after the isocyanate oligomer crosslinker has penetrated into the latex or polyurethane dispersion particle or polymer. Thus in the realm of leather finishing, use of polyisocyanate crosslinkers in most cases results in the formation of an interpenetrated polymer network or IPN, where, according to this explanation, the isocyanate polymerizes in and around and in the presence of an acrylic or polyurethane, but does not actually react with the polymer to which this extreme form of entanglement is associated.

AVAILABILITY

These slides summarize how most of the available water-dispersible polycarbodiimides and polyisocyanates are manufactured, and their main features.

Both polycarbodiimides and polyisocyanates start with a diisocyanate as the basic building block.

isocyanates, they can also be supplied in water. Aqueous polycarbodiimides can be manufactured with zero VOC.

In use, both types of crosslinkers can be hotpotted, that is mixed into the aqueous finish before being applied, the practice necessitating some reasonable potlife for the mixture. Or both types of crosslinkers can be mixed into the rest of the finish formulation in-line ahead of or actually in the application device, usually a spray gun, thus overcoming any potlife limitations.

DOSAGE

The term stoichiometry as applied to the use of a polyisocyanate crosslinker with a typical water-based leather finish having no hydroxyl or other isocyanate-reactive groups is not a useful concept. The situation for polycarbodiimide crosslinking is quite different since most of the aqueous polymers that we use, whether acrylic or polyurethane, do have available functionality (carboxylic acid) that can react with a carbodiimide. Even though one can in principle address carbodiimide crosslinker dosage in stoichiometric terms, it is not useful to do so. Two main reasons are that few endusers will be in a position to calculate a stoichiometry without intimate knowledge of the makeup and functionality, not only of the main polymeric binders, but also of the carboxy-functional materials that may be present in the form of thickeners and dispersants. One is compelled to run dosage ladders to determine optimum crosslinker levels. The second reason is based on the empirical observation that in soft coating systems, such dosage ladders often produce optimum crosslinker levels that bear no relationship to stoichiometry. In other words, studies with stoichiometry as the independent variable have revealed no special virtue as regards performance in the use area of leather finishing. For leather finishing, typical use levels are often below stoichiometric.

The dosage rule is simple: Run a ladder, start low – more is not always better -- and don't sweat the little differences. Comparing a high-solids material to a low-solids one, but if the differences, say in solids, are small (40% solids vs. 50% solids) it may not pay to make the adjustment.

DETECTING CROSSLINKING

There are three very simple ways of detecting the existence of crosslinking. One is to determine stress-strain behavior. Here we see idealized stress-strain curves for a soft vs. a slightly harder polymer, or a soft polymer which has been lightly crosslinked. These are typical curves for polyurethanes; acrylics might differ somewhat, though many will behave as shown. Initial slope increases with crosslinking – more force to elongate a given amount, and at various percents elongation (strain) we will expect to see higher stress for the crosslinked coating. In one convention, we often refer to stress at 100% elongation as 100% modulus, at 200% elongation as 200% modulus, etc. The other feature we might look for is how much we can elongate before the specimen breaks. Crosslinking will generally reduce ultimate elongation.

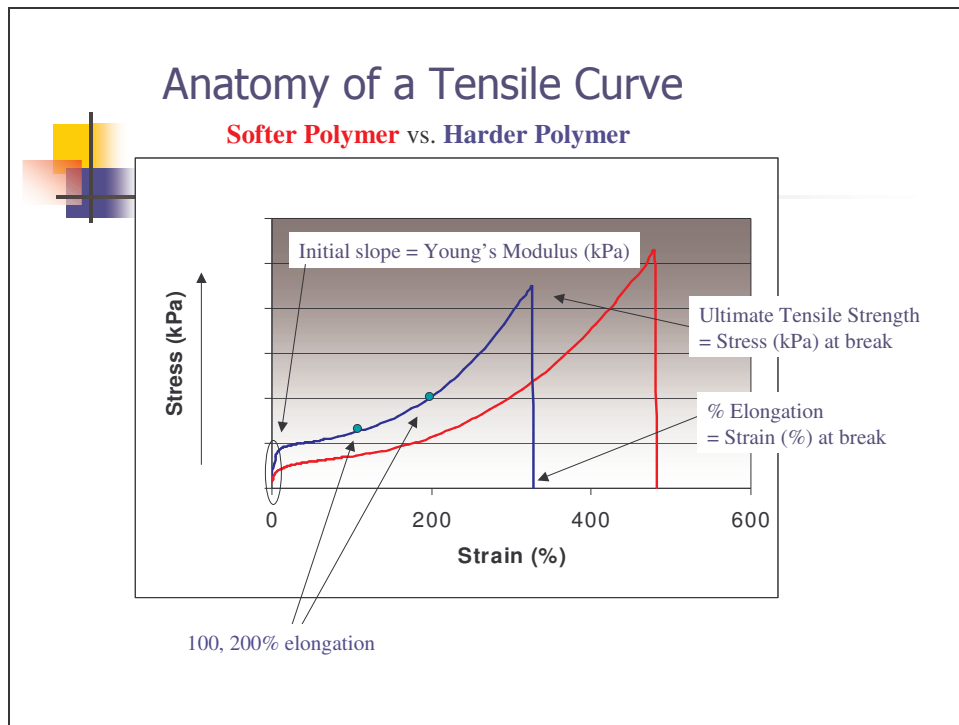


Fig. 6 – idealised Stress-Strain curves comparing a softer vs. a harder polymer, but showing features similar to a comparison of soft & uncrosslinked to crosslinked

Fig. 7 through 9, we see the tensile properties of uncrosslinked and crosslinked films from anionic (carboxyl-functional) latex acrylic polymers, one with normal (low carboxyl) content, the other with very high carboxyl content, and one anionic (also carboxyl functional) polyurethane dispersion. The following abbreviations are used on the slides:

CDI = oligomeric waterdispersible polycarbodiimide

CDI++ = multifunctional, higher performing water dispersible solvent-borne polycarbodiimide

NCO or NCO olig = oligomeric water dispersible polyisocyanate

In the Xlinker (crosslinker) column, percents are of crosslinker product not solids, calculated on total mixture

Notice how (Fig. 7) for the low carboxyl-content acrylic even low levels of polycarbodiimide increase moduli -- stress at given elongations -- and how in this case elongation is lower as crosslinker level increases. We are in a stoichiometry range here below 1.00. The two polycarbodiimides are one (identified as simply CDI) supplied at 40% aqueous (and zero VOC), and the other identified as CDI++, supplied 50% in solvent. CDI++ is a higher performance multifunctional polycarbodiimide useful in certain heavier-duty industrial applications.

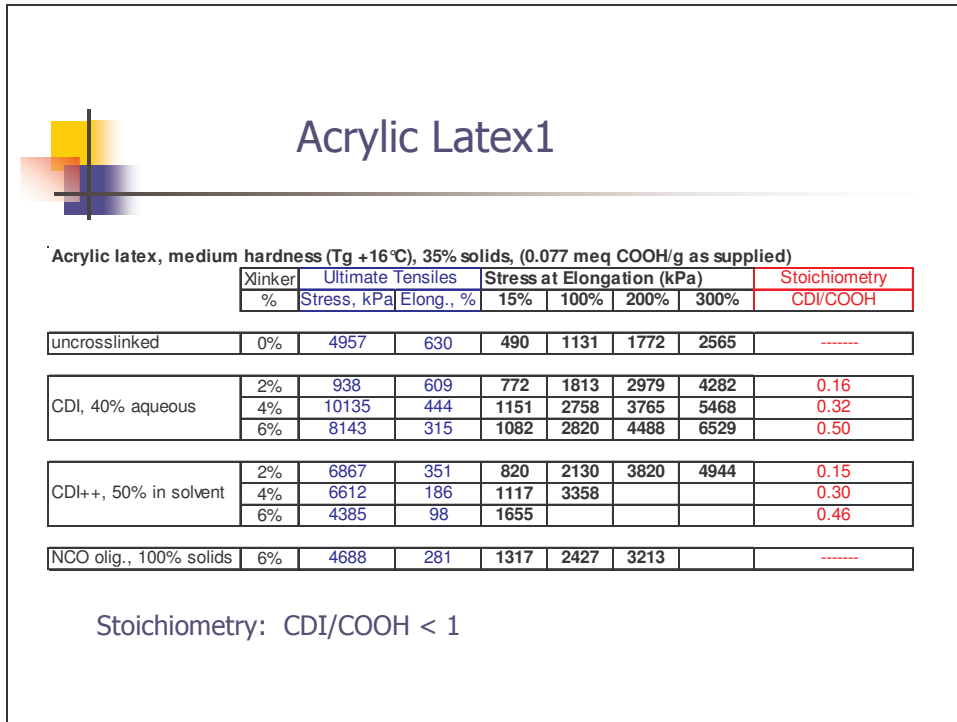


Fig. 7 – Medium hardness acrylic latex

In Fig. 8 we see similar behavior for a typical anionic (carboxyl-functional), soft aqueous polyurethane dispersion, again covering a stoichiometry range below 1.00

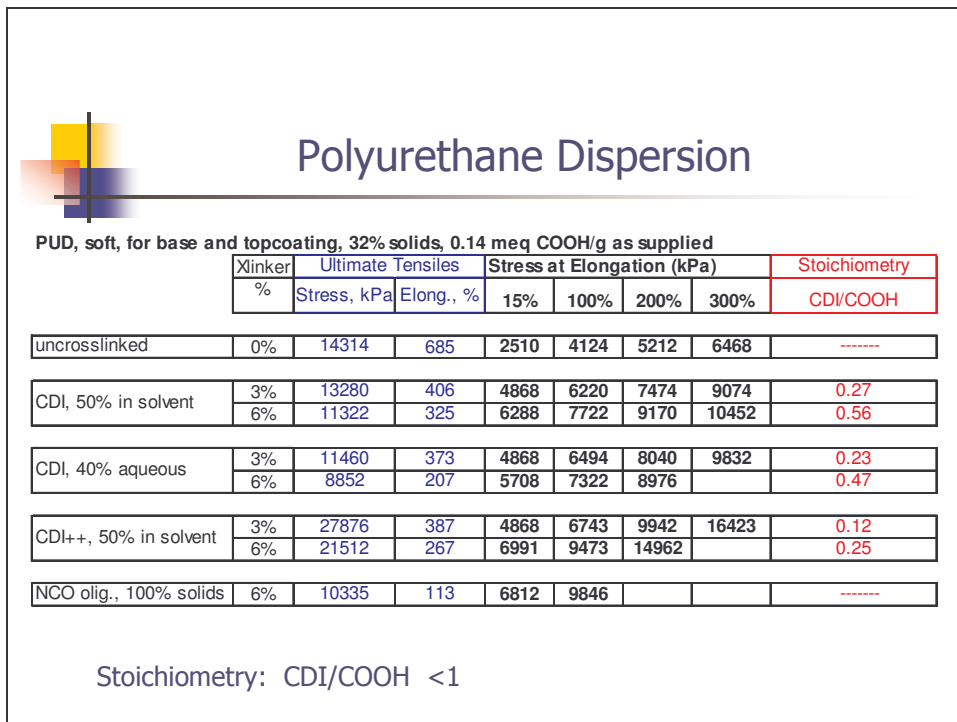


Fig. 8 – Soft aqueous polyurethane dispersion

Fig. 9 shows stress strain behavior is of a high acid acrylic latex formulated with 2-6% polycarbodiimide crosslinkers, at very low resulting carbodiimide to carboxylic acid stoichiometry, and where we see an effect is with the higher-performance

multifunctional polycarbodiimide (CDI++) only. The amount, 2-6% of crosslinker product, that is, the dosage level is important, rather than the stoichiometry.

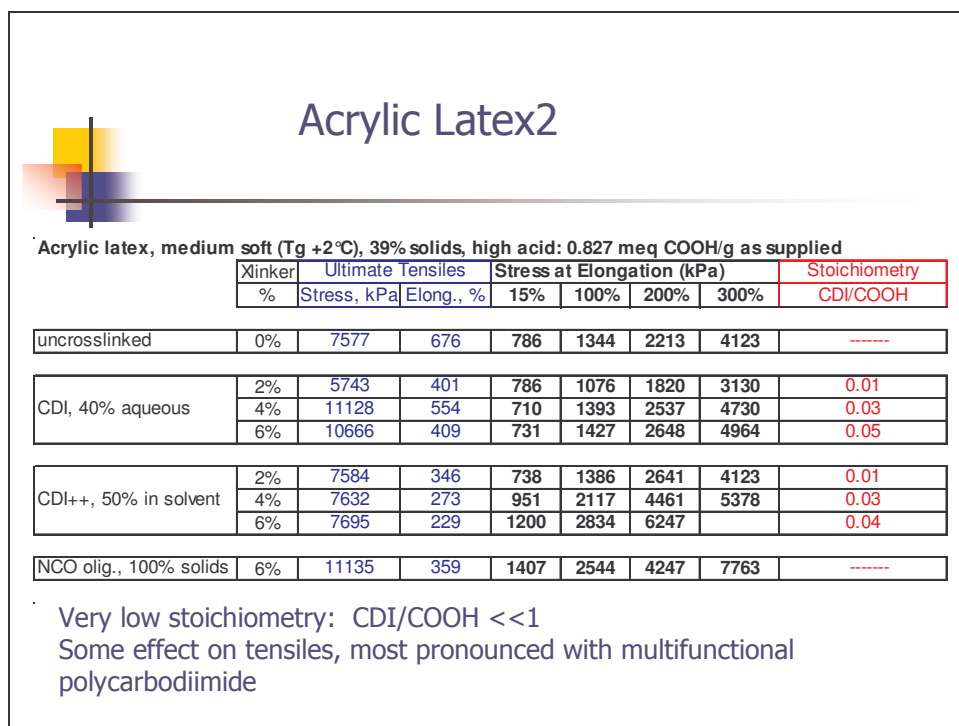


Fig. 9 – Soft, high acid acrylic latex

POTLIFE

These next two figures (Fig. 10, Fig. 11) represent efforts to quantify what happens with carbodiimide functionality in a leather finish by using Fourier Transform Infrared (FTIR) measurements to assay for carbodiimide functionality. Carbodiimide/Carboxyl stoichiometry is very high: CDI/COOH = 4.4.

Fig. 10 is a surface FTIR scan of leather, freshly topcoated, scanned immediately after it was dried in one pass through a typical drying tunnel, then rescanned after it was allowed to rest at ambient temperature for two weeks. Only the slightest trace of carbodiimide remains after two weeks. Conventional wisdom would hold that three-quarters of the initial carbodiimide should remain unreacted.

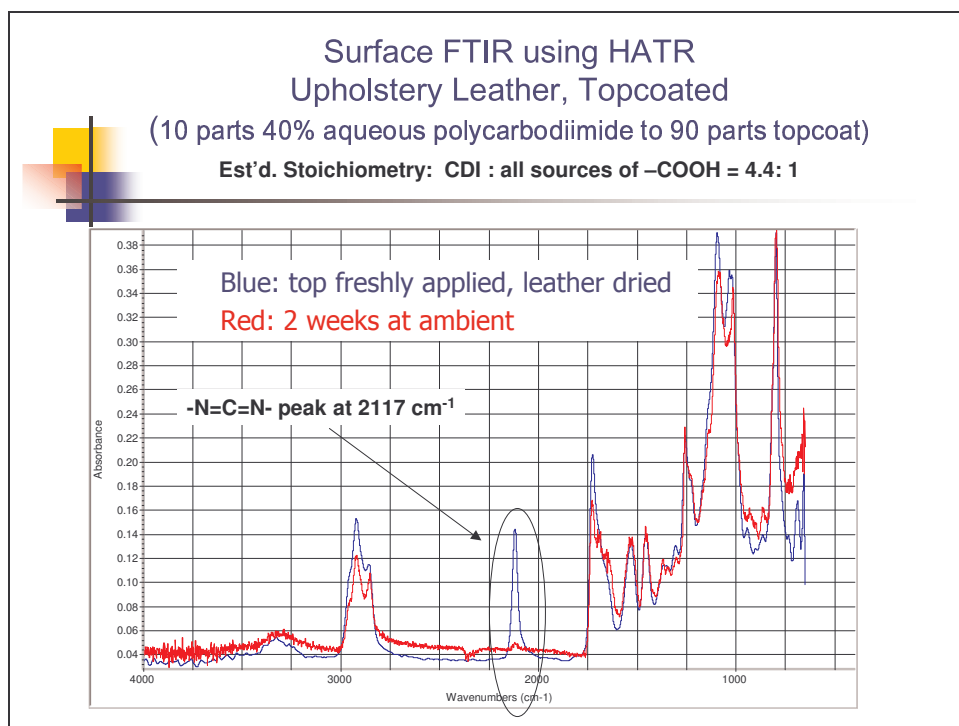


Fig. 10 – Topcoat automotive upholstery leather, after being dried right after application, and two weeks later, stored at ambient

This behavior was observed with a several coating formulas and with acrylic latex polymers and unformulated polyurethane dispersions, and in all cases examined where CDI/COOH stoichiometry was in excess of 1.00 – and of course in all cases where it was less than 1.00 -- we observed loss of the excess carbodiimide functionality over time. Some were more rapid than others, and in one case, the result was spectacular.

This most impressive example (refer Fig. 11) of failure of conventional wisdom to hold up was obtained in the case of an acrylic latex synthesized with almost no carboxylic acid but containing a proprietary functionality that from the classical understanding of carbodiimide reactivity would be expected to be unreactive. The FTIR scan is of an ambient cured polymer latex-plus-polycarbodiimide crosslinked film that has remained at ambient two weeks. In fact it loses carbodiimide faster than any other polymer we have looked at, and produces a significant improvement in tensile properties as it does, all as if – indeed suggesting – efficient reaction with carbodiimide, or some other chemistry mediated by the proprietary functionality. The diagram indicates stoichiometry – CDI/COOH ratio to be $\gg 10:1$ which is correct. In fact, CDI/COOH ratio was 28:1 and CDI/(COOH+other functionality) was high as well, 10:1, so the loss, reaction, or destruction of $-N=C=N-$ must have been catalytically driven.

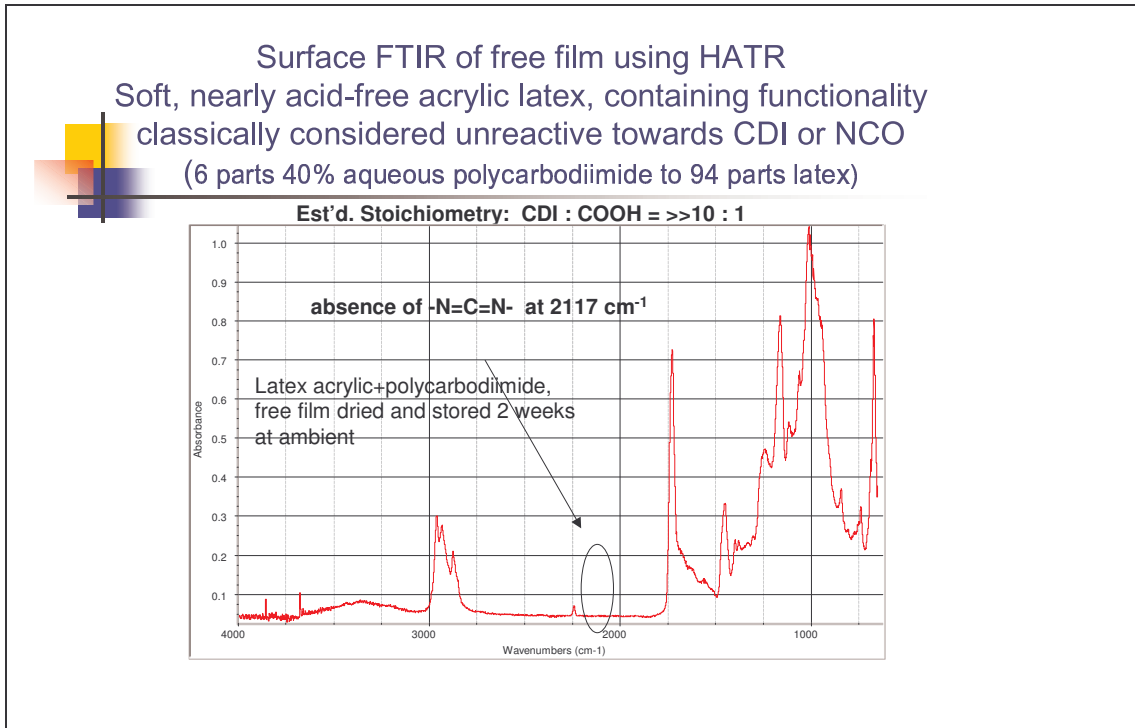


Fig. 11 -- FTIR scan is of an ambient cured polymer latex-plus-polycarbodiimide crosslinked film that has remained at ambient two weeks.

LEATHER FINISH RESULTS

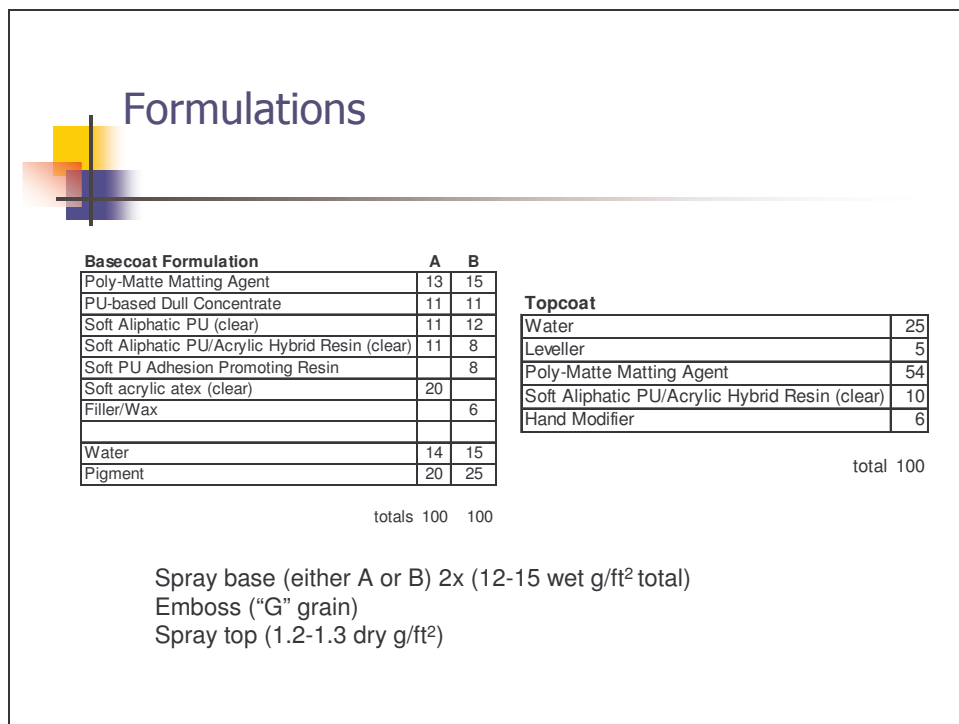


Fig. 12 – Formulations

Formulations shown in Fig. 12 were used to test out some of the capabilities of polycarbodiimides as crosslinkers for leather finishing and specifically to analyze the effect of using a polycarbodiimide to crosslink a basecoat. Basecoats A and B differ

in performance, B being the higher performing of the two. The topcoat is a good performing topcoat. Neither system on the crust selected will pass automotive wet abrasion specifications if there is no crosslinker in base or in topcoat but over the better performing basecoat, crosslinking the topcoat with isocyanate oligomer will pass wet abrasion, and crosslinking with polycarbodiimide will not.

Thus we can, with this combination of basecoats, topcoat and crosslinker, evaluate very sensitively the capabilities of polycarbodiimide as a crosslinker.

In Fig. 13 we compare basecoat A – the lesser performing one – with and without 3% of a 40% aqueous polycarbodiimide crosslinker. The single testing criterion is Veslic wet abrasion cycles to failure.

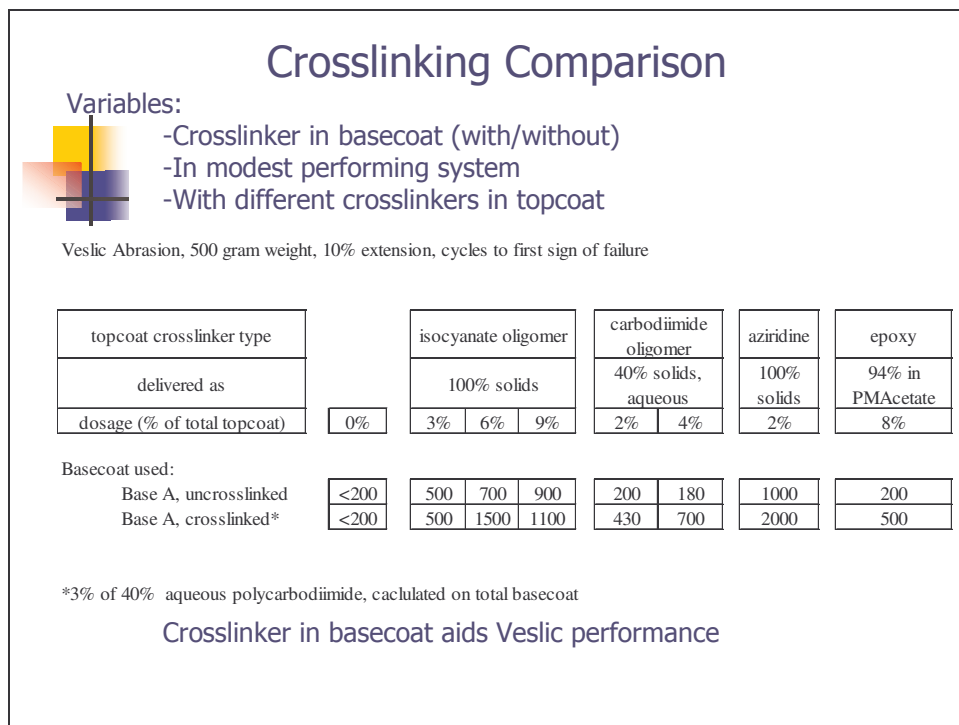


Fig. 13 – Wet abrasion results showing example of utility of polycarbodiimide crosslinker in basecoat

With no crosslinker in the topcoat we experience failure before 200 cycles, basecoat crosslinked or not. Using different crosslinkers in the topcoat, we see better performance for a crosslinked basecoat than uncrosslinked, and we see the expected performance ranking of aziridine crosslinker >> oligomeric isocyanate in the topcoat > polycarbodiimide. Similar trends – better performance with carbodiimide in the basecoat than with none was observed with basecoat B, and we could meet goals with carbodiimide as crosslinker in the topcoat

In Fig. 14 we seek improvement by going to a better-performing basecoat, crosslinking that also with polycarbodiimide, trying to see if, after improvement there, we can reach a desired performance level with polycarbodiimide crosslinking, rather than polyisocyanate, in the topcoat. We also made comparison of all aqueous vs. solvent-borne water-dispersible polycarbodiimides as crosslinkers for the better performing basecoat (B)

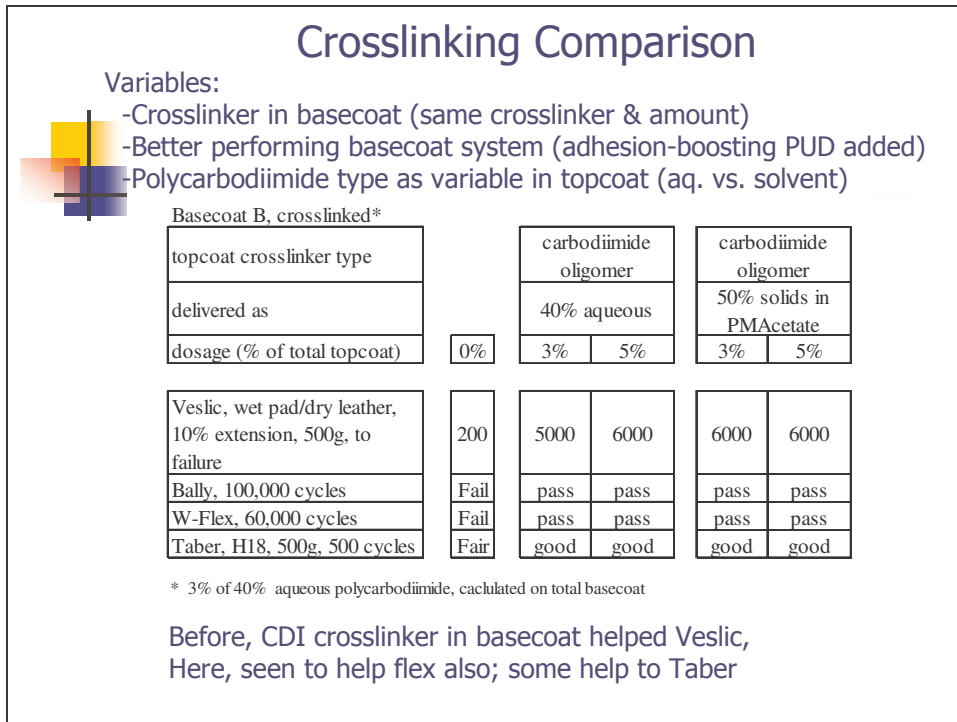


Fig. 14 – Better basecoat, crosslinked, plus carbodiimide crosslinking in topcoat

Fig. 15 represents a repeat and extension of the experiment represented in Fig. 14: Basecoat B with 3% of 40% aqueous polycarbodiimide, and compares polyisocyanate oligomer and polycarbodiimide oligomer crosslinkers, with an extended ladder of crosslinker in the topcoat ranging from 0 to 10%.

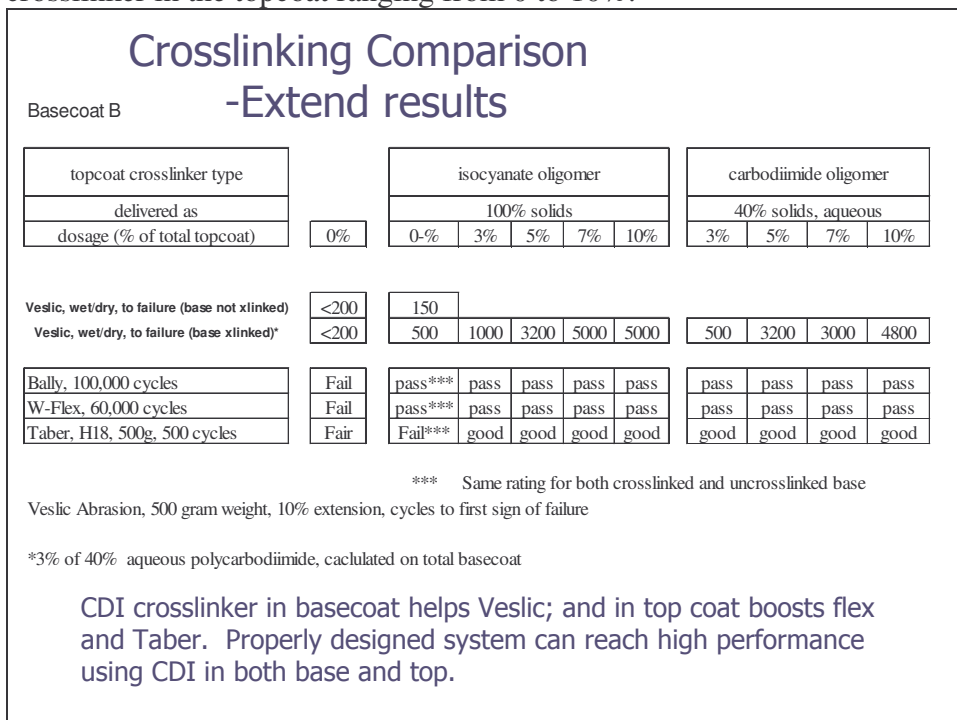


Fig. 15. --Extension of the experiment represented in Fig. 14: Basecoat B with 3% of 40% aqueous polycarbodiimide, comparing polyisocyanate oligomer and

polycarbodiimide oligomer crosslinkers, with an extended ladder of crosslinker in the topcoat ranging from 0 to 10%.

It is very clear that good performance can be had with polycarbodiimides as crosslinkers.

MORE ON POTLIFE

Fig. 16 graphically represents data regarding stability of a leather top coat that was hotpotted – formulated with different isocyanate or carbodiimide crosslinkers – and periodically assayed for isocyanate or carbodiimide content. Quantitative tracking of the carbodiimide and isocyanate groups over time was done using Fourier Transform Infrared techniques.

You will note that carbodiimides are much more stable in water than isocyanates as expected. We state normal potlife for water-dispersible polyisocyanates to be 4 to 8 hours, depending on the potlife. For the more hydrolytically resistant polycarbodiimides represented by the new technology of the water-borne material shown here, useful potlife is at least several days, to a week or more, as the next slide illustrates.

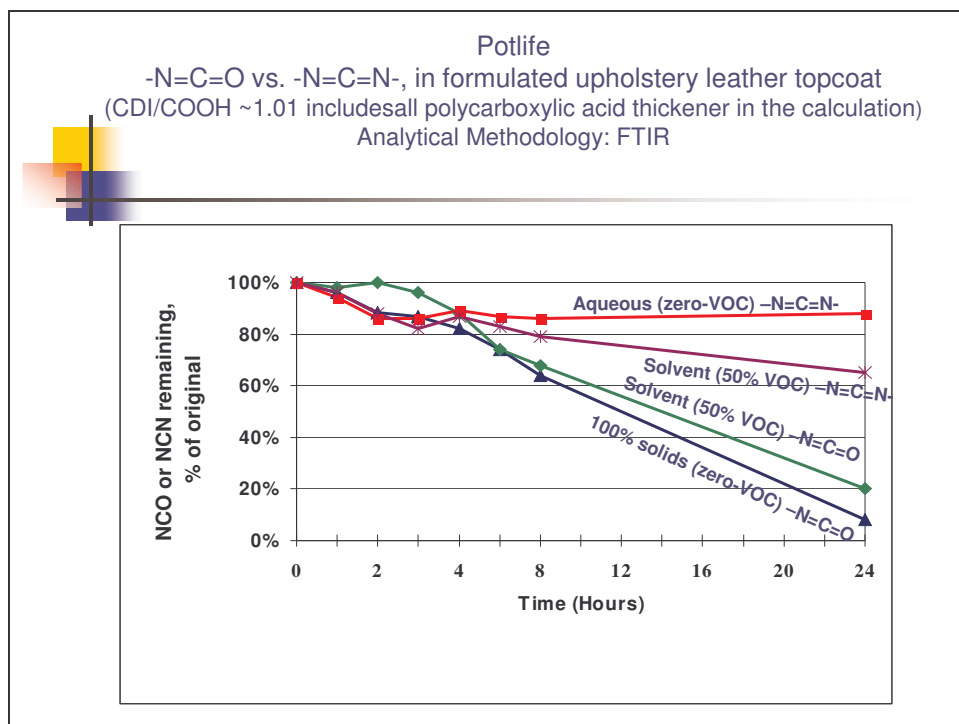


Fig. 16 – Potlife. Decay of crosslinker reactive functionality over time in a formulated aqueous topcoat system

In a different system, formulated more typically, that is at lower carbodiimide to carboxyl stoichiometry, we followed loss of carbodiimide spectroscopically and tried to gauge useful potlife also (Fig. 17). How we have done this is to apply the aged formula as a topcoat to ready-for-topcoating basecoated automotive upholstery leather, and then to age that leather coated with aged formula at room temperature, testing the leather at daily or more prolonged intervals to determine how many days

room temperature post-cure is needed to pass 500 wet/dry Veslic abrasion cycles (wet pad, dry leather, 10% extension of the leather, 1 kg load). Formulated topcoat aged up to about 13 days passes this go/no-go test after under 2 days aging, and then with older formulated mix longer cure time is required. Still, though cure time is lengthened to 5 days when 30-day-old topcoat formulated with carbodiimide crosslinker is applied, there is ability to pass the test.

Typical useful potlife for isocyanate oligomers is 4-6 hours.

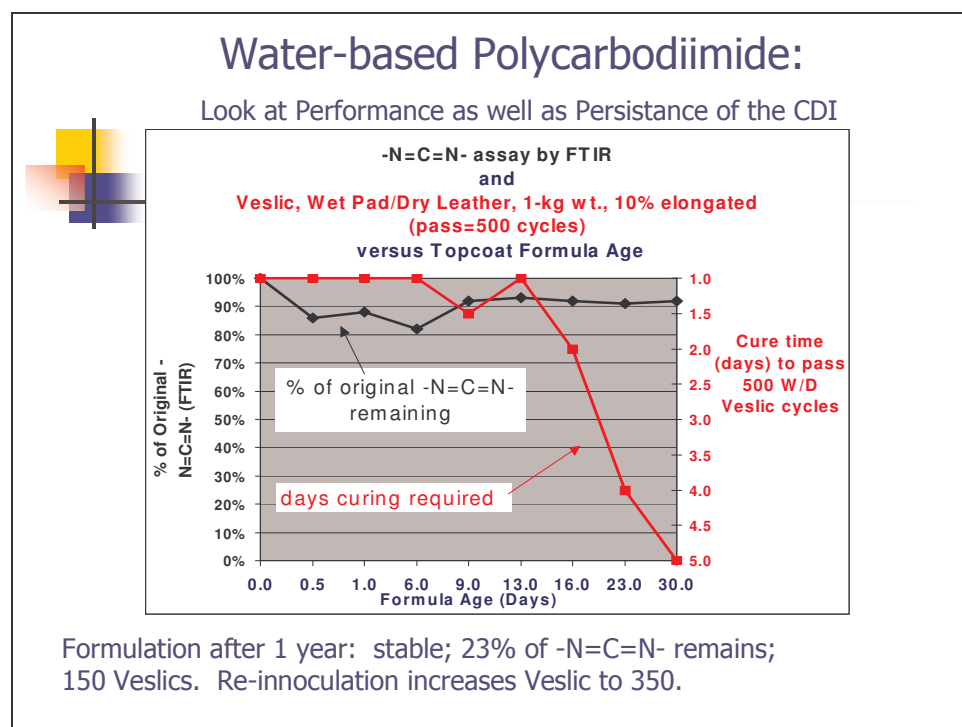


Fig. 17 – Stability (-N=C=N- remaining) and performance versus time for a crosslinked topcoat formulation subjected to aging

HIGHER PERFORMANCE MULTIFUNCTIONAL POLYCARBODIIMIDES

We have presented some data (Fig. 7, 8, 9) that referred to a high performance multifunctional polycarbodiimide identified simply as CDI++. It is a solvent based polycarbodiimide that is suitable in industrial coating applications where a top finish will not need to be recoated, which thus leaves out most of leather finishing. CDI++ had enjoyed some initially good success for leather finishing because it achieves a considerably higher degree of crosslinking and property improvement compared to any other type of polycarbodiimide, and whereas we often accept the generality that polyisocyanates will outperform polycarbodiimides, CDI++ is in fact sometimes added to finishes that use polyisocyanates as crosslinkers to improve crosslinking and properties. CDI++ actually does satisfy a small part of the leather finish market where the maximum in wet abrasion resistance, hydrolysis resistance, sweat resistance, chemical resistance and UV-durability are sought. The most easily recognizable of these segments of the leather finishing market is for finishes for steering wheel covers, and there it is most often used not in place of but to enhance crosslinking by isocyanate oligomers. The binder of choice in that end use is a polyurethane dispersion based on polycarbonate diol, prized for its UV and hydrolytic stability.

New multifunctional polycarbodiimides that greatly minimize the downside recoat problem and that have other benefits will be the subject of a future presentation.

CONCLUSIONS

We can conclude from this work that polycarbodiimides can be very practical in leather finishing. The most obvious use is in basecoats, at low levels of 2-4%, to build properties from the ground up. It is often common practice to expect the topcoat to do most of the work and to use crosslinkers only there. Anything done to improve the performance of the basecoat, whether by crosslinking or not, should obviously help overall performance and reduce test and performance variability. An advantage of aqueous polycarbodiimides is that while they can be used in-line, as is mostly the case with polyisocyanates, unlike polyisocyanates their long potlife recommends them for hotpotting.

We have also seen that if attention is paid to the basecoat – either a better basecoat system or that plus some crosslinking -- it is possible with polycarbodiimides in the topcoat to also achieve acceptable performance. For topcoats, somewhat higher levels are recommended (7-10%).than in basecoats. Again, formulate from dosage ladders, not to stoichiometry.

There is also a high performance multifunctional polycarbodiimide available which for a variety of reasons are not optimum for leather finishing. New ones will shortly be available that we are confident will elevate carbodiimide crosslinking to greater prominence.

It is interesting and useful to note that polycarbodiimide and polyisocyanate crosslinkers can be used together. We surmise that the high reactivity of the polycarbodiimide with carboxylic acid promotes an early cure, enhancing early property development, while the slower moisture cure of the polyisocyanate works itself to completion.

Finally, there is the issue of what precisely is the chemistry of disappearance of carbodiimide when used at levels much above 1 to 1 stoichiometry with carboxyl. We lack all of the answers. This is an area of continuing investigation, important because we find from mechanical film performance evidence that the use of excess can contribute to additional property development. Once again, it is not some particular stoichiometry that must be respected; it is dosage that is found to be important.