Carbodiimides in Leather Finishing II: Recent Advances*

by

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Abstract

The first paper in this series outlined the then-known chemistry of water-dispersible polycarbodiimides and demonstrated conclusively their utility for leather finishing, but at the same time revealed unexpected gaps in some of the chemical detail.

This presentation represents an update to an important leather industry audience and is one more in what is a longer series devoted to developing a consensus understanding of the chemistry and benefits that accrue to the use of polycarbodiimide crosslinkers for specialty coatings. The search for continued performance improvement in the most demanding areas of leather finishing continues, and the thrust of this paper and others in the series is to promote a more precise understanding of the complex chemistry of polycarbodiimides, to distill out from that larger chemical picture what reactions are most likely and deserve further study, and to ally that knowledge with what is taught by experience for the purpose of proposing, explaining, and justifying how best to use them to produce more cost-effective performance outcomes for the leather finisher.

Resumen

El primer documento de esta serie esbozó la química entonces conocida de la dispersión en agua de la policarbodiimida y demostrado de manera concluyente su utilidad para el acabado del cuero, pero al mismo tiempo se puso de manifiesto las deficiencias inesperadas en algunos detalles químicos.

Esta presentación representa una actualización a un importante público en la industria del cuero y es una más en lo que ya es una serie dedicada a la elaboración de un consenso en la comprensión de la química y los beneficios que se obtienen con el uso de reticulantes de policarbodiimidas para recubrimientos especiales. La búsqueda de una mejoría en el perfil de rendimiento de las más exigentes áreas del acabado del cuero continúa, y la idea central de este trabajo y otros de la serie es promover una comprensión más precisa de la compleja química de las policarbodiimidas, para destilar de ese amplio panorama de los productos químicos cuales de las reacciones son las más probables y merecen un estudio más a fondo, y la posibilidad de aliarse con el conocimiento de que lo que se enseña por la experiencia con el fin de proponer, explicar, y justificar la mejor forma de utilizarlos para obtener resultados más rentables y eficientes en el cuero acabado.

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INTRODUCTION

It was earlier proposed that failure in the mid to late 1980's of newly introduced water-dispersible polycarbodiimides to capture favorable market acceptance was in part due to the fact that they were promoted as replacements for polyaziridines to cure relatively hard acrylics. The choice to pursue such a difficult objective was unfortunate, and polymer type and hardness together combined to make the task more daunting. For leather finishing we use softer polymers, and whether we use acrylics or polyurethanes or combinations, both polymer types are good candidates for crosslinkability with polycarbodiimides. There are nevertheless differences between how these two competing backbones behave towards carbodiimides which we need to appreciate and which we will attempt to explain. Hardness also plays a role.

Experience has taught that in regard to leather finishing specifically, use of low levels of polycarbodiimide crosslinker was actually preferable to use of higher levels and in fact what evolved from that was a strategy of using low levels at least in undercoats, and thus building performance from the foundation up. Now polycarbodiimides are often used in topcoats as well, supplementing, less commonly replacing, polyisocyanate oligomers. In practice, however, basecoat use of polycarbodiimide crosslinkers permitted in many instances the economical reduction of how much of the widely used isocyanate needed to be added to the topcoat, resulting in improvements in overall cost as well as contributing to overall performance improvement.

THE CHEMISTRY

The principal crosslinking reaction between polycarbodiimides and acrylic latexes or polyurethane dispersions (PUD's) is between carboxylic acid functionality in the latex or PUD and carbodiimide to form an N-acyl urea (Fig. 1), but this proceeds through the intermediacy of an unstable and very reactive O-acyl urea, which unlike the carbodiimide itself, can react rapidly with amines and any alcohols that may be present. If there is available additional carboxylic acid, the O-acyl urea can react with that to form anhydride (Fig. 2). The anhydride provides another pathway allowing amines and alcohols, even the urethanes and ureas in the PUD and ureas formed from the primary reaction of carboxylic acid with the carbodiimide to enter the reaction scheme. All of these side reactions can occur and as shown by positions of infrared bands (Fig. 3), when important can be reasonably tracked.

What we can now rationalize out of this complexity is the occasional excess consumption of carbodiimide beyond what would be predicted solely from just availability of carboxylic acid.

It is now well established that aliphatic polycarbodiimides react with carboxyl groups only when the carboxyl group is in the un-ionized form (-COOH), not when it is present as a salt, in which case it exists in the form of a carboxylate anion ($-COO^-$). This readily explains why formulated coatings containing polycarbodiimides on the alkaline side can have good potlife, and why, when the acid is protected as an amine salt in the wet coating, it can cure so readily when the coating is dried when the amine gets driven off. We can now report that this simple picture, with a little more detail added, assigns a previously unheralded role to carboxyl group acidity, allowing one to explain on the basis of pKa why carboxyl-functional acrylic latexes react faster than carboxyl-functional polyurethane dispersions and are less likely to enjoy as good potlife.

It should be noted that the argument which will be developed does not mean that acrylic latexes are not good candidates for crosslinking by polycarbodiimides, but rather helps with rationalization of the anecdotal reports that overall seem to favor PUD's for both pot life and cure efficacy, though not for cure speed.

Fig. 4 presents structures and lists the pKa's of the most common acid monomers used in manufacture of carboxyl-functional acrylic latexes and PUD's. pKa's of the acid monomers all increase upon conversion to polymers by several pKa units, making them weaker acids when they are incorporated into polymers. Carboxylic acid groups in PUD's turn out to be stronger acids than their cousins in acrylic latexes. The stronger an acid is, the more of it will be in the salted form at any given pH. The more a carboxylic acid is partitioned into its salted form, the less available it will be to react with carbodiimide crosslinker in a wet formulation, leather finish formulations almost always being on the alkaline side. Consequently, simple analysis of the consequences of these pKa considerations leads one to understand why (1) carboxyl-functional PUD's exhibit better pot-life (less reaction in the wet formulation) than acrylic latexes, and (2) considering coating, drying, and the critical film-formation process as sequential steps in the creation of a sound coating, why timing of reaction of the carboxyl functionality with carbodiimide is likely to occur later in the film formation and curing process for a PUD than for an acrylic latex. This could mean film formation and coalescence has a chance to be further along for a PUD before crosslinking takes over.

Polymer hardness was earlier mentioned. In the realm of leather finishing, both acrylic latexes and PUD's in common use are quite soft when compared to coatings for wood, metal, or more rigid substrates where carbodiimide crosslinkers were first promoted over two decades ago. Ease of forming good films from either type of polymer is well accepted in our industry, and an inescapable conclusion can be reached that polycarbodiimide crosslinkers provide an admirable adjunct to leather finishing.

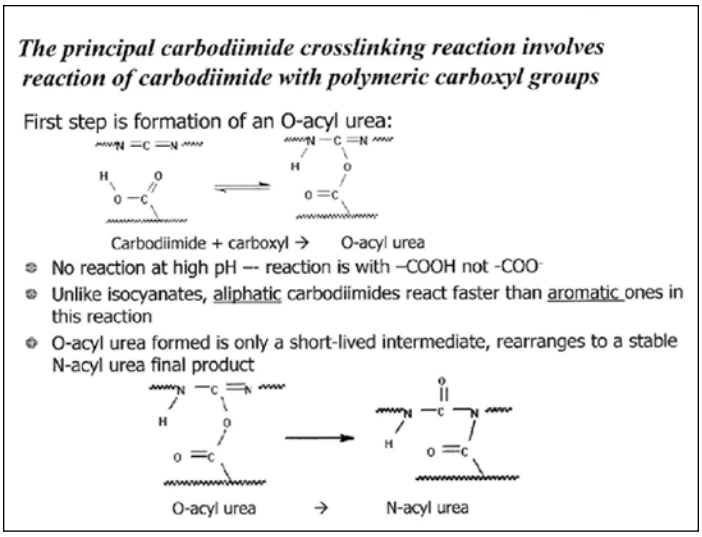

Figure 1: First step in crosslinking a carboxyl functional latex or PUD with a polycarbodiimide: A distinct intermediate is formed that rearranges to the final reaction product.

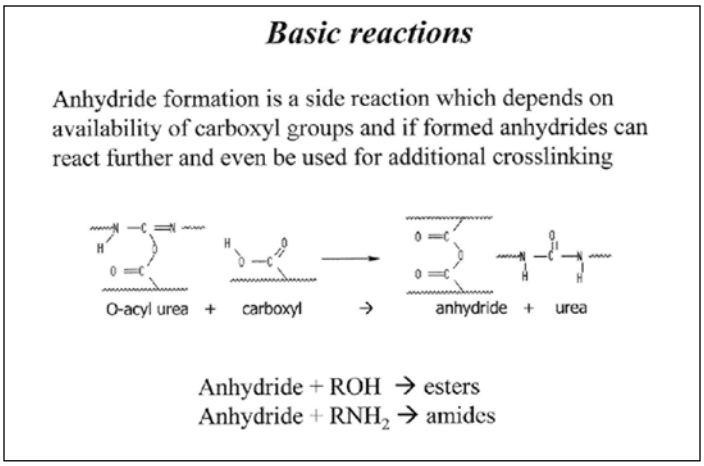

Figure 2: The O-acyl urea can be diverted to anhydride by reaction with excess carboxylic acid giving rise to additional side reactions and other potential crosslinking mechanisms.

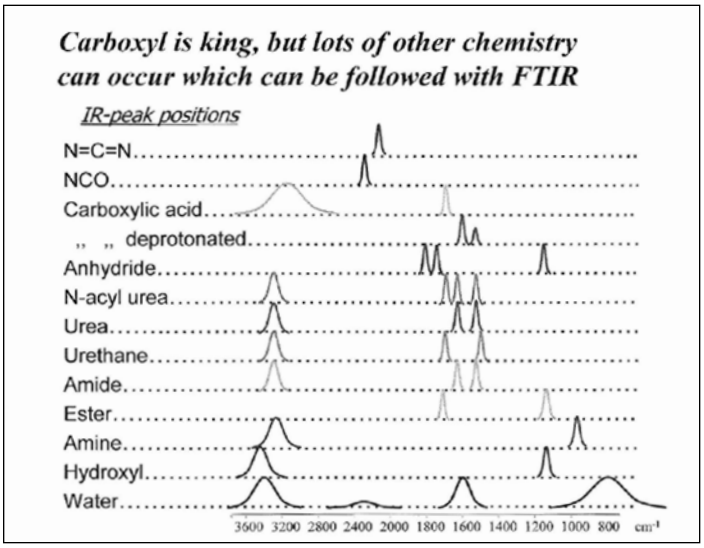

Figure 3: Important peak positions in Fourier Tranfer Infrared spectroscopy that permit main- versus side reactions to be detected and quantified.

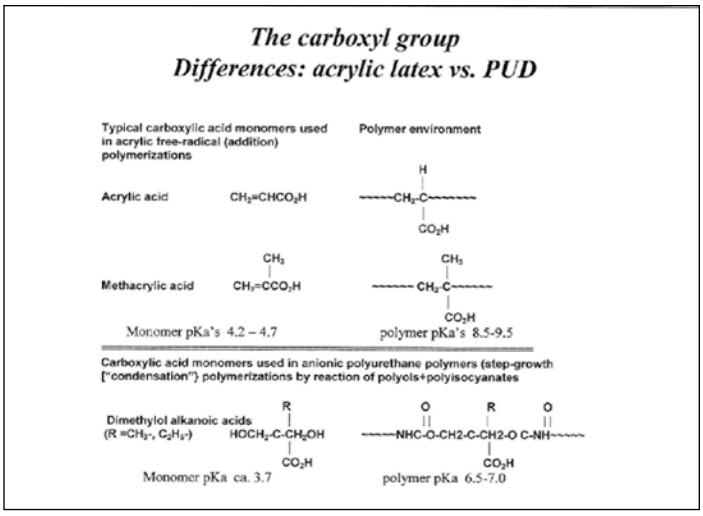

Figure 4: Typical pKa's of carboxylic acid monomers and how they change in the polymeric environment (acrylic latexes vs. PUD's)

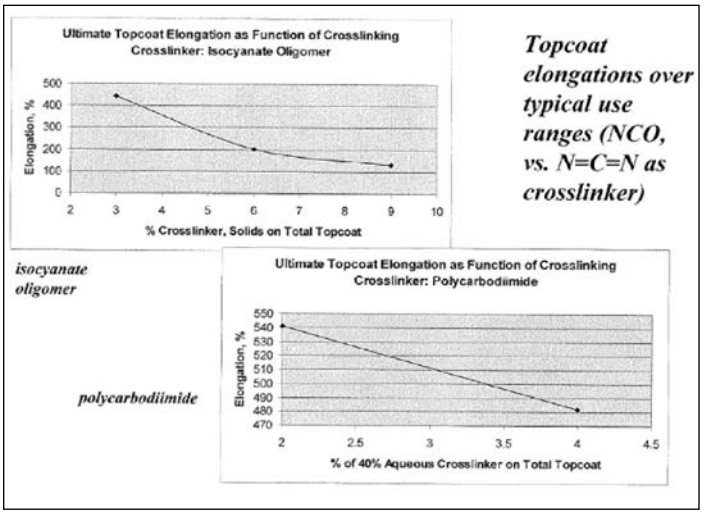

Figure 5: PUD Polymer elongation and how it is affected by crosslinking with isocyanate oligomer (upper) and polycarbodiimide (lower) crosslinkers. Compare each crosslinker in its typical dosage range (2-5% for polycarbodiimides; 8-10% for polyisocyanates)

Dosage Levels are Different for Polycarbodiimides and Polyisocyanayes

Polyisocyanate crosslinkers when they were first introduced were used in topcoats at levels of 15 to 20%, and now are typically used at 6 to 8 or 10% (calculated on finish). Polycarbodiimides used to be recommended at up to 8-15%, and now recommendations for use in basecoats range much lower, towards 2 to 3 or maybe 5%. Fig. 5 compares film elongation for the same PUD for a dosage for each type of crosslinker bracketing typical use ranges. It is clear that at the 2 to 5% recommended for polycarbodiimide, there is less loss of film flexibility and elongation than for a polyisocyanate at the higher recommended use rate for the latter. There are reasons why each crosslinker optimizes at a different dosage level. A good case is made for using each appropriate to its best character, or maybe the two used together in a topcoat, but at different use rates appropriate to each chemistry.