Effect of Crosslinker Reaction Rate on Film Properties for Thermoset Coatings

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With thermoset coatings that employ room temperature crosslinkers, there is often a competition between film formation and crosslinking. In order to meet the early use/handling requirements for the coated substrate, formulators sometimes need to use crosslinkers with very fast room temperature reaction rates. However, when the coatings are based on aqueous latex resins, sufficient time must be allowed for latex particle coalescence to occur prior to crosslinking, or the resulting films will be partially or completely precrosslinked, which is detrimental to many coatings properties. In this paper the effect of the crosslinker reaction rate on various film properties of coatings based on acrylic and acrylic/styrene latex resins will be investigated using several model carbodiimide-functional crosslinkers which have different reaction rates.

INTRODUCTION

Thermoset coatings play an important role in the coatings industry. By crosslinking the resin used in the coating, many properties can be greatly improved over the corresponding thermoplastic coating. Among these properties are such things as hardness, mar resistance, abrasion resistance, solvent resistance, and stain resistance. While there are many different types of thermoset coatings, they all have one thing in common: the chemical reaction used to crosslink the system must not occur to a substantial extent until after the paint has been applied to the substrate. Sometimes this requirement is achieved by selecting crosslinking reactions that will not take place until the coated substrate is heated or exposed to UV radiation. In these systems the applicator has almost complete control over when the crosslinking occurs. In other systems, however, the reaction begins immediately after the coating is applied, or maybe even immediately after an external crosslinker is added to the coating. In these cases the rate of the reaction must be slow enough to allow the coating to be applied to the object to be coated. When the coating in question is based on waterborne emulsion polymers, there is a further requirement on the rate of the crosslinking reaction; it must be slow enough to allow for some measure of latex particle coalescence to take place in the drying coating before sufficient crosslinking has occurred to halt the film formation process. In short, the crosslinking reaction must in some sense be slower than film formation.

Film formation in a coating based on a crosslinking latex is quite complicated.[1-3] There are several processes that take place and many of these occur simultaneously; this is shown schematically for a model coating in *Figure* 1. The model coating is based on an emulsion polymer with a glass transition temperature (T_g) near or above room temperature. To aid film formation, the coating contains coalescing solvents, which may be water-soluble, water-insoluble, or a mixture of both. Finally, there is an external crosslinker which reacts with some functionality on the backbone of the polymer. Upon application of the coating, water begins to evaporate, which ultimately brings the individual emulsion particles in contact with each other. Ideally, this is followed by deformation of the particles to fill the interstices between them, and finally coalescence of the particles to form a continuous film. Coalescence of the particles involves diffusion of individual polymer molecules across particle boundaries and subsequent entanglement of the polymer molecules. It is this molecular entanglement which holds the film together and gives the coating many of its beneficial properties. At some point during the film formation process, the coalescing solvents will also begin to evaporate. If water-soluble solvents are used, evaporation begins as soon as the paint is applied, and there is an inherent competition with water evaporation. For the

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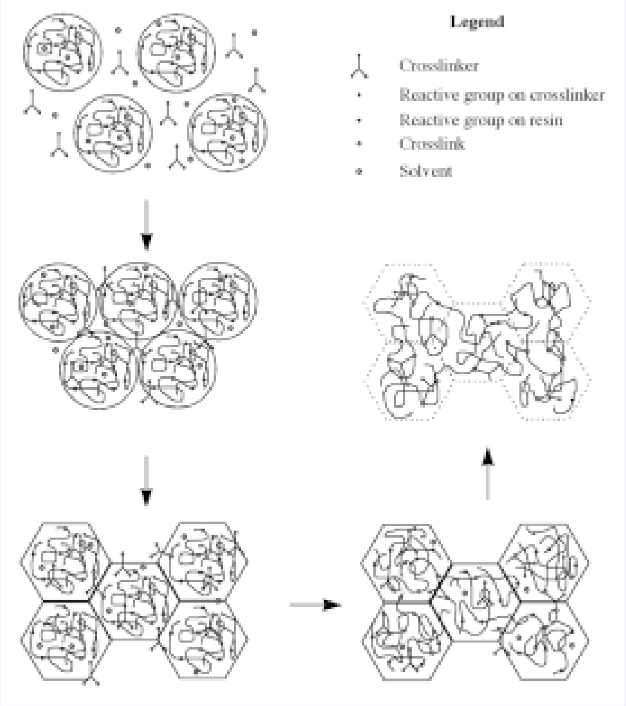

Figure 1—Film formation in a crosslinking latex-based coating.

Table 1—Preparation of Carbodiimide Crosslinkers

	al-CDI	ar-CDI	shar-CDI
Stage 1[a]			
MPEG350	15.7 g	25.1 g	4.8 g
NCO	39.78 g IPDI	50.0 g TDI	20.0 g MDEPI
Stage 2[b]			
PMA	48.5 g	34.5	22.7 g
MPPO	0.8 g	0.044	0.17 g
reaction time	18 hr	5.5 hr	16 hr
reaction temp	140°C	120°C	140°C
Solids	50.1%	39.4%	40.1%
Mn (g/mole)	2170	1786	3292

(a) Stage 1—Into a 150 ml three-neck round-bottom flask outfitted with an N_2 sparge tube, thermocouple, magnetic stirrer, and reflux condenser was placed the polyethylene glycol monomethyl ether Mn=350g/mole (MPEG350) and diisocyanate (IPDI=isophorone diisocyanate, TDI=tolylene 2,4-diisocyanate, MDEPI=4,4′-methylenebis(2,6-diethylphenyl isocyanate)). The flask was sparged with N_2 at the rate of 5cc/min and heated to 80°C for 30 min.

(b) Stage 2—The propylene glycol methyl ether acetate (PMA) and 3-methyl-1-phenyl-2-phospholene-1-oxide (MPPO) were added to the flask. The sparge rate was increased to 20cc/min, and the temperature increased as given. The flask was heated until no residual NCO could be seen in the FTIR spectrum (reaction times given).

solvent to be effective, a sufficient quantity of it must remain to bring the minimum film formation temperature (MFFT) below the drying temperature after the latex particles have come into contact with each other. Regardless of the type of coalescent used, once the water has left the coating, there is a competition between solvent evaporation and film formation. Film formation is not an instantaneous process, and to effect good film formation, the solvent must remain in the latex particles, and thus lower the MFFT for a long enough period of time to allow significant polymer diffusion to occur. Obviously, this can be accomplished by choosing very slow evaporating solvents, but where early use or handling is required, one generally uses the fastest solvents possible. The presence of the crosslinker further complicates the picture. If for simplicity we assume that the crosslinker begins reacting with the latex upon application of the coating, then the mobility of the polymer molecules, and thus the ability of the latex to film form, begins to be reduced as soon as the coating is applied. Clearly, to achieve a good film, the rate of this crosslinking reaction needs to be slow enough to allow for good film formation.

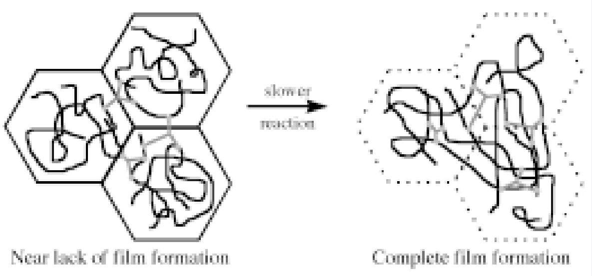

Figure 2—Extremes of film formation in a crosslinked coating.

This discussion raises two questions: (1) just how fast is film formation and (2) how much film formation is required to have a good film? Unfortunately, neither question has a simple answer. The rate of film formation depends on, among other things, the difference between the drying temperature and the latex T_g.[4] The latex T_g depends not only on the polymer composition and molecular weight, but also on the amount of coalescent remaining in the system[5] and the extent of crosslinking which has already occurred. These latter factors are time dependent. Thus the rate of film formation is steadily decreasing as the coating dries. Both the initial rate of film formation and the decrease in the rate of film formation depend on the neat polymer T_g and molecular weight, the level, evaporation rate, and water solubility of the coalescing solvent(s) used, and the rate and starting time of the crosslinking reaction. Feng et al. addressed some of these issues in a study of latex film formation in films crosslinked by the acetoacetoxy/diamine reaction[6]; however, the rate of this reaction is so rapid that all of the crosslinked films studied were likely severely precrosslinked, which would presumably be detrimental to a practical coating.

The question of how much film formation is necessary to get a good coating is also not straightforward, and the answer depends in large part on what types of properties the coating must have. In an extreme case, a thermoset coating created from a latex can look something like what is depicted on the left side of *Figure* 2; while the film will look perfectly continuous to the eye, there will be minimal interdiffusion of latex particles, and the film will be held together by only a few interparticle entanglements along with interparticle crosslinks. Such a coating may meet appearance and hardness requirements, but if one begins to stress the system, it will easily fail. The situation depicted on the right side of

Figure 2 is ideal, with complete loss of particle identity, but is probably unrealistic and unnecessary to achieve the requirements placed on a real world coating. However, just what position between these two extremes one can accept depends on just how much stress, and types of stresses, to which the coating will be subjected.

The goal of this paper is to provide some insight into the questions of what properties are affected, and by how much, by incomplete film formation in a crosslinked latex-based coating. We will also attempt to answer the question of just how fast the crosslinking reaction can be without negatively impacting film properties.

EXPERIMENTAL

The carbodiimide crosslinkers were made by heating two moles of polyethylene glycol monomethyl ether (Mn = 350g/mole) with eight moles of the appropriate diisocyanate in the presence of a phospholene oxide catalyst[7] (see *Table* 1 for the synthesis details). The crosslinkers were made at 40-50% solids in propylene glycol methyl ether acetate and were added to the coatings as 1/1 mixes with water. In the case of the sterically hindered aromatic CDI (shar-CDI) crosslinker (see *Figure* 3), two percent of a non-ionic surfactant was included in the crosslinker/water mixture to help emulsify the crosslinker. Crosslinkers were added in a stoichiometric amount on polymer acid.

The three polycarbodimide (pCDI) crosslinkers used in this study are shown in *Figure* 3. All of the crosslinkers are, on average, 7 functional and contain polyethylene oxide endgroups to make them compatible with waterborne coatings. The resins employed were either acrylic or acrylic/styrene copolymers and contained either methacrylic acid (MAA) or sulfoethylmethacrylate (SEM) as the reactive functionality. Polymer/crosslinker reaction rates were determined by measuring the concentration of unreacted CDI groups in a drying film utilizing FTIR spectroscopy; the CDI group absorbs at ~2140cm^{-1}, well away from any other peaks in the system (see *Figure* 4).

Polymer and coating MFFTs were measured at 0% RH. The required coalescent level for an MFFT below 0°C was determined by measuring the MFFT for a series of coatings with increasing amounts of solvent and extrapolating to the desired temperature (see *Table* 2 for an example).

Table 2—Determination of Coalescent Level for Desired MFFT

Weight of Latex (41%)	Weight of Coalescent	MFFT (° C)
20.0 g	0.00 g	56.7
20.0 g	0.42 g	42.5
20.0 g	0.84 g	28.5
20.0 g	1.24 g	17.0

Coalescent is a mixture of 3 parts ethylene glycol butyl ether/1 part diethylene glycol butyl ether. Linear least squares fit of data yields the relationship. Weight of coalescent = 1.75 –0.031*MFFT. In the work leading to the results shown in *Figure* 16, the coatings were coalesced to an MFFT of –5° C, which from the equation was predicted to require 1.9 g of coalescent per 20 g of latex.

Films were coated on ACT A600 treated Al at a WFT of 7 mil (DFT of ~1 mil) except for in the following cases: for the impact test, the substrate was Bonderite 1000 treated cold-rolled steel; for the abrasive scrub test, the substrate was a black vinyl chart from Leneta Co. and films were cast at 5 mil WFT (DFT of ~1 mil); and for the solvent spot test and stain tests, the substrate was maple veneer boards. Films were dried at 25°C and 65% RH for seven days prior to testing.

MEK rubs were determined with a crockmeter from Atlas Electric Devices, using a swatch of cotton cloth saturated with MEK. Mar resistance was determined by striking the coating with a fingernail and observing the coating for damage. Stain resistance was a composite result of four stain tests including water, 50% ethanol, Formula 409 household cleaner, and nine percent aqueous acetic acid. The staining agents were left in contact with the coating for 16 hr, and the results recorded 24 hr after the staining agents were removed. The acetone spot test involved placing acetone on the film for 15 min, covering it, blotting away the excess acetone, and rating the film after a 24-hr recovery. Taber abrasion was measured using 200 cycles with 50 g weights and CS-10 wheels. Abrasive scrub resistance was measured using a Gardner Laboratories Abrasion Tester with a brass shim placed under the panel (results reported as number of

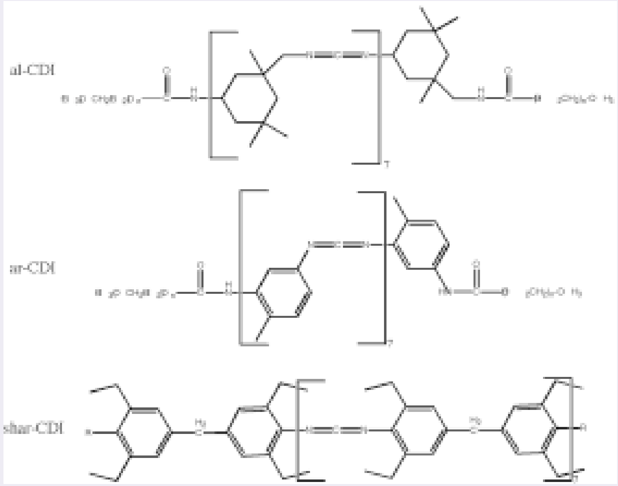

Figure 3—pCDI crosslinker structures.

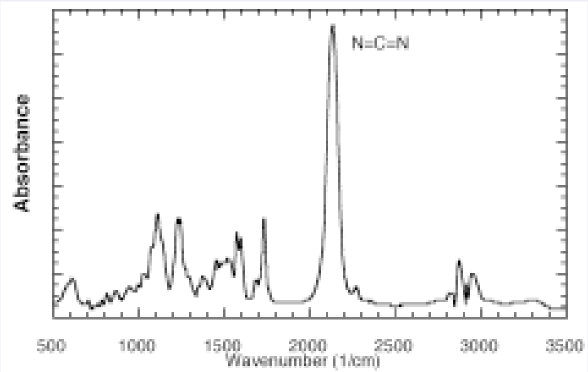

Figure 4—IR spectrum of pCDI crosslinker.

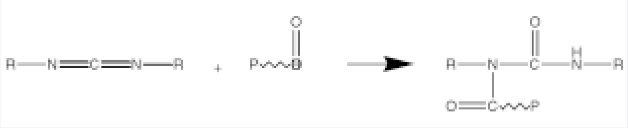

Figure 5—CDI/Acid crosslinking reaction.

scrubs to cut through one continuous line across shim). MEK swell ratios are volume swell ratios measured by immersing a 1.2 cm square of coating in MEK for 16 hr, then using the equation: swell ratio = (length of one side of swollen film/1.2).[3]

RESULTS AND DISCUSSION

The crosslinkers chosen for this study were based on pCDIs, which react with acid groups contained in the latex particles[8,9] (see *Figure* 5 for the pertinent reaction). Polycarbodiimide crosslinkers were selected for this work because the rate of their reaction can be varied by changes in the crosslinker structure. Aliphatic pCDIs (al-CDI) are highly reactive, whereas their aromatic counterparts are considerably less so.[10] Also, the reaction rate can be further decreased by introducing steric hindrance near the CDI groups. Finally, pCDIs react with strong acid groups such as sulfonates and phosphonates at a slower rate than with weak acid groups such as carboxylic acids. By combining different polymer acid groups with different pCDI structures, one can achieve a broad range of crosslinking reaction rates. A further advantage of pCDI crosslinkers is that the reaction with the acid groups on the resin is very slow in the presence of water.[10] Given that all of the paints evaluated in this study were used within 30 min of adding the crosslinker, it is a very good approximation to say that the crosslinking reaction does not begin until the majority of the water has left the film, i.e., at the same time that film formation begins.

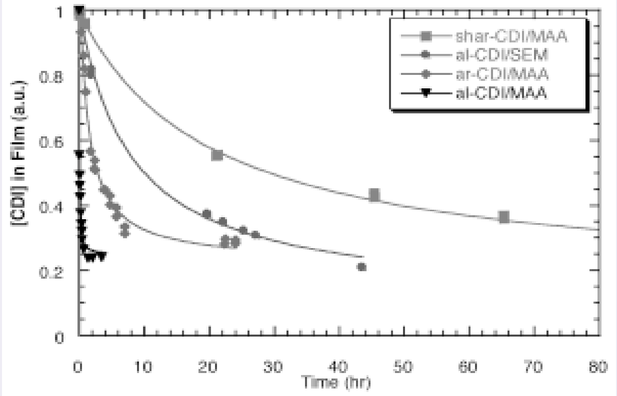

Figure 6—Reaction rates of pCDI crosslinkers in film.

Table 3—Half-Lives of pCDI Crosslinkers

Crosslinker	Acid Type	Half-Life
al-CDI	MAA	8.4 min
ar-CDI	MAA	4.4 hr
al-CDI	SEM	6.6 hr
shar-CDI	MAA	17 hr

Note: Half-lives are for reaction with a resin with an acid number of 15.3. See *Figure* 4 for definitions of crosslinkers.

Table 4—Comparison of Film Properties with al-CDI and ar-CDI Crosslinkers

Crosslinker	None	al-CDI	ar-CDI
Aqueous stain tests[a]	7	9	10
Solvent spot tests[a]	1	2	9
MEK swell ratio	dissolves	3.1	3.0
Mar resistance[a]	2	1	5
Knoop hardness	4.5	6.2	6.5
Sward hardness (s)	39	43	43

Note: The resin was acrylic/styrene, acid # = 27, T_g = 30° C.
(a) Scales: 0-10, 10=no damage

Although the exact reaction rate will be different for each polymer, depending on such factors as acid level, T_g, and molecular weight, a feeling for the order of magnitude of the reaction rates for the different crosslinker/acid combinations can be obtained by examining the reaction profiles for representative polymers (these are shown in *Figure* 6). Reaction half-lives were obtained by fitting the data for the early stages of the reaction to the second order rate equation $1/[CDI]-1/[CDI]_0 = k^*t$ (these are given in *Table* 3). It is necessary to note here that the reactions do not strictly follow second order kinetics because polymer mobility decreases throughout the reaction as crosslinking occurs, making the rate constant itself time dependent (which is why only the early time data is included in the fit), but the half-lives given in *Table* 3 are still useful in a comparative sense. Also, one should remember that half-lives for a second order reaction are inversely proportional to the reactant concentrations; doubling the level of acid in the polymer will halve the half-life. The half-lives given in *Table* 3 assume a resin with an acid number of 15.3.

As we see from an examination of the data in *Figure* 6 and *Table* 3, the reactions studied in this paper range from extremely rapid for the case of the al-CDI with carboxylic acids ($\tau_{1/2}$ = 8.4 min), to quite slow for the case of the shar-CDI ($\tau_{1/2}$ = 17 hr). This allowed us to perform property tests on crosslinked coatings in which one would expect very little film formation to have occurred, coatings in which one would expect that near complete film formation had occurred, and points in-between.

The first coating property results are given in *Table* 4. These results are for clear coatings made from an acrylic/styrene resin with a T_g of 30°C and an acid number of 27. The coatings were coalesced with a mixture of three parts ethylene glycol butyl ether (EB)/one part diethylene glycol butyl ether (DB) to an MFFT of –20°C. Only the two fastest crosslinker/acid combinations, i.e., al-CDI/MAA and ar-CDI/MAA, were included in this experiment. Two important conclusions can be drawn from the results in *Table* 4: first, for coatings properties that are primarily determined by resin composition and bulk crosslink density, the rate of the crosslinking reaction does not seem to be important. This makes sense, because the property depends only on how much crosslinking took place, not on when it took place. Properties in this category include solvent swell ratios, Knoop hardness, and Sward hardness. Note that to a first approximation, none of the tests for these properties involve stressing the films. Since the boundaries between the polymer particles are not being stressed much, the extent of film formation is relatively unimportant. It seems to matter only that enough coalescence has occurred to make a film. On the other hand, if one looks at the tests in *Table* 4, which subject the coating to significant stresses such as the solvent spot or mar resistance tests, then one finds that the coating crosslinked with the al-CDI performs much worse than the coating crosslinked with the slower reacting ar-CDI. For example, with mar resistance, which depends on both surface hardness and film integrity, the ar-CDI crosslinked coating shows marked improvement over the uncrosslinked control, while the al-CDI crosslinked coating is actually worse than the control. By contrast, with Sward hardness, which depends solely on surface hardness, both the al-CDI and ar-CDI crosslinked coatings show the same improvement over the control. With resins having an acid number of 27, the half-life of the crosslinking reaction with the al-CDI would be predicted to be around five minutes; clearly this crosslinker in this coating reacts too quickly to allow for sufficient film formation to occur to develop properties such as mar resistance.

While the discussion shows the loss of properties which can happen when the crosslinker reacts too rapidly for a given coating, it only touches upon the issues of just how fast the reaction can be without property loss, and how this maximum reaction rate depends on the resin composition and/or coating formulation. Intuitively, it seems clear that, given equal coalescent levels, a coating made from a softer resin would be able to tolerate a faster crosslinker than one made from a harder resin. Likewise, a lower molecular weight resin would be expected to be able to work with a faster crosslinker than a higher molecular weight resin. However, in practice, one would generally not formulate resins with different T_gs or molecular weights the same; rather the level of coalescing solvent would be adjusted so that the coatings have equal MFFTs. So the question then is whether two coatings based on resins with different T_gs, but formulated to equal MFFTs, would work similarly with a given crosslinker, considering that the hardness of the latex particles, and hence the rate of film formation, may be changing at different rates as the coalescents evaporate.

The experiments presented in *Figures* 7-14 attempt to provide some insight into this question. Four polymers of similar composition in which the T_g was varied from 23° to 47°C and the molecular weight was either ~500,000 g/mol or 50,000 g/mol were studied; the properties of the resins are given in *Table* 5. Both clear and pigmented coatings were made from each polymer; a coalescent package of three parts EB/one part DB was used, and each coating was formulated to an MFFT of –5°C. The pigmented coatings (used only for direct impact resis-

Table 5—Resin Properties

Resin T_g (° C)	Resin Mw (g/mole)	Acid Number	Acid Type
30	~500,000	15.3	MAA
30	~500,000	15.3	SEM
23	50,000	15.3	MAA
47	~500,000	15.3	MAA

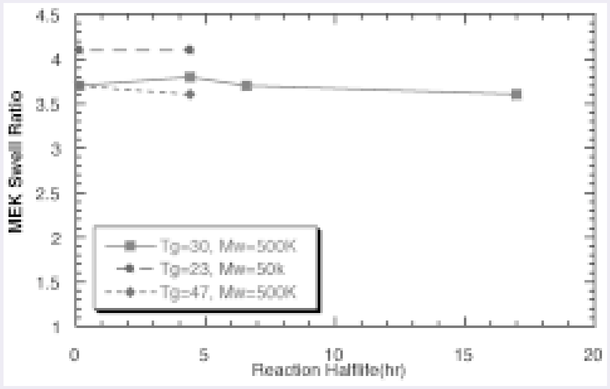

Figure 7—Swell ratios vs. reaction rate.

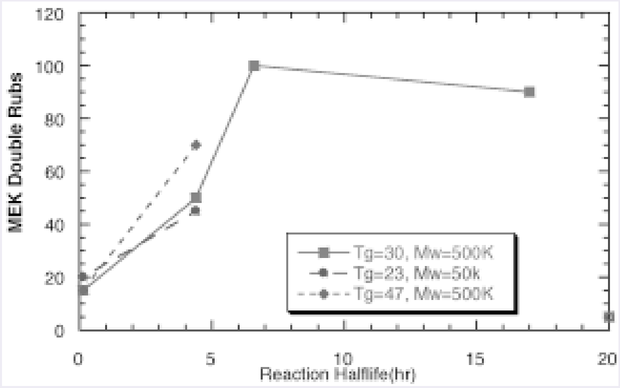

Figure 8—MEK double rubs vs. reaction rate.

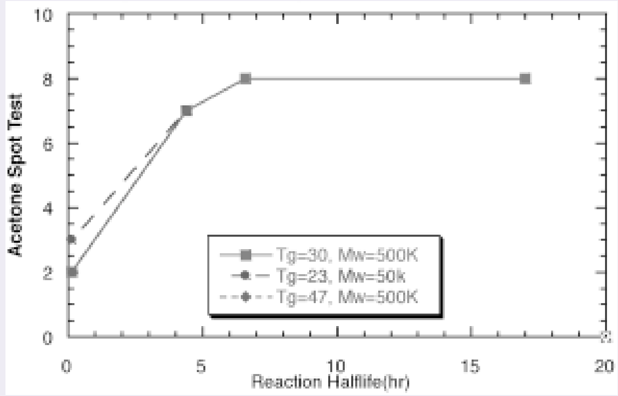

Figure 9—Solvent spot test vs. reaction rate.

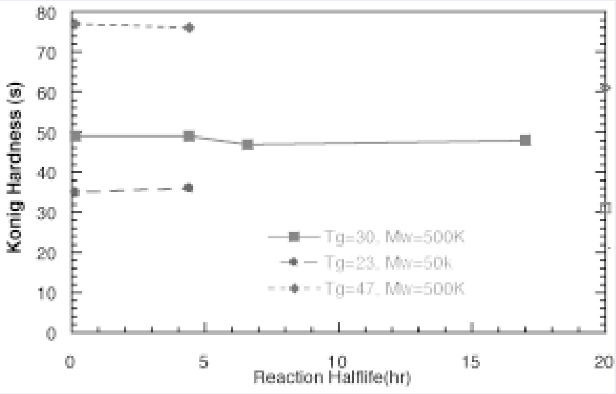

Figure 10—Konig hardness vs. reaction rate.

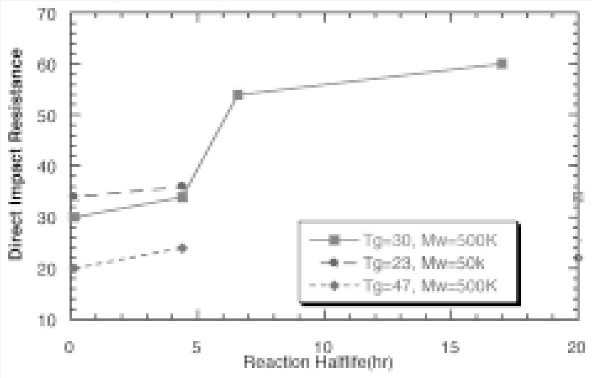

Figure 12—Impact resistance vs. reaction rate.

tance and abrasive scrub resistance) were pigmented to 15 PVC with TiO_2. *Figures* 7-9 show the results of several solvent resistance tests (results for the uncrosslinked controls are shown as open symbols on the right hand side of the graphs; in the MEK swell ratio test, the uncrosslinked controls dissolved). Just as was seen in the previous experiment, the MEK swell ratios, a test which does not depend on film formation, show no dependence on crosslinker reaction rate for any of the polymers. However, for both solvent double rubs and solvent spot tests, tests which stress the coating, dramatic improvement is seen as the crosslinker reaction rate is slowed to a half-life of 6.6 hr. A further decrease in $\tau_{1/2}$ to 17 hr shows no further improvement in properties, suggesting that for these coatings a crosslinker with a half-life of ~6 hr or longer is slow enough to achieve maximum solvent resistance. There does not appear to be much difference in the way that the coatings based on the harder or lower molecular weight resins behave in going from the al-CDI crosslinker to the ar-CDI. Although these resins were not evaluated with the al-CDI/SEM and shar-CDI crosslinkers, from the available data, there does not appear to be much, if any, effect of resin T_g or molecular weight on property development versus crosslinker reaction rate. This is probably a result of the coatings having been coalesced to equal MFFTs, with the details of the resin's molecular architecture and the coating's formulation being less important than the resulting polymer mobility.

Figures 10-14 show the results of several hardness/abrasion resistance tests (again, results for the uncrosslinked controls are shown as open symbols on the right hand side of the graphs). The same trends seen for the solvent resistance tests are repeated here, with the film formation insensitive property (König hardness) showing no dependence on crosslinker reaction rate, while the film formation sensitive tests (mar resistance, impact resistance, Taber abrasion, and abrasive scrubs) showing improvement with decreasing reaction rate up to $\tau_{1/2}$ = 6.6 hr. Again, little dependence of resin T_g or molecular weight on property development versus crosslinker reaction rate is evident. The exceptions are the low molecular weight resin in the Taber abrasion test, which is most likely an experimental anomaly, and the poor result for the SEM-functional coating in the abrasive scrub test, which was probably caused by the hydrophilicity of the SEM monomer.

As discussed previously, in a real world coating, the drying/curing process is a complicated one with several events occurring simultaneously. For example, the work suggests that for a coating coalesced to –5°C, a crosslinker should not react much more quickly than the al-CDI/SEM pair (with a $\tau_{1/2}$ of 6.6 hr) or else film formation will

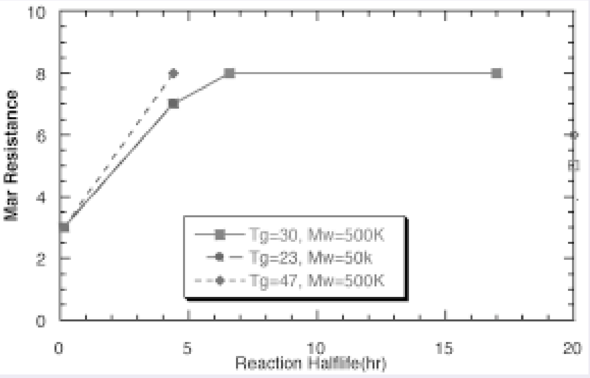

Figure 11—Mar resistance vs. reaction rate.

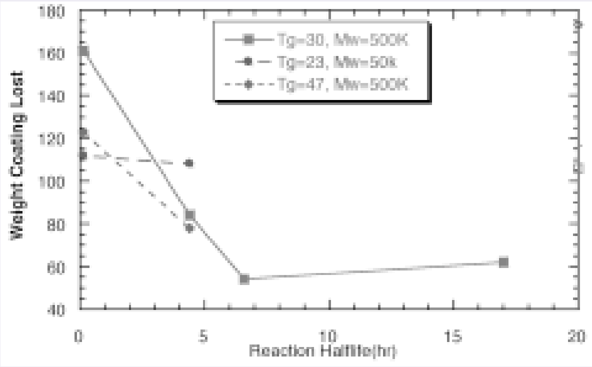

Figure 13—Taber abrasion vs. reaction rate.

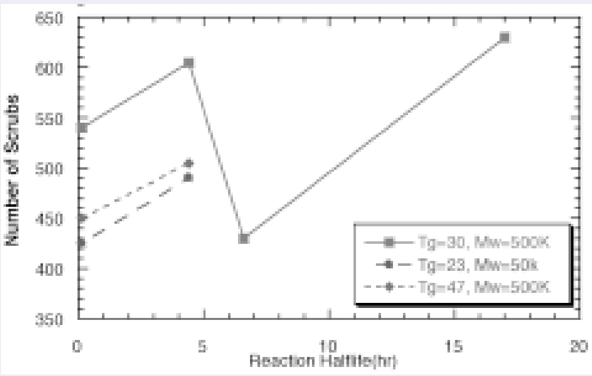

Figure 14—Abrasive scrub resistance vs. reaction rate.

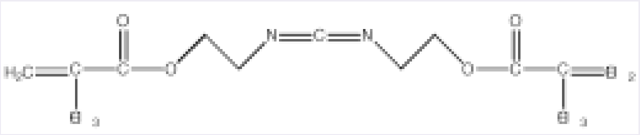

Figure 15—UV-curable CDI resin modifier.

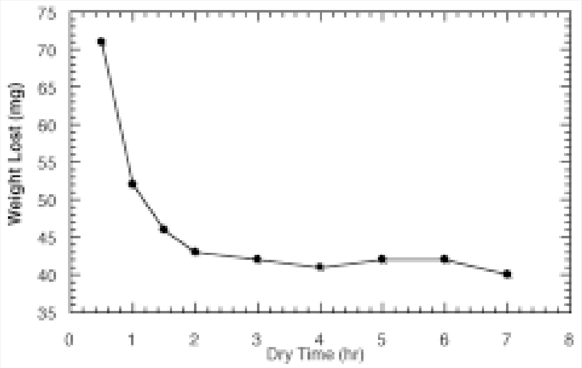

Figure 16—Taber abrasion for UV-cured coatings.

be compromised. This does not mean, however, that complete film formation in a coating coalesced to –5°C requires on the order of six hours, because in a real coating the formation of crosslinks is interfering with film formation even in the very early part of the reaction. To attempt to answer the question of just how long does complete film formation take, a different approach was used. In this final experiment, a relatively high acid (acid number = 50) acrylic/styrene resin was formulated as a clear coating which included enough of the UV-curable resin modifier shown in *Figure* 15 to react with 66.7% of the acid on the resin backbone. The formulation also included 0.7% of the photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one. Because the UV-curable resin modifier had one and only one CDI group per molecule, it reacted very quickly with the resin to graft methacrylate groups onto the polymer backbone after the coating was applied, but without causing any crosslinking to occur. Thus, unlike the previous experiments, film formation was (initially) allowed to occur unencumbered by the formation of crosslinks. However, after various drying intervals, the coatings were exposed to UV light, which polymerized the methacrylate groups introduced onto the resin backbone and almost instantaneously crosslinked the coating. Given the high level of crosslinking introduced, one would expect film formation to stop after exposure to the UV light, essentially freezing the polymer chains in place. By testing the cured films for some application property, which is sensitive to film formation, we hoped to be able to determine how much time was required to develop complete film formation, at least in terms of the amount of film formation required to achieve full property development.

The results for such an experiment are shown in *Figure* 16, where the Taber abrasion resistance of the coatings was measured as a function of the dry time before curing. Again, the coatings were coalesced with a mixture of three parts EB/one part DB to bring the MFFT of the coating down to –5°C (the T_g of the neat resin was 47°C). Care was taken in curing the coatings to not allow the heat generated in the UV oven from significantly warming the coatings and speeding film formation; the panels were only slightly warmer to the touch after exiting the UV oven. The coatings were cured by three separate passes through the UV oven, with cooling between passes, for a total UV dose of 1500 mJ/cm^2. An examination of data in *Figure* 16 shows that the amount of coating abraded off of the panel decreased up until the coating had had two hours to dry prior to curing. If one views this result in light of the pCDI crosslinker/acid combinations evaluated earlier, one finds that with the al-CDI/SEM coatings, after two hours of drying approximately 18% of the CDI groups had reacted; this corresponds to approximately 1.3 CDI groups/crosslinker molecule, which would have effected a very low level of crosslinking. Recall that this was the reaction rate at which property development did not appear to be affected by a loss of film formation. By comparison, for the coatings with the ar-CDI/MAA pair, after two hours of drying 42% of the CDI groups had reacted, which corresponds to approximately 2.9 CDI groups/crosslinker molecule. These latter coatings showed a small loss of properties due to incomplete film formation.

Most of the work presented here employed coatings coalesced to –5°C using the solvent mixture of three parts EB/one part DB. Although it is expected that the general conclusions found in this study would be applicable to coatings employing alternate coalescent packages, the exact numerical results would be expected to change. For example, coatings coalesced to lower MFFTs would be expected to tolerate faster crosslinkers without loss of properties. However, the magnitude of these changes is not currently known, and their study was beyond the scope of this work.

CONCLUSIONS

In crosslinked latex-based coatings, if the rate of crosslinking is sufficiently fast to interfere with film formation, then coatings properties which stress the coating, such as solvent rubs and abrasion or impact tests, will be compromised. The maximum reaction rate for a crosslinker that does not compromise film formation appears to be independent of resin T_g and molecular weight for coatings which are coalesced to equal MFFTs. For coatings coalesced to an MFFT of –5°C, this maximum reaction rate corresponds to a reaction half-life of between 4.4 and 6.6 hr for a resin with an acid number of 15.3. The amount of time necessary for a coating coalesced to –5°C to achieve complete film formation seems to lie between 1.5 and 2 hr, a period of time in which little crosslinking occurs with crosslinkers that react at or slower than the maximum allowable reaction rate for complete property development.

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