# Crosslinking Reactions of Acrylic Polymers Containing Carboxyl Groups with Melamine Resins*

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## Synopsis

The mechanism of cure has been studied in coating systems comprising blends of ammonium salts of acrylic acid–acrylic ester copolymers and alkoxymethylmelamines. Experiments were conducted both on the resin components themselves and on model compounds having analogous chemical structures. Curing of the resin begins with loss of ammonia to regenerate free carboxyl groups, rather than loss of water to form amides. The alkoxy group is eliminated, and ester crosslinks are formed between the carboxyl and the methylolmelamine. Base binding studies on cured films show that the extent of crosslinking depends on the exact composition of the resin system and the presence or absence of an acidic catalyst. These variables can be adjusted to provide essentially quantitative crosslinking in the cured coating, as shown by the complete disappearance of unreacted carboxyl groups.

## Introduction

In recent years, water-soluble or water-dispersible surface coatings have been extensively studied. These systems offer the inherent advantages of nonflammability, nontoxicity, lack of odor, ease of cleaning, etc. One water-soluble coating system recently disclosed[1] comprises essentially a mixture of the ammonium salt of an acrylic acid–acrylic ester copolymer and an ether of a methylolated melamine. It is converted by baking from the water-soluble state to an insoluble crosslinked material. Numerous examples of carboxyl-containing acrylic polymers as a basis for crosslinked surface coatings have been described by other workers.[2]

In order to elucidate the chemical reactions involved in the crosslinking, a study of the curing mechanism was undertaken. First, a qualitative examination was made of the chemical reactions which occur. Second, quantitative measurements were obtained to indicate the change in carboxyl content of the resin when cured under various conditions. The present paper describes the findings obtained in both approaches to the problem.
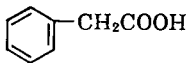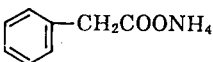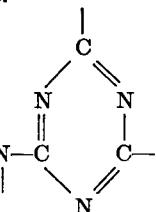
## Mechanism Studies Based on Model Compounds

The conversion of the acrylic–melamine system from a soft water-soluble state to a hard, chemically resistant film by baking is an attribute of great industrial value. But this very property makes a study of the curing reaction itself extremely difficult. The cured film cannot, of course, be dissolved in order to carry out chemical tests without decomposing it. Infrared spectroscopic examination is hampered by the large variety of chemical structures in the resin, and hence the complexity of its spectrum. Opportunities for competitive and side reactions, such as those between melamine residues, are numerous. Under these circumstances, it appeared helpful to design a group of relatively simple monofunctional compounds having the same types of reactive groups as exist in the resin system, and to bring these compounds together under typical curing conditions.

Structures (I) show the two components of the water-soluble resin under investigation. The fully etherified compound hexakis(methoxymethyl)-melamine (HMM), is a particularly useful melamine derivative.[3] It can be prepared in a pure state as a crystalline low-melting solid. Since it contains six identical reactive sites, complications due to reactions of hydrogen or unsubstituted methylol groups on the side-chain nitrogens of the melamine are avoided.



Acrylic copolymer

Hexakis(methoxymethyl)melamine

(I)

It was readily proven that neither the alpha hydrogens nor the ester functions on the acrylic chain are significant in the crosslinking reaction. Esters of acrylic acid or methacrylic acid were homopolymerized and the polymers blended with HMM. In neither case was crosslinking obtained under typical curing conditions (e.g., 30 min. at 150°C.), even in the presence of a strong acid catalyst. Films from such blends were opaque, soft, incompatible, and soluble in organic solvents. Thus, neither ester groups nor alpha hydrogens provide crosslinking sites. Only the carboxyls, or their ammonium salts, can be regarded as reactive. Accordingly, the only model compound required as analog of the acrylic polymer is the ammonium salt of a carboxylic acid. Ammonium phenylacetate was selected since

the parent acid is fairly nonvolatile, and the salt, unlike salts of long-chain aliphatic acids, did not cause objectionable foaming in aqueous solution.
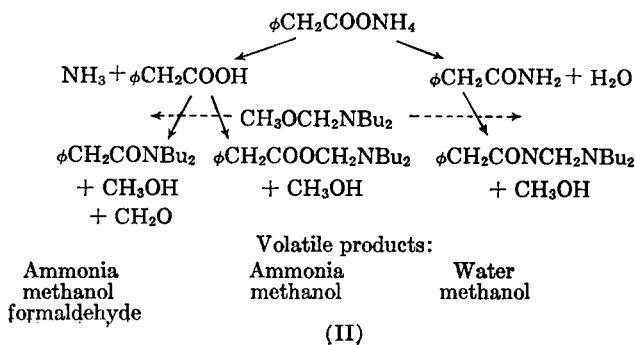
As a model compound for HMM, a monofunctional triazine derivative was first tried. In a pilot experiment, 2-methoxymethylamino-4,6-di-methoxy-s-triazine was heated in aqueous solution with strong acid. Acid was added since, in the actual resin, curing is promoted by acidic catalysts. Under the conditions of this experiment, infrared evidence indicated that the triazine structure had been destroyed; this is not the case with cured melamines. Presumably, isomerization to an isocyanurate had occurred, as is frequently observed on heating alkoxytriazines (cyanurates).[4] Other triazine model compounds may have better stability; nevertheless, it was deemed preferable to select a simpler model for the melamine component, namely methoxymethyldibutylamine.

The resin constituents and their small molecular counterparts are indicated in Table I.

TABLE I
Model Compounds for Crosslinking Reactions

| Resin constituent | Model compound |
| --- | --- |
| Acrylic acid–acrylic ester copolymer. Reactive group: —COOH | $\bigcirc$—CH$_2$COOH |
| Ammoniated copolymer. Reactive group: —COONH$_4$ | $\bigcirc$—CH$_2$COONH$_4$ |
| Methoxymethylated melamine. Reactive group: CH$_3$OCH$_2$N—C (triazine ring) | CH$_3$OCH$_2$N(C$_4$H$_9$)$_2$ |

Numerous reaction possibilities exist even among the model compounds under the influence of heat, with or without the addition of catalysts. These reactions are given in (II).

$\phi$CH$_2$COONH$_4$

NH$_3$ + $\phi$CH$_2$COOH                    $\phi$CH$_2$CONH$_2$ + H$_2$O

CH$_3$OCH$_2$NBu$_2$

$\phi$CH$_2$CONBu$_2$    $\phi$CH$_2$COOCH$_2$NBu$_2$    $\phi$CH$_2$CONCH$_2$NBu$_2$
+ CH$_3$OH            + CH$_3$OH                + CH$_3$OH
+ CH$_2$O

Volatile products:

| Ammonia | Ammonia | Water |
| methanol | methanol | methanol |
| formaldehyde | | |

(II)

Ammonium carboxylates can either lose ammonia to revert to the parent carboxylic acid or lose water to form the amide. Methoxymethyldibutylamine can yield either of two products by reaction with the acid, depending on the bond which cleaves. If it reacts with the amide, however, only one reaction is considered probable, following from cleavage between the methanol and formaldehyde moieties. For, if cleavage occurred between the formaldehyde and amine residues, the amine so liberated would be most unlikely to react with an amide. In the actual resin, this would be equivalent to the direct reaction of melamine itself with an amide, which has been shown not to occur.[5] On the other hand, formaldehyde itself readily methylolates amides,[6,7] and a methylolmelamine might reasonably be expected to do the same.

The only side reaction which need be considered here is a possible condensation between two molecules of the amine, analogous to self-condensation of the HMM:

$$2CH_3OCH_2N(C_4H_9)_2 + H_2O \rightarrow [(C_4H_9)_2N]_2CH_2 + 2CH_3OH + CH_2O$$
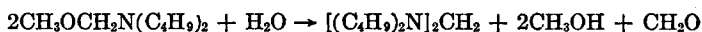
In order to determine which reactions actually occur, all of the reactants and possible products shown in Figure 2 were synthesized independently.

## Experimental

**Reactants.** Phenylacetic acid was obtained from Distillation Products Industries. Ammonium phenylacetate was prepared by mixing equimolar quantities of the acid and concentrated ammonia, filtering the resulting slurry, and air-drying the filter cake. To prepare methoxymethyldibutylamine, 1 mole of dibutylamine was added dropwise to 1 mole of formaldehyde (as formalin) at 5–10°C., followed by 1 mole of methanol, and the desired compound recovered from the organic layer by distillation at 65° and 12 mm.

ANAL. Calcd. for $C_{10}H_{23}ON$: N 8.09%, O 9.25%. Found: N 8.23%, O 9.52%.

Hexakis(methoxymethyl)melamine was of commercial grade (marketed by American Cyanamid Co. as Cymel 300), recrystallized from heptane, m.p. 49–51°. Acrylic copolymers were synthesized following the procedure of Daniel.[1]

**Model Reactions.** Phenylacetic acid and methoxymethyldibutylamine in equimolar amounts were heated 20 min. at 150° with 2% p-toluenesulfonic acid monohydrate as catalyst in a small flask whose exit tube was connected to a receiver immersed in dry ice. All products, both volatile and nonvolatile, were collected, separated by solubility or gas chromatography, and identified. A similar experiment was conducted with ammonium phenylacetate and the amine, and control experiments were carried out with single compounds.

## Results and Discussion

The results of the experiments were as follows:

*(1)* Ammonium phenylacetate, heated at 150° with catalytic amounts of strong acid, yielded phenylacetic acid and ammonia. No amide was detected under these conditions.

*(2)* Methoxymethyldibutylamine similarly heated gave no reaction. The self-condensation suggested above did not occur.

*(3)* Ammonium phenylacetate and methoxymethyldibutylamine, heated together in equimolecular amounts with *p*-toluenesulfonic acid as catalyst at 150°, gave a volatile fraction containing about 90% methanol and 6% ammonia. No formaldehyde was detected. The nonvolatiles, which comprised 90% of the starting weight, were inspected by infrared, since attempts to achieve clean-cut separations of the reaction mixture by selective extraction failed. The principal constituent of the mixture was phenylacetic acid, which is inconclusive in determining the reaction path. Between 60 and 70% of the mixture was unidentifiable, although the spectra of the suspected constituents were available for comparison.

*(4)* Equimolecular amounts of phenylacetic acid and methoxymethyl-dibutylamine, heated with acidic catalyst at 150°, gave 6% of distillate and 93% of residue. The distillate was essentially pure methanol, with no more than a trace of formaldehyde. Based on infrared evidence, the residue contained 60% of starting phenylacetic acid; the starting amine was undetectable. There was indication of both *N*,*N*-dibutylphenylacetamide and dibutylaminomethyl phenylacetate as well, but in small amount. These were noted in scheme (II) as the products of alternative reactions.

*(5)* The acrylate ester–acrylic acid copolymer itself, in the form of its ammonium salt, was heated in the absence of HMM as a thin film. It decomposed into the acidic polymer and free ammonia. No amide was formed, as shown by the absence of nitrogen in the residue. No ionized carboxyl or amide bands were found in the infrared spectra.

*(6)* An 8-g. quantity of copolymer, neutralized with ammonia, and stirred with 4 g. of HMM plus sufficient water to make a 50% solids solution, to which 80 mg. of *p*-toluenesulfonic acid had been added, was evaporated under vacuum at room temperature on the inner wall of a rotating 500-ml. round-bottomed flask. The flask was then immersed in an oil bath at 150° and volatile reaction products were collected in a Dry Ice trap. The volatiles weighed only 10 mg., insufficient for VPC analysis; the odor was that of methanol. While it is likely that more than this amount of volatile product had been formed, it appears that release from the crosslinked film is very slow.

The results of these tests, although not completely unequivocal, do permit fairly definite conclusions to be drawn. Experiments 1 and 5 show that under curing conditions the ammonium carboxylate reverts to the free acid and does not form amide. The postulated reaction path shown on the right side of scheme (II) thus does not occur. Furthermore, no water—a product of this reaction—was actually detected.

In choosing between the other two paths, VPC analysis of the volatile fraction seems more helpful than infrared examination of the nonvolatiles, since the latter contained much unreacted starting material and defied attempts to separate them into their individual components. It should be emphasized that the composition of the volatile fraction is different for each of the three proposed reaction paths.

The volatiles were shown to contain methanol but no significant amount of formaldehyde, although in one of the postulated paths it should be produced in substantially equal amount with the methanol. On the whole, therefore, the path shown in the center of structure (II) is judged to account best for the observations. The path on the right has been rejected, and the one at the left, if it occurs at all, makes only a minor contribution.

If these findings are carried to the actual resin system, the crosslinking mechanism for the acrylic–melamine system is as depicted in reaction (III).
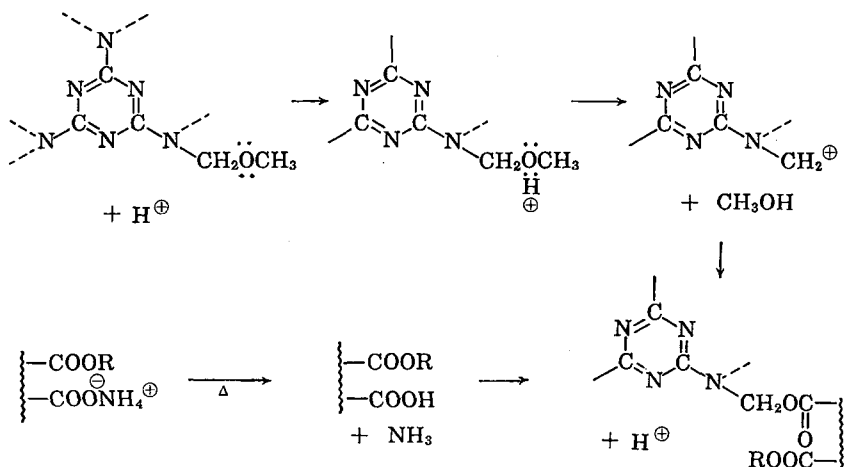
The reaction is initiated by loss of ammonia from the backbone acrylic copolymer, liberating free carboxylic acid groups. Protons from the strong acid catalyst, or from some of the carboxyls if no catalyst is used, react with the alkoxy group of the HMM. The alkoxy is ejected as methanol, while free carboxyls combine with the melamine residue to form a methylene ester linkage. Since the melamine derivative is polyfunctional, the ultimate result is a highly crosslinked network.

Conclusions based on studies of model compounds are always to be drawn with caution, and the shortcomings inherent in such an approach are recognized. In the present case, however, it did not appear possible to gain adequate understanding of the crosslinking process by examination of the polymer system alone.

One of the difficulties with model compounds which has already been noted was the large proportion of material remaining unreacted under conditions which promoted curing in the resin itself. This observation, although surprising, is in agreement with studies on related systems. Nord-

høy and Ugelstad[8] have investigated the acid-catalyzed hydrolysis of alkoxymethylureas:

$$CH_3OCH_2NHCONH_2 + H_2O \rightarrow CH_3OH + HOCH_2NHCONH_2$$

$$HOCH_2NHCONH_2 \rightarrow NH_2CONH_2 + CH_2O$$
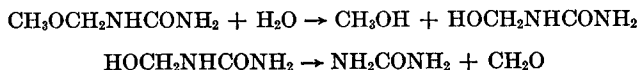
The rate of cleavage of methoxymethylurea was 1650 times that of methoxymethylbenzamide, which was their "model compounds." With both of these substances, the initial step was the same as the principal reaction of the present study, i.e., ejection of the alkoxy group as alcohol. In the work of Nordhøy and Ugelstad, this ejection from alkoxymethylureas was approximately 15 times as rapid as the subsequent elimination of formaldehyde. The evidence of the present investigation indicates that the reactions in the melamine series are at least qualitatively similar.

## Degree of Crosslinking from Base Binding Measurements

Since curing in the melamine–acrylic system is initiated by the creation of free carboxyl groups which are esterified as the crosslinking reaction proceeds, it should be possible to determine the extent of crosslinking by a titrimetric procedure. Such measurements would have an obvious practical value, since they would enable the resin chemist to select compositions and curing conditions for which crosslinking would be a maximum. The cured resin would then contain a minimum of free carboxyl groups and would be expected to have the greatest chemical resistance. In order to carry out these determinations, the cured resin was considered as a cation exchange polymer of unknown base-binding capacity. Acrylic ester–acrylic acid copolymers were prepared at several ester/acid ratios, converted to ammonium salts, and blended with different proportions of HMM and acidic catalyst. Films were cast on glass plates with each of these blends, and baked for 30 min. at 150°C. The cured films were scraped off the glass and powdered. Weighed samples were shaken for 72 hrs. with standard $0.1N$ sodium hydroxide, and the excess alkali was back-titrated with hydrochloric acid. The degree of crosslinking was then calculated. This quantity is defined, for the present purposes, as 100% minus the ratio of the free carboxyl concentration in the cured resin to that in the original soluble polymer. The reproducibility of the method was very satisfactory, duplicate determinations agreeing to ±1 or 2% in degree of crosslinking.

Since the crosslinks have been shown to be methylene esters, it might be thought that saponification during lengthy contact with dilute alkali would cause serious interference with the determination of free carboxyls. Such inteference does not, in fact, seem to occur. In many cases, as will be seen shortly, essentially no free carboxyls could be detected; that is, no alkali was consumed by any kind of reaction with these cured films. It is possible that in very poorly crosslinked systems some saponification does take place, but such films have little practical interest.
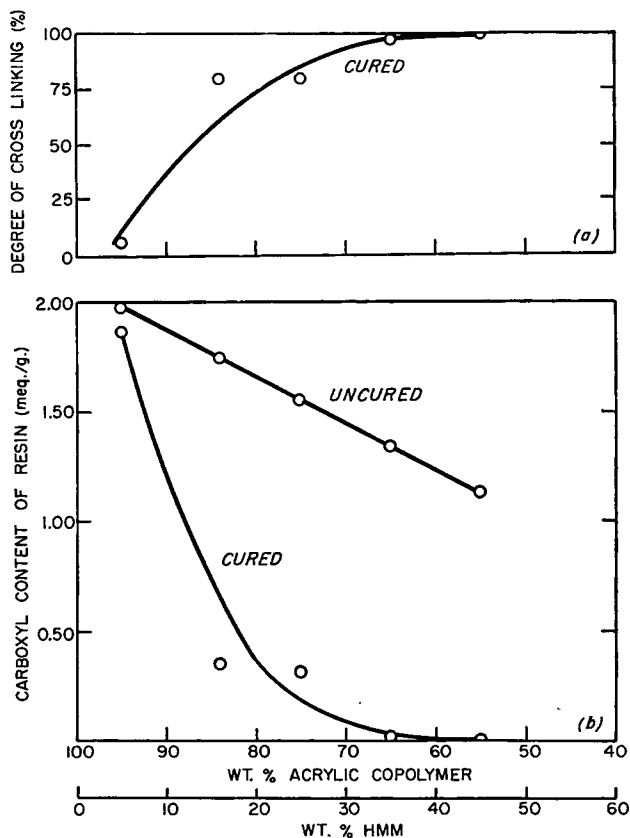
Fig. 1. Effect of acrylic copolymer–HMMA ratio on degree of crosslinking: (a) expressed as per cent of maximum crosslinking; (b) expressed as titratable carboxyl content.

The graphs which follow show the dependence of the degree of crosslinking upon the composition of the system or the conditions of cure. Figure 1 indicates the effect of different amounts of HMM in curing the same acrylic ester–acrylic acid copolymer, which contains 23 mole-% acid. To achieve essentially quantitative curing, as shown by the disappearance of titratable carboxyl groups from the cured film, approximately 1 part of the melamine component is required for each 2 parts, by weight, of the acrylic copolymer. This corresponds to 1 mole of HMM per 1.5 moles of acid in the copolymer. If the HMM were truly hexafunctional, as its formula would suggest, 1 mole should obviously completely esterify 6.0 moles of acid. Undoubtedly, the restriction of molecular motion during the curing of the resin prevents the reaction of all six possible sites on the HMM. Self-condensation of some of the HMM is also a possibility which would reduce the functionality relative to the acrylic polymer. While such reaction was not found to occur in the experiments on model com-
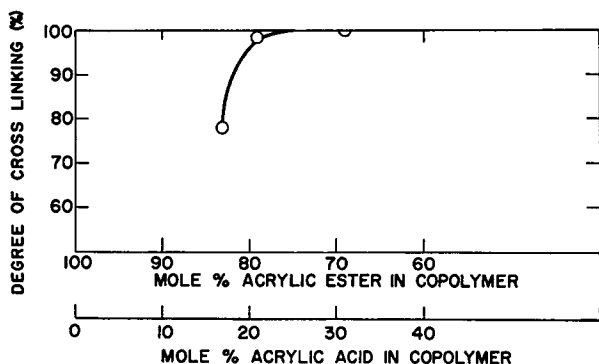
Fig. 2. Effect of dilution of acrylic acid with acrylic ester in copolymers on degree of crosslinking; acrylic acid/HMM mole ratio constant at 2.15:1.
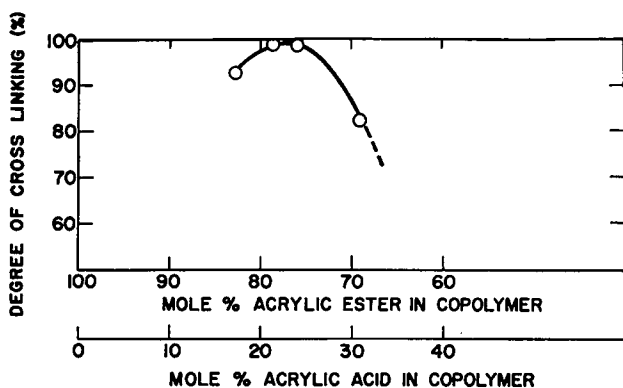


Fig. 3. Effect of acrylic copolymer composition on degree of crosslinking; copolymer/HMM weight ratio constant at 65:35.

pounds, it cannot be entirely rejected on this ground, and may take place to an appreciable extent.

Even apart from this possibility, the apparently low functionality of the HMM in this system is consistent with the studies of Wohnsiedler et al.[9] on simple melamine–formaldehyde resins. When a 1:2 melamine–formaldehyde resin was completely cured (as judged by a leveling off of physical properties), only 1.2–1.3 moles of formaldehyde had reacted per mole of melamine, 0.7–0.8 moles being left as noncrosslinked methylol groups. In view of the rigidity, insolubility, and infusibility of conventional melamine resins achieved with this low functionality, it is evident that the effective functionality of 1.5 for HMM under the specified reaction conditions is also ample to provide a highly crosslinked network.

The crosslinking efficiency of HMM is further examined in the experiments presented in Figure 2. The compositions of these systems were selected so that the mole ratio of acrylic acid to melamine in each case is 2.15:1, but the ratio of acrylic ester to acrylic acid in the

backbone copolymer has been varied. Thus the crosslinkable groups have been diluted with differing amounts of inert acrylic ester. Where the acrylic ester content is high, the degree of crosslinking is found to be low, even though on a stoichiometric basis all three of the formulations have the same opportunity to generate crosslinks. But this is to be expected, since where acid groups are relatively widely spaced along the chain, a single HMM molecule will be less likely to react with more than one carboxyl group than will an HMM molecule in a carboxyl-rich environment.

In Figure 3 the ratio of acrylic copolymer to HMM has been held constant at 65:35 by weight, and the acrylic acid content of the copolymer varied over a fairly narrow range. It was not practical, with the particular monomers selected, to extend the range of acid content; at lower contents, the uncured resin appeared insoluble in ammonia water and hence could not
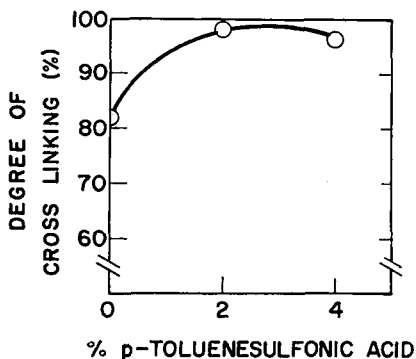


Fig. 4. Effect of catalyst concentration on degree of crosslinking in a typical acrylic–melamine system.

be cast into films in the usual way. At the other extreme, when the acid content was increased while the HMM content was kept unchanged, the cured film appeared to be so poorly crosslinked that it swelled excessively on prolonged exposure to $0.1N$ NaOH. Even within the narrow range examined, the degree of cure began to decrease in this series of copolymers when the acid content exceeded 25 mole-%.

Figure 4 shows the effect of different catalyst concentrations in promoting the cure of one typical copolymer at one level of HMM concentration. Under conventional curing conditions (30 min. at 150°C.) but without catalyst, 82% of the titratable carboxyl groups was transformed into crosslinks. It would appear desirable in practical surface coatings to obtain a higher degree of conversion of carboxyls in order to secure the maximum in alkali resistance. Under the same conditions of cure, addition of small amounts of strong acid to the system leads to essentially quantitative crosslinking. It should be mentioned that since p-toluenesulfonic acid, a nonvolatile compound, was chosen for these experiments, it was assumed that a certain fraction of the titratable acidity in the films was due to the

catalyst, and an appropriate correction was made in calculating the degree of crosslinking. This was usually of the order of 2% absolute.

The results obtained in these binding experiments depend on the ability of sodium and hydroxyl ions to penetrate the crosslinked polymer structure. It may be argued that where crosslinking is very extensive a certain fraction of free carboxyls may be trapped inside a tightly bound network, through which the titrant ions will be unable to penetrate, and hence the shielded groups will remain undetected by this procedure. There is some merit in this argument, but there is obviously no chemical means of determining its validity, and spectral detection of these groups would be unlikely unless they were present in relatively high concentration. Any shielded carboxyls would, of course, make no detrimental contribution to the behavior of the coating under actual service conditions as long as the crosslinks themselves remained intact.

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## Résumé

On a étudié le mécanisme de vulcanisation dans des enduits formés de mélanges de sels d'ammonium des copolymères acide acrylique–ester acrylique et d'alcoxyméthylmélamines. On a fait des expériences sur les composants mêmes de la résine et sur des composés modèles ayant des structures chimiques analogues. La vulcanisation de la résine commence par la perte d'ammoniaque pour régénérer les groupes carboxyliques libres, plutôt que par la perte d'eau pour former des amides. Le groupement alcoxylé est éliminé et des pontages sont formés entre les groupes carboxyliques et les groupes méthylmélamines. Des études sur la liaison fondamentale dans des films vulcanisés indiquent que le degré de pontage dépend de la composition exacte de la résine et de la présence ou l'absence d'un catalyseur acide. Ces variables peuvent être réglées pour donner essentiellement un pontage quantitatif dans l'enduit vulcanisé ce qui est prouvé par la disposition des groupes carboxyliques qui n'ont pas réagi.

## Zusammenfassung

Der Häartungsmechanismus in Überzugssystemen aus Mischungen von Ammonium-salzen von Acrylsäure–Acrylestercopolymeren und Alkoxymethylmelaminen wurde untersucht.   Versuche wurden sowohl an den Harzkomponenten selbst, als auch an Modellverbindungen mit analoger chemischer Struktur ausgeführt.   Die Härtung des Harzes beginnt mit einem Ammoniakverlust unter Regenerierung freier Carboxyl-gruppen und nicht mit einem Wasserverlust unter Amidbildung.   Die Alkoxygruppe wird eliminiert und zwischen dem Karboxyl und dem Methylolmelamin bilden sich Estervernetzungen.   Versuche über die Bindung von Basen an gehärtete Folien zeigen, dass das Vernetzungsausmass von der exakten Zusammensetzung des Harzsystems und der Gegenwart oder Abwesenheit eines sauren Katalysators abhängt.   Diese Variablen können so gewählt werden, dass im gehärteten Überzug im wesentlichen quantitative Vernetzung eintritt, wie das vollständige Verschwinden freier Karboxylgruppen zeigt.