

Thermosetting Vinyl and Acrylic Copolymers

D. P. KELLY, G. J. H. MELROSE, and D. H. SOLOMON, *Research Laboratory, Balm Paints Pty., Ltd., Clayton, Victoria, Australia*

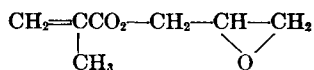
Introduction

Experience has established that the durability of a polymeric surface coating is directly related (among other things) to its molecular weight.¹ Two distinct methods are used to achieve the desired high molecular weight final coating. First, the polymer is preformed and applied as a solution in a suitable solvent which simply evaporates to form a film (lacquer). However, this approach inherently gives low solids at a given viscosity, since viscosity is proportional to the solids and also to the molecular weight of the polymer in solution.² The second approach utilizes systems in which two or more relatively low molecular weight polymers are applied from a solution and subsequently the polymers interreact to form a high molecular weight film (enamel).

Acrylic (and vinyl) copolymers have been used extensively in lacquers and have shown advantages of gloss retention and general durability,³ but until recently⁴ they have not been used in enamels. The work described in this paper arose from a search for an acrylic-based enamel which would interreact at schedules of 135°C./30 min. or less and yet, in spite of this reactivity, be stable at ambient temperatures.

The reaction between alkyd resins (fatty acid-modified polyesters) and melamine or urea-formaldehyde condensates (nitrogen-formaldehyde resins) leads to reasonably durable films.⁵ Moreover, the system reacts in the region⁵ of 135°C./30 min. and is stable at room temperatures.⁵ Here, the functional groups are hydroxyl and carboxyl on the one hand, and amido, methylol, and methylol ether on the other, and hence, from analogy, it was decided to investigate the reactions of acrylic copolymers which contained these groups. Since a method chosen for the synthesis of hydroxyl-containing copolymers (see below) involved epoxy-substituted copolymers as intermediates, these were also studied.

Preparation of Copolymers



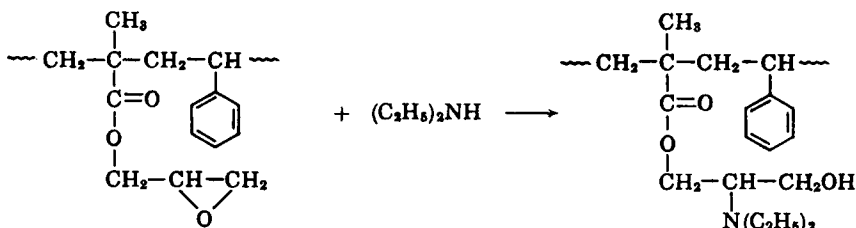
Glycidyl methacrylate

Epoxy-, carboxyl-, and amido-substituted acrylic copolymers were prepared simply, by copolymerizing glycidyl methacrylate, acrylic acid, and

acrylamide, respectively, with styrene in the conventional free-radical solution processes. In contrast, the direct synthesis of hydroxyl-substituted acrylic and vinyl copolymers is difficult. At the time of the investigation, the only commercially available monomer was allyl alcohol which must be expected to homopolymerize rather than copolymerize with acrylic or vinyl monomers.⁶

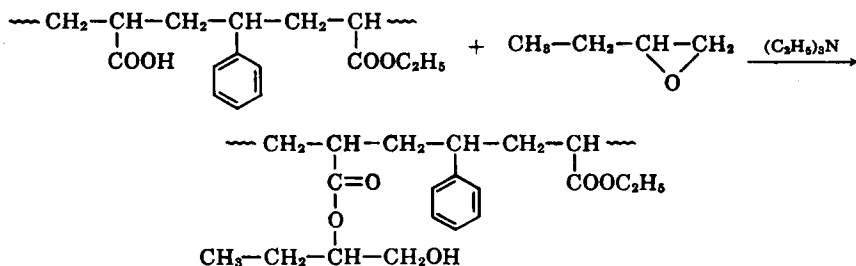
Thus, it became necessary to synthesize the hydroxy copolymers in directly from other commercially available monomers. Two principal syntheses were used.

First, glycidyl methacrylate and styrene were copolymerized in solution and the resulting copolymer was heated under reflux with diethylamine until the infrared spectrum⁷ of the product had strong hydroxyl absorption near 3300 cm^{-1} but no epoxide absorption⁸ near 910 cm^{-1} . (Although both *primary* and *secondary* hydroxyl groups may be formed, we have chosen to illustrate the primary hydroxyl only.)



A *secondary* amine is used in the above synthesis, since a *tertiary* amine has, obviously, no labile hydrogen, while a *primary* amine would react to form a *secondary* amine group. This product could then lead to gelation by crosslinking with unchanged macromolecules containing epoxy groups.

In the second method, copolymers of the type ethyl acrylate-acrylic acid-styrene were reacted quantitatively under basic catalysis, with butylene oxide:



In view of the superior quality of acrylic surface coatings, it was considered desirable to use the reaction between hydroxyl and methylol (and/or methylol ether) groups in a completely acrylic enamel. That is, to stove hydroxy-acrylic copolymers with acrylic copolymers containing methylol groups. However, this has a serious limitation: it is difficult to find two completely compatible copolymers.⁹ The alternative approach of

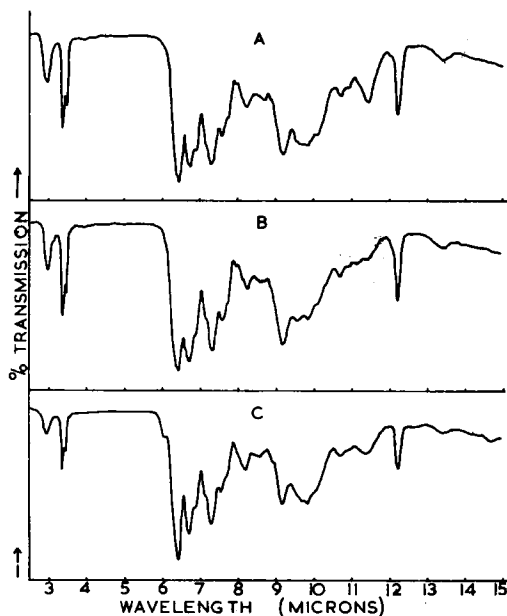
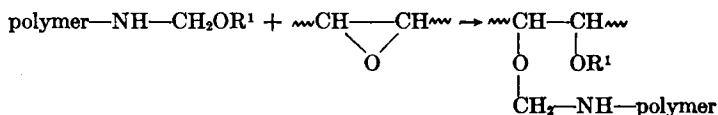


Fig. 1. Infrared spectra of a butylated melamine-formaldehyde resin: (A) after evaporation of solvent at 45°C. for 1 hr. with reduced pressure; (B) after heating at 120°C. for 30 min.; (C) after heating at 120°C. for 30 min. with *p*-toluene sulfonic acid (2%).

Figures 1A-1C, 2A-2D and 3A-3C illustrate the crosslinking of a butylated melamine-formaldehyde resin with a copolymer prepared from equal parts of glycidyl methacrylate and styrene. The reaction was presumably of the following type,



where "polymer" is a nonreactive portion of a melamine-formaldehyde resin and R^1 is H or C_4H_9 . This reaction was followed by the disappearance of the epoxy group absorption at 910 cm^{-1} . Figures 1A-1C and 2A-2C show that crosslinking was negligible at 120°C./30 min. except in the presence of 2% of *p*-toluene sulfonic acid. The reaction appears to be approaching completion under 4% catalysis with 10% of butylated melamine-formaldehyde resin (Fig. 2D). The ease of the condensation between methylol and epoxy groups under the influence of acid catalysis is seen in a comparison of Figures 3A and 3B which indicate that crosslinking proceeds little further on raising the temperature from 105 to 150°C. This is also supported by Figures 3A and 3C, little change being apparent on increasing reaction time. Thus, it appeared that the epoxy-substituted copolymer with nitrogen-formaldehyde resin, when catalyzed by a latent acid catalyst such as morpholine *p*-toluene sulfonate might be used as a basis for the

desired enamel. However, further experiments were not made after it was found that copolymers of this type were generally incompatible with both butylated melamine-formaldehyde and urea-formaldehyde resins.

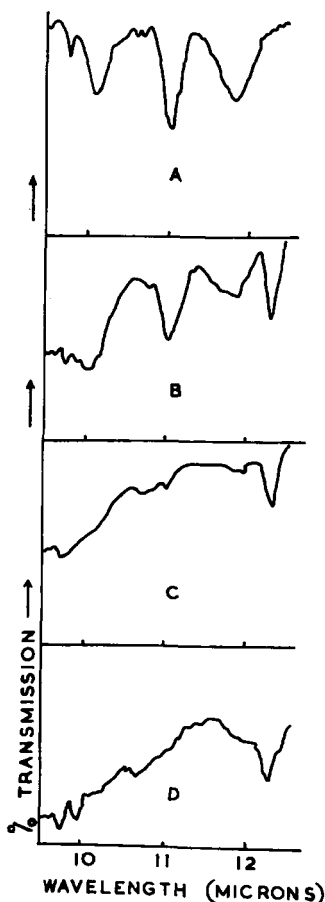
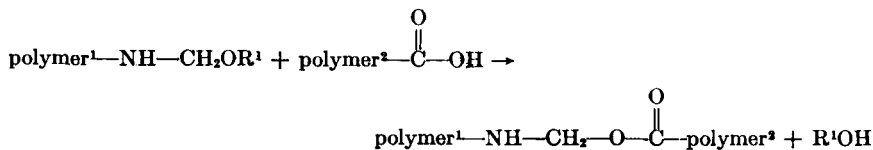


Fig. 2. Infrared spectra of blends of epoxy-substituted copolymer (ESC) with butylated melamine-formaldehyde resin (MF) after heating: (A) ESC (80 parts) and MF (20 parts) at 105°C. for 30 min. with *p*-toluene sulfonic acid (2 parts); (B) ESC (80 parts) and MF (20 parts) at 150°C. for 30 min. with *p*-toluene sulfonic acid (2 parts); (C) ESC (80 parts) and MF (20 parts) at 105°C. for 1 hr. with *p*-toluene sulfonic acid (2 parts).

Two other reactions were followed by infrared analysis. First, a polymer which was prepared from acrylic acid (4 parts) and styrene (96 parts) was found to crosslink with the melamine-formaldehyde resin:



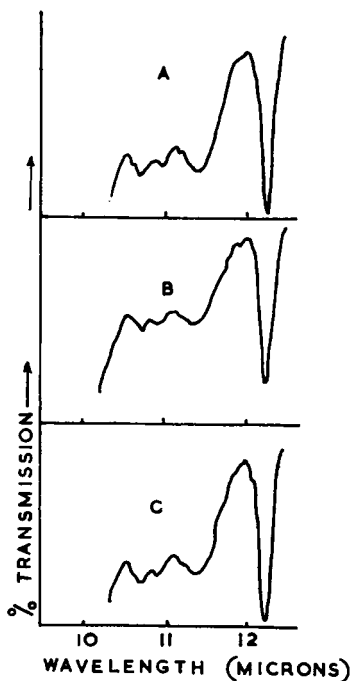


Fig. 3. Infrared spectra of epoxy-substituted copolymer (ESC) and blends with butylated melamine-formaldehyde resin (MF) after heating: (A) ESC at 120°C. for 30 min.; (B) ESC (90 parts) and MF (10 parts) at 120°C. for 30 min.; (C) ESC (90 parts) and MF (10 parts) with *p*-toluene sulfonic acid (2 parts) at 120°C. for 30 min.; (D) ESC (90 parts) and MF (10 parts) at 120°C. for 30 min. with *p*-toluene sulfonic acid (4 parts).

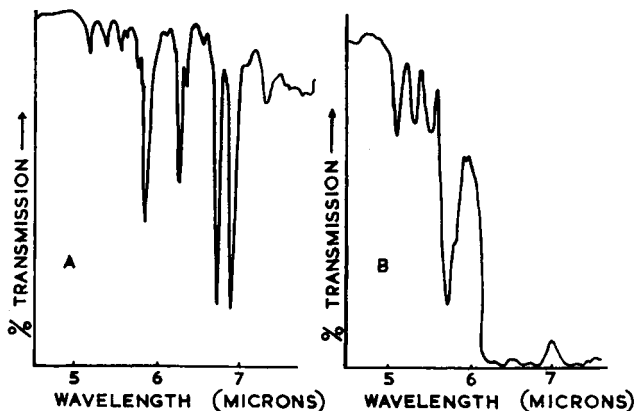


Fig. 4. Infrared spectra of carboxyl-substituted copolymer (CSC), and blends with butylated melamine-formaldehyde resin (MF); (A) CSC (100 parts) and MF (30 parts) after evaporation of solvent at 45°C. for 1 hr. with reduced pressure; (B) after heating of CSC (100 parts) and MF (30 parts) at 120°C. for 30 min.

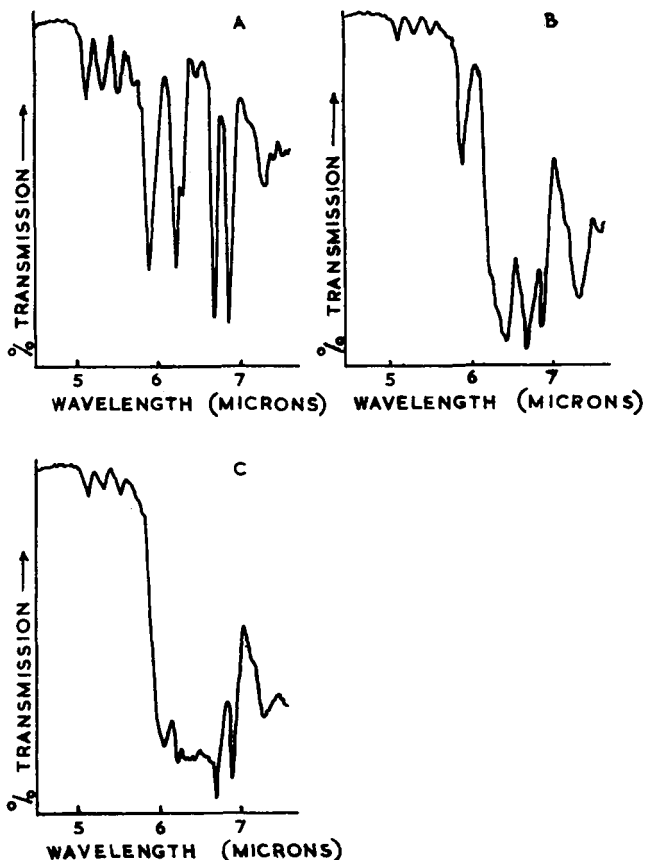
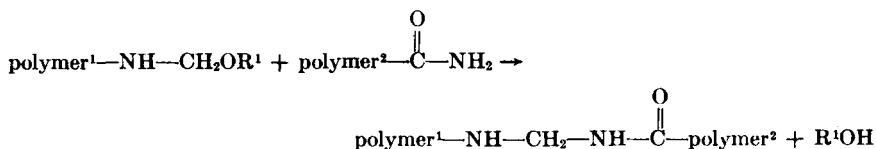


Fig. 5. Infrared spectra of amido-substituted copolymer (ASC), and blends with butylated melamine-formaldehyde resin (MF) after heating: (A) ASC at 120°C. for 30 min.; (B) ASC (80 parts) and MF (20 parts) at 120°C. for 30 min.; (C) ASC (80 parts) and MF (20 parts) at 120°C. for 30 min. with *p*-toluene sulfonic acid (2 parts).

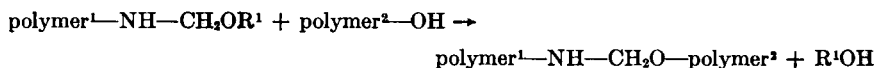
where "polymer¹" is a nonreactive portion of melamine-formaldehyde resin, "polymer²" is a polystyrene backbone, and R¹ is H or C₄H₉. This is evident from the formation, on heating at 120°C. for 30 min., of a strong ester band near 1730 cm.⁻¹ (Figs. 4A and 4B). Second, the acid-catalyzed reaction given below,



where "polymer¹" and R¹ are as above and "polymer²" is a polystyrene backbone, was followed (Figs. 5A-C) by a change from *primary* amide absorption near 1680 cm.⁻¹ to substituted amide absorption near 1650 cm.⁻¹

when 80 parts of a copolymer, prepared from acrylamide/styrene (1:9) were heated with *p*-toluene sulfonic acid catalyst (4 parts) and butylated melamine-formaldehyde resin (20 parts). In spite of the reactivity of these particular systems, they were discarded also, because it was later found that similar polymers were generally incompatible.

The reactions of hydroxy copolymers with butylated nitrogen-formaldehyde resins were difficult to follow by infrared spectroscopy owing to the overlap of the —NH and —OH stretching bands near 3400 cm.⁻¹. However, the insolubility in butyl acetate of the films prepared by stoving hydroxy copolymers with butylated melamine-, urea-, or benzoguanamine-formaldehyde resins indicated crosslinking:



where "polymer¹" is a nonreactive portion of melamine-formaldehyde resin, "polymer²" is an addition polymer backbone, and R¹ is H or C₄H₉. Moreover, the films were generally compatible. Also, the systems are stable. For these reasons further efforts were concentrated on the reactions of polymers containing hydroxyl and methylol groups.

Evaluation of Copolymers

A series of hydroxy copolymers were pigmented with rutile titanium dioxide and heated with butylated melamine-formaldehyde resin, sometimes with morpholine *p*-toluene sulfonate as catalyst. The products were evaluated as domestic appliance coatings, durability in boiling soap solution (4%) being one of the standard screening tests (Table I).

TABLE I
Mean Durabilities of Films in Boiling Soap Solution (4%)

Copolymer, SEAAA ratio ^a	Film durability, hr.	
	Catalyzed	Uncatalyzed
90:0:10	100	100
72:18:10	1	60
45:45:10	0	2
0:90:10	0	0

^a S = styrene, EA = ethyl acrylate, AA = acrylic acid.

Understandably, the durability is decreased when the proportion of alkali-sensitive groups is increased by substitution of ethyl acrylate for styrene. Table I also shows the down-grade of durability when the enamel is acid-catalyzed. This effect is apparently due to excess *p*-toluene sulfonic acid being leached out of the film as salts.

Experimental

General

Weights specified in the descriptions of the blending of polymers are of 50% solutions by weight of polymer in organic solvent. Purities of monomers and solvents were checked by gas-liquid chromatography and distillation was carried out when necessary. Inhibitor (0.01–0.10%) and polymer contents (nil) of monomer samples were checked by standard tests.¹² Peroxide assays of benzoyl peroxide and cumene hydroperoxide were 96% and 75%, respectively.

Solids Determinations. These represented the per cent residue after a solution of the polymer (ca. 1.0 g.) was evaporated on a 4 cm. diameter Petri dish in a forced-draught oven at 105°C. for 3 hr.

Infrared Analyses. A blend of solutions of a copolymer and a butylated melamine-formaldehyde resin and, in some cases, *p*-toluene sulfonic acid catalyst, was applied to a rock salt plate and the spectrum was recorded after drying under vacuum at ca. 50°C., and then again after heating the film and plate at a given schedule.

Stability Determinations. Copolymer (70 parts) was blended with butylated melamine-formaldehyde resin (30 parts) and reduced with xylene to viscosity A (Gardner-Holdt scale). The blend was labeled "stable" if the increase in viscosity was less than 7 scale units after standing at 45°C. for 3 months.

Compatibility and Solubility Determinations. A blend of the copolymer (80 parts) and the nitrogen-formaldehyde resin (20 parts) was drawn on a 6 in. × 4 in. glass panel by means of a 0.0042 in. doctor blade. After heating at 120°C. for 30 min. the panel was cooled and the film inspected. It was compared with a corresponding film of the copolymer, any increase in opacity of the blend being indicative of incompatibility. The solubility of the experimental film was observed after contact with butyl acetate for 20 sec.

Copolymers

Epoxy-substituted Copolymer. Xylene (450 g.) and butyl alcohol (50 g.) were heated under reflux while a solution of benzoyl peroxide (2 g.) in glycidyl methacrylate (250 g.) and styrene (250 g.) was added over 2 hr. Reflux was continued for 2 hr., when a solids determination showed that copolymerization was complete. The copolymer had infrared maxima near 910 (epoxy), and 770 and 700 cm.^{-1} (aromatic).

Carboxyl-substituted Copolymer. A copolymer was prepared in a manner similar to that given above, with styrene (480 g.) and acrylic acid (20 g.). The copolymer had strong carboxyl absorption near 1710 cm.^{-1} and aromatic absorption near 770 and 700 cm.^{-1} . A solids determination gave 50%.

Amido-substituted Copolymer. Acrylamide (40 g.) and styrene (460 g.) were copolymerized in a manner similar to that described above, in butyl alcohol (400 g.) and xylene (400 g.). The copolymer had infrared maxima near 1680 (amido), and 770 and 700 cm.^{-1} (aromatic). A solids determination gave 38%.

Hydroxyl-substituted Copolymer. 1. Styrene (20 g.), glycidyl methacrylate (30 g.), toluene (800 g.) and benzoyl peroxide (19 g.) were heated at 80–100°C. while styrene (234 g.), glycidyl methacrylate (302 g.) and benzoyl peroxide (14 g.) were added dropwise over 4 hrs. After cooling, diethylamine (450 g.) was added and the solution heated under reflux for 14 hrs. After this time the spectrum of the copolymer no longer showed epoxide absorption near 910 cm.^{-1} . Solvent (700 g.) was distilled under reduced pressure. The resulting polymer had infrared absorption maxima near 3300 (hydroxyl), 1730 (ester), and 770 and 700 cm.^{-1} (aromatic). A solids determination gave 54%. A mixture of the copolymer (70 parts) with butylated melamine-formaldehyde resin (30 parts) was stable. 2. Xylene (600 g.) and butyl alcohol (400 g.) were heated under reflux while styrene (416 g.), acrylic acid (288 g.), and benzoyl peroxide (20 g.) were added over 3 hr. Reflux was continued for 1 hr. Butylene oxide (500 g.) and triethylamine (40 g., 30% solution in xylene) were added, and the solution was heated (12 hr.) until the infrared absorption band near 3300 cm.^{-1} (hydroxyl) no longer increased and the carboxyl band (1710 cm.^{-1}) disappeared. Unchanged butylene oxide and solvent (300 g.) were distilled. A solids determination gave 49%. The acid value (number of milligrams of potassium hydroxide equivalent to 1 g. of solid copolymer) was 0.4.

Similarly, copolymers of ethyl acrylate-styrene-acrylic acid (butylene oxide) were prepared. Generally, films derived from blends of hydroxy copolymers and butylated nitrogen-formaldehyde resins were softened—insoluble in butyl acetate.

Hydroxy-Methylolamido-substituted Copolymer. Acrylamide (50 g.), *tert*-dodecyl mercaptan (15 g.), butyl alcohol (700 g.), and hydroquinone (200 mg.) were brought slowly to 80°C. and filtered. Xylene (800 g.), vinyl toluene (1500 g.), acrylic acid (30 g.), and cumene hydroperoxide (15 g.) were added to the filtrate and the whole was heated under reflux for 5 hr., more catalyst (10 g.) being added after the second and fourth hours. After cooling, paraformaldehyde (90 g.) and triethylamine (80 g., 30% solution in xylene) were added and the solution was heated under reflux for 2 hr. The reaction product was cooled to 75°C. and butylene oxide (25 g.) added before the solution was again brought to reflux for 1 hr. Solvent (715 g.) was distilled and replaced by xylene (600 g.). Solids of the product were 52%. The infrared spectrum of the copolymer had maxima near 3300 (hydroxyl and methylolamido) and 1710 cm.^{-1} (carboxyl). A clear and solvent-resistant film was obtained when the copolymer was heated at 120° C. for 30 min.

Nitrogen-Formaldehyde Resins

Melamine-Formaldehyde Resin. The butylated resin (viscosity V in Gardner-Holdt units at 50% solids, acid value 2, water content 0.5%) was made by the conventional process from a charge of melamine (29 parts), formaldehyde solution (40%, 96 parts), butyl alcohol (122 parts), and toluene (42 parts).

Urea-Formaldehyde Resin. Urea (33 parts) and formaldehyde solution (40%, 100 parts) were reacted in butyl alcohol (32 parts) and toluene (18 parts) to yield a resin (viscosity L in Gardner-Holdt units at 50% solids, acid value 5, water content 2%).

Benzoguanamine-Formaldehyde Resin. Imperial Chemical Industries' Paralac 7001 was used.

Evaluation of Copolymers

Films for evaluation in boiling soap solution (4%) or boiling detergent solution (0.5%) were prepared in the following manner. A blend of copolymer (70 parts) and butylated melamine-formaldehyde resin (30 parts) and, in some cases, *p*-toluene sulfonic acid (2 parts) was pigmented with rutile titanium dioxide (100 parts blend to 80 parts pigment) and sprayed to a dry thickness of 0.00015 in. on 6 in. × 4 in. phosphated steel panels. After heating at 120°C. for 30 min. and aging for 1 day, the panels were immersed in the soap or detergent solution. Breakdown was taken as the time for the formation of film blisters. A mean of eight determinations for each blend was recorded.

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Synopsis

Infrared spectra indicate that carboxyl-substituted acrylic copolymers react appreciably with a butylated melamine-formaldehyde resin when heated at 120°C. for 30 min., but under these conditions acid catalysis is needed before epoxy- or amido-substituted copolymers will crosslink with the melamine-formaldehyde resin. Two methods have been used to synthesize hydroxyl-substituted acrylic copolymers. First, a glycidyl methacrylate copolymer was reacted with diethylamine. Second, an acrylic acid copolymer was heated under reflux with butylene oxide in the presence of a basic catalyst. This second method was used to esterify a vinyl toluene-acrylic acid-acrylamide copolymer which was subsequently treated with paraformaldehyde. The resulting hydroxy-methylolamido copolymer intercondensed when heated at 120°C. for 30 min., somewhat as did the hydroxy copolymer with melamine-formaldehyde resin blends.

Résumé

L'analyse des spectres infrarouge montre que les copolymères acryliques substitués au carboxyle réagissent d'une façon appréciable avec une résine butylée mélamine-formaldéhyde lorsqu'on chauffe à 120°C./30 min., mais dans ces conditions, une catalyse acide est nécessaire avant le pontage des copolymères époxy ou amidosubstitués avec la résine mélamine-formaldéhyde. Deux méthodes ont été utilisées pour synthétiser des copolymères acryliques substitués à l'hydroxyde. La première en faisant réagir un copolymère de méthacrylate de glycidyle avec la diéthylamine. La seconde en chauffant à reflux un copolymère de l'acide acrylique avec l'oxyde de butylène en présence d'un catalyseur basique. La seconde méthode a été employée pour estérifier un copolymère de vinyl toluène/acide acrylique/acrylamide lequel a été traité ensuite avec le paraformaldéhyde. La copolymère hydroxy-méthylolamide qui en résulte a été condensé par chauffage à 120°C./30 min. d'une façon analogue à celle du mélange de copolymère hydroxylé avec la résine mélamine-formaldéhyde.

Zusammenfassung

Infrarotspektren zeigen, dass carboxyl-substituierte Acrylcopolymere beim Erhitzen durch 30 Minuten auf 120°C in beträchtlichem Ausmass mit einem butylierten Melamin-Formaldehydharz reagieren, dass aber unter diesen Bedingungen zur Vernetzung von epoxy- oder amido-substituierten Copolymeren mit dem Melamin-Formaldehydharz Säurekatalyse notwendig ist. Zwei Methoden wurden zur Synthese hydroxyl-substituierter Acrylcopolymerer verwendet. Erstens wurde ein Glycidylmethacrylatcopolymeres mit Diäthylamin zur Reaktion gebracht und zweitens wurde ein Acrylsäurecopolymeres mit Butylenoxyd in Gegenwart eines basischen Katalysators unter Rückfluss erhitzt. Diese zweite Methode wurde zur Veresterung eines Vinyltoluol-Acrylsäure-Acrylamidcopolymeren benützt, das nachher mit Paraformaldehyd behandelt wurde. Das gebildete Hydroxymethylamidocopolymere kondensierte beim Erhitzen durch 30 Minuten auf 120°C in analoger Weise wie das Hydroxy-Copolymere mit Melamin-Formaldehydharzmischungen.

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