

## NOTES

*Polycondensates of Hexakis(methoxymethyl)melamine  
as Crosslinking Agent*

## INTRODUCTION

Hexakis(methoxymethyl)melamine (HMM) is a unique and useful crosslinking agent. It is superior to the conventional melamine resins in that the self-condensation does not proceed, thus a smaller amount of HMM is required to cure the coexisting film formers.<sup>1</sup> HMM is recommended as a crosslinking agent for emulsion systems since it does not destabilize the emulsion.<sup>2</sup>

It was believed that polycondensates of HMM would also show these two properties of HMM, as long as all the methylol groups are still blocked by methanol. It was found that such polycondensates are better crosslinking agents than HMM when used at the same weight level. An acrylic resin cured with the polycondensates had higher surface hardness and higher crosslinking densities than those cured with HMM.

## EXPERIMENTAL

Polycondensation of HMM was carried out by two methods, with the use of a commercial grade HMM (Nippon Carbide Co., Ltd., mol. wt. 434, free CH<sub>2</sub>O content less than 0.1%) without further purification. In the first method, HMM was heated in the presence of 80% HCOOH (2.5 wt.-%) at 130–140°C. for 35 hr. under a nitrogen atmosphere, the temperature then gradually being raised to 170°C. during the course of 1 hr. in order to distil off the volatile products formed. The molecular weight of the resinous product (PHMM) was 891. The infrared spectrum of the product PHMM is shown in Figure 1. The gas chromatographic analysis of the volatile products showed the presence of methanol only.

In the second method a mixture of 248 parts ethylene glycol (0.40 mole), 7800 parts HMM (2.0 mole), and 80% HCOOH (0.1 wt.-%) was heated to 120–130°C. for 3 hr., the temperature then being raised to 180°C. during the course of 2 hr. in order to remove the volatile products formed. The molecular weight of the resinous product (EGHMM) was 975. The gas chromatographic analysis of the volatile products showed the presence of only methanol and no ethylene glycol. The infrared spectrum of EGHMM is shown in Figure 1. The yields of PHMM and EGHMM are shown in Table I. The molecular weights were measured with a vapor-pressure osmometer (Model 301A, Mechrolab Inc.).

The acrylics to make paint films were synthesized by adding a mixture of 1800 parts glycidyl versatate (Cardura-E, Shell Oil Co.) 420 parts styrene, 780 parts methacrylic acid, and 60 parts benzoyl peroxide dropwise into 600 parts of boiling isobutanol during

TABLE I  
Yields of PHMM and EGHMM

	PHMM	EGHMM
Resinous product, %	92.3	92.0
Volatile products, %	6.6	6.4
Total, %	98.9	98.4

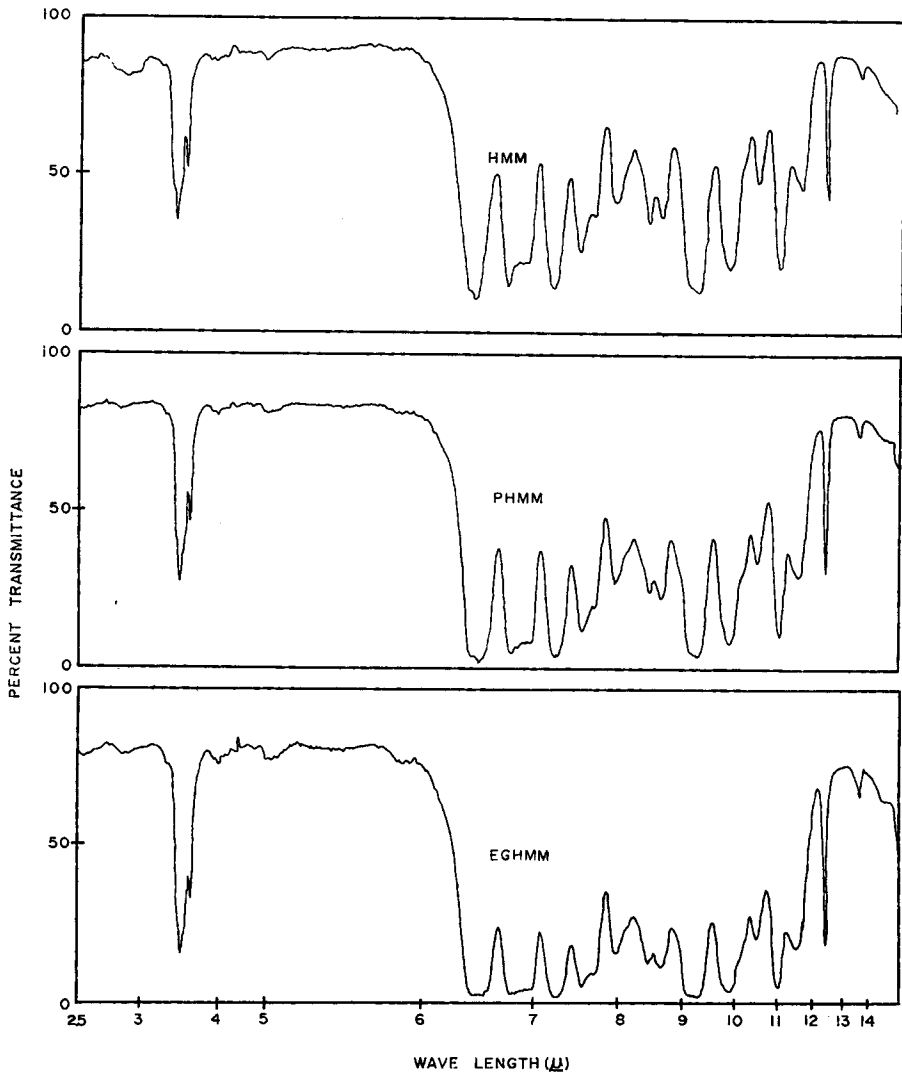


Fig. 1. Infrared spectra of HMM, PHMM, and EGHMM.

the course of 2.5 hr. The resin acid value was 35, and the calculated OH equivalent is about 425. This acrylic resin was blended with each of the hardeners, and enamels with  $\text{TiO}_2$  pigment/binder ratio of  $1/2$  were applied onto galvanized steel panels with a doctor blade, kept at room temperature overnight, and then baked at  $160 \pm 2^\circ\text{C}$ . for a specified period. The thickness of the films was about  $70 \mu$ .

For the purpose of estimating the relative crosslinking efficiencies of HMM, PHMM, and EGHMM, the damping versus temperatures curves were measured by a pendulum hardness tester on the paint films. This method of estimating the relative crosslinking density and glass transition temperature  $T_g$  has been widely used by Japanese paint chemists.<sup>3,4</sup>

The weight of the pendulum was 62 g, and it was loaded on the film through two spherical indentors (2 mm. diameter) located 30 mm. apart. The center of gravity of the pen-

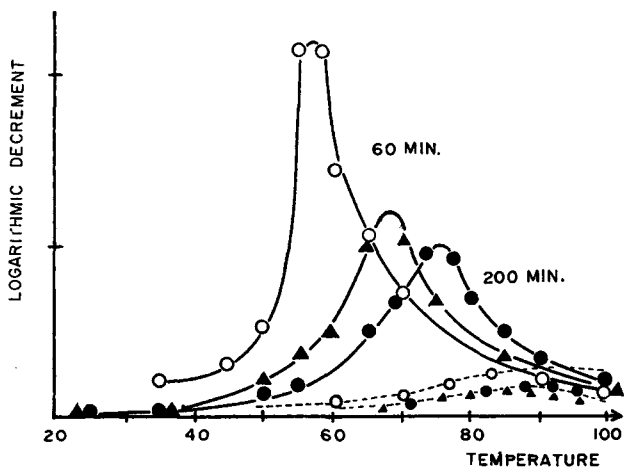


Fig. 2. Relative logarithmic decrement as a function of baking time of the films derived from three kinds of hardeners: (○) HMM; (▲) PHMM; (●) EGHMM. Hardener/acrylics ratio = 30/70.

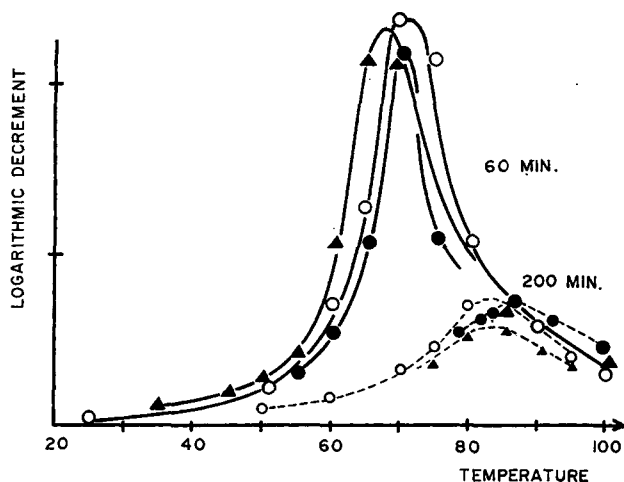


Fig. 3. Relative logarithmic decrement as a function of baking time of the films derived from three kinds of hardeners: (○) HMM; (▲) PHMM; (●) EGHMM. Hardener/acrylics ratio = 10/90.

dulum was 30 mm. below the loading points. The number of oscillations between two amplitudes was measured at various temperatures. More details of the apparatus and the theoretical backgrounds of the method are given elsewhere.<sup>3,5,6</sup>

### RESULTS AND DISCUSSION

The decreased absorption in the range 2.5–3.2  $\mu$  in the infrared spectra of PHMM and EGHMM would indicate that the concentrations of OH or NH groups are less than those of the commercial grade HMM; thus it appears reasonable to assume that practically all the functional groups of the polycondensates are still  $\text{CH}_3\text{OCH}_2-$ . Attempts to self-condense pure HMM (m.p. 48.8–51.7°C., mol. wt. 382), or to react the pure HMM with

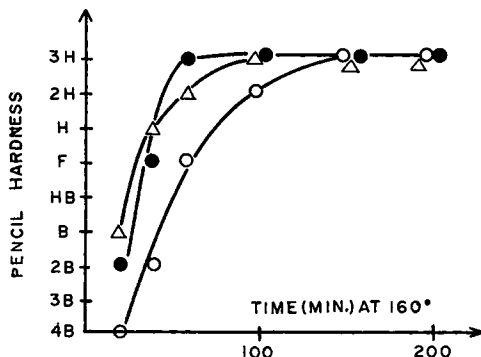


Fig. 4. Pencil hardness as a function of baking time of the films derived from three kinds of hardeners: (O) HMM; ( $\blacktriangle$ ) PHMM; ( $\bullet$ ) EGHMM. Hardener/acrylics ratio = 30/70.

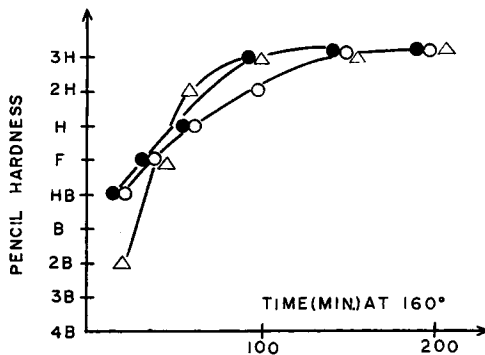


Fig. 5. Pencil hardness as a function of baking time of the films derived from three kinds of hardeners: (O) HMM; ( $\blacktriangle$ ) PHMM; ( $\bullet$ ) EGHMM. Hardener/acrylics ratio = 10/90.

ethylene glycol without the use of strong catalyst such as *p*-toluenesulfonic acid all failed.<sup>7</sup> Therefore, the methylol or NH groups which were probably present must have been consumed by the condensation reactions. The results of the measurements of crosslinking density are shown in Figures 2 and 3; those of pencil hardnesses at 20°C., in Figures 4 and 5.

The fact that the position of the peak, corresponding to  $T_g$ , is shifted towards a higher temperature accompanied by a decrease in the peak height in Figure 2 indicates that the crosslinking density of the films is in the order, EGHMM > PHMM > HMM.<sup>3,4,8</sup> As the HMM content is increased from 10% to 30% the  $T_g$  is decreased, which is perhaps consistent with the decrease in pencil hardness from H to F. One possible explanation would be that 30% of HMM was too great an excess to be tolerated by 70% of the acrylics. If this were the case, the excess HMM molecules would merely act as diluent or as branching agent at best, in either case lowering  $T_g$ .<sup>8-10</sup> This, however, is probably not the case. After 200 min. at 160°C. the crosslinking densities of the 30/70 systems appear to be higher than those of the 10/90 systems, as suggested by the fact that after 200 min. peak heights for the 30/70 systems are lower than those for the 10/90 systems.

All of the above arguments seem to lead to the conclusion that the polycondensation of HMM enhances the efficiency as crosslinking agent, despite the fact that the number of the molecules should be decreased by the polycondensation when used at the same

weight level. When the polycondensation of HMM was carried out further, the efficiency started to decrease.<sup>7</sup> In short, the number of functional groups per molecule of HMM appears to be small to be the most effective crosslinking agent, at least for the acrylics used in the present study. The generality of the results will be reported in the near future, together with a more vigorous viscoelastic study of the resins cured with HMM or its polycondensates.

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