Effect of Temperature on Properties of Aqueous Dispersions of Poly (Vinyl Methyl Ether)–Maleic Anhydride Half Amide

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In connection with the development of photosensitive coatings for the production of images on lithographic plates, the temperature-viscosity relationship of poly-(vinyl methyl ether)–maleic anhydride half amide copolymer dispersions was investigated.

Photosensitive coatings have long been employed in the field of lithography (*1*, *6*). Some of the earliest coatings developed for lithographic use consisted of an aqueous solution of a colloid such as gum arabic, egg albumin, gelatin, casein, or glue together with ammonium or potassium bichromate and in some instances ammonium hydroxide. The basic reaction responsible for image formation is the light hardening or tanning of the colloid, sensitized by the presence of bichromate. Although the reaction involves oxidation and reduction, the mechanism is incompletely understood (*7*). Modifications of this basic coating solution are in use today. Development efforts have been focused from time to time on the evaluation of new types of colloidal material, especially those of synthetic origin. With the view toward finding a suitable substitute for gum arabic, this laboratory initiated an investigation to determine the solution properties of a rather new and unique copolymer—viz., poly(vinyl methyl ether)–maleic anhydride half amide (PVM/MA-HA).

The solution properties of greatest interest in this study were density, viscosity, color, and pH. Preliminary studies indicated that temperature and time of heating had a marked effect on the color and viscosity of PVM/MA-HA dispersions. Further work also disclosed some batch-to-batch variation in copolymer composition which necessitated adjustments in temperature to produce a satisfactory dispersion for coating preparation. For production application, therefore, rigid quality control was exercised. The present report is concerned primarily with only one aspect of the study—the effect of temperature on the properties of PVM/MA-HA dispersions.

EXPERIMENTAL

The PVM/MA-HA used in this investigation consisted of a very light, creamy-white, hygroscopic powder which was obtained from General Aniline and Film Corp. and designated as Type 10. The rate at which the copolymer was dispersed depended on the temperature and the time of heating. At low temperatures, incomplete dispersion resulted and solutions of high viscosity were obtained, which often contained very small particles of gelatinous material. The presence of the latter usually caused slight imperfections in the dry coating. Dispersion at higher temperatures, on the other hand, resulted in solutions of low viscosity and greater clarity. However, prolonged heating at elevated temperatures resulted in a darkening of the solution.

Typical behavior of PVM/MA-HA dispersions prepared at different temperatures and heated for varying periods of time is illustrated in the following experiments.

Changes in Properties with Time for the Same Batch of Copolymer Prepared and Held at Various Temperatures. Two-gallon quantities of PVM/MA-HA, Type 10, Lot 176-1, containing 5.4 ounces of copolymer per gallon, were prepared with vigorous agitation at temperatures of 110°, 130°, 150°, and 170° F. Each preparation was divided into two portions in order to study changes in properties with time. One, the control, was reserved for analysis when cooled to room temperature, while the other was subjected to prolonged agitation at the temperature of preparation. Viscosity determinations were made with the Zahn G2 viscometer (*4*) and reported as flow time in seconds. Viscosity curves, together with notations on appearance of these dispersions, agitated for varying periods of time at their temperature of preparation, are shown in Figure 1.

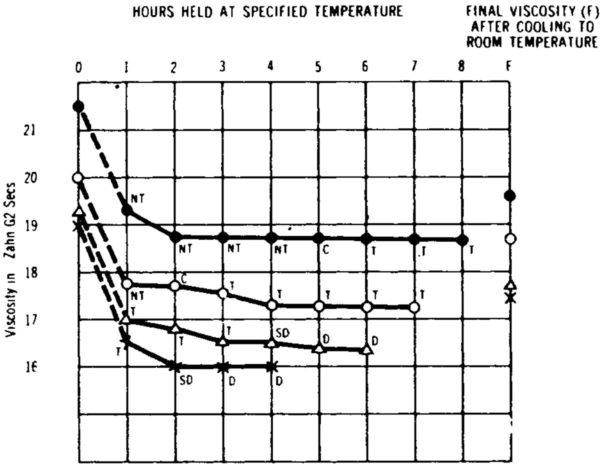


Figure 1. Viscosity and appearance with time for the same batch of PVM/MA-HA copolymer dispersed and heated at different temperatures for varying periods of time

● 110°F.
○ 130°F.
△ 150°F.
× 170°F.
--- Drop from room temperature viscosity
NT. Not transparent (light and opaque)
T. Transparent
C. Clearing
SD. Darkening
D. Dark

With the exception of the final viscosity, *F* , and the viscosity reported at zero hours, all determinations were made at the specified temperature. Room temperature viscosities were made at 72° ± 1.0°F. Analyses of the dispersions after cooling to room temperature are shown in Table I. These include observations of appearance as well as determinations of density, pH, and viscosity.

On the basis of these data (Figure 1 and Table I) it appears that a given batch of copolymer, when dispersed at concentrations of 5.4 ounces per gallon, yielded solutions the viscosity of which varied markedly with temperature of preparation and slightly with time of heating. The appearance of the solutions, on the other hand, varied both with temperature of preparation and with time of heating.

In general, dispersions prepared at lower temperatures yielded the highest viscosities and were somewhat opaque in appearance. Increased transparency accompanied by some lowering of viscosity could be obtained by heating at an effective low temperature for a longer time.

Dispersions prepared at slightly elevated temperatures and agitated for a short period of time resulted in trans-

Table I. Tests at Room Temperature on Similar Copolymer Dispersions Prepared at Different Temperatures

Preparation Temp., °F.	Samples Taken Immediately after Preparation				Samples Taken after Holding Designated Hours at Preparation Temperature				
	Appearance	°Bé.	pH	Zahn G2 visc., sec.	Hours held	Appearance	°Bé.	pH	Zahn G2 visc., sec.
110	Light and opaque	2.0	6.8	21.4	8	Light and transparent	2.0	7.0	19.6
130	Light and less opaque	2.0	6.8	20.0	7	Light and transparent	2.	6.9	18.8
150	Light and transparent	2.1	7.0	19.2	6	Dark and transparent	2.0	7.2	17.7
170	Very transparent	2.0	6.9	19.0	4	Dark and transparent	2.0	7.15	17.5

parent solutions of slightly lower viscosity. However, continued heating with agitation at elevated temperatures caused discoloration and lowered the viscosity below the optimum required for satisfactory preparation of plate coating solutions. Dispersions made at 170°F. were generally transparent but, on continued heating, the solution darkened and the viscosity dropped below the optimum required.

The densities of the solutions were practically unaffected by changes in temperature or by reasonably prolonged heating, while pH values were increased very slightly by prolonged heating. Partial hydrolysis of the amide group to ammonia may account for a slight rise in pH on prolonged heating. However, the extent to which the amide groups break down was not ascertained.

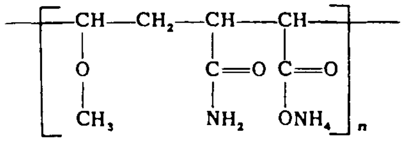
Changes in Viscosity with Increase and Decrease of Temperature of the Same Dispersion Prepared at Different Temperatures. Dispersions of PVM/MA-HA copolymer were further investigated as to behavior when heated from room temperature to 170°F. and cooled back again to room temperature. Figure 2 illustrates the changes in viscosity with temperature of a solution prepared at 110°F., and Figure 3 shows similar changes of a solution prepared at 170°F. The solution prepared at the lower temperature showed a wider spread in viscosity when heated over the same temperature range than that prepared at higher temperature.

Both Figures 2 and 3 show the effect of extending the time of heating on the final viscosity. In both experiments the time of heating was approximately 5 hours and the effect of this is shown in the difference between initial and final viscosities at room temperature. Although data for more concentrated solutions are not included in this report, the temperature-viscosity relationship was similar except that the viscosities were higher.

DISCUSSION

The observed decrease in viscosity of PVM/MA-HA copolymer dispersions with increasing temperature and time of heating indicates a possible degradation of the chain structure by an oxidative mechanism. Because the polymer chains are saturated, the most likely points of attack are the tertiary hydrogen atoms derived from the maleic anhydride portion of the copolymer.

The half amide is prepared from PVM/MA copolymer and may be represented by the following unit structure:



$$\left[-\underset{\substack{|\\ O\\ |\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ C=O\\ |\\ NH_2}}{CH}-\underset{\substack{|\\ C=O\\ |\\ ONH_4}}{CH}-\right]_n$$

The nitrogen content varies between 10.5 and 12.5%, indicating that approximately three fourths of the anhydride groups have been converted to amide and ammonium groups (2).

The PVM/MA copolymer from which the amide is prepared

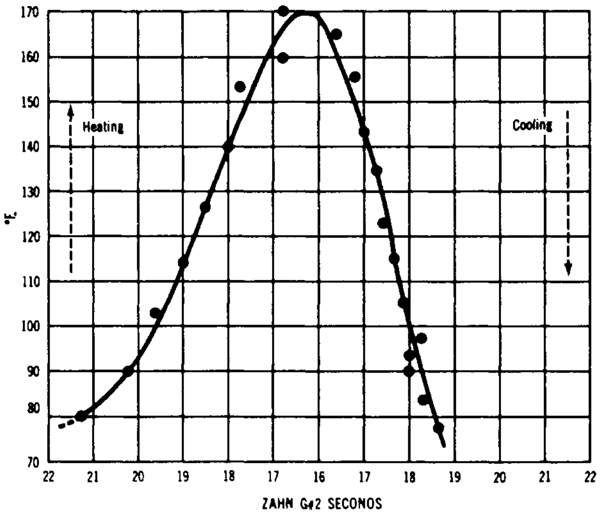
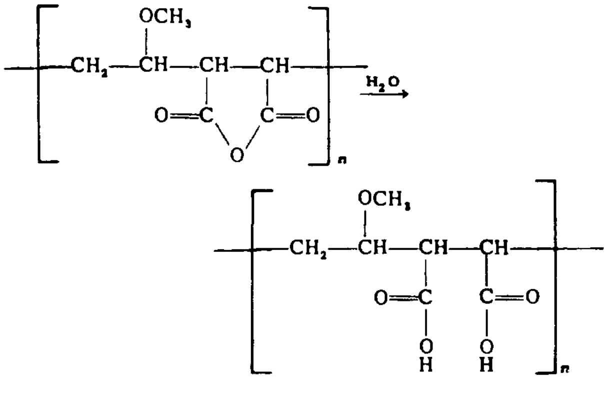


Figure 2. Changes in viscosity with increase and decrease in temperature in a PVM/MA-HA dispersion prepared at 110°F.

consists of linear chains of methyl vinyl ether and maleic anhydride units. When dissolved in water, the copolymer is hydrolyzed to a polymeric acid (3).



A 10% aqueous solution of PVM/MA, heated for 45 minutes at 212°F., yields pH 2.0, indicating the formation of a polymeric acid. Variation in the viscosity of this solution may be brought about by increasing the pH by the addition of sodium hydroxide. For example, the viscosity increases from a minimum at pH 2.0 to a maximum at pH 6.0 and then falls off gradually as the alkalinity is further increased to pH 8.0 (3).

Similarly, the addition of ammonium hydroxide raised the viscosity from 17.5 seconds (Zahn G2) at pH 2.0 to 28 seconds at pH 6.6. Unlike the addition of sodium hydroxide, however, further addition of ammonia, to pH 9.3, increased the viscosity of the solution to 32 seconds. At

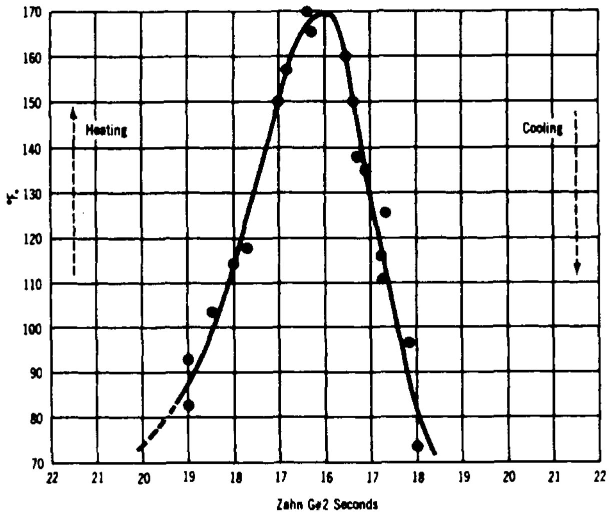


Figure 3. Changes in viscosity with increase and decrease in temperature in a PVM/MA-HA dispersion prepared at 170° F.

this point the solution became slightly more turbid and assumed an amber color (*5*).

No appreciable change in viscosity was observed when PVM/MA copolymer solutions were heated at different temperatures for varying periods of time (*5*). Thus, if the decrease in viscosity, observed in the case of solutions of the half amide, is due to oxidative degradation, it is possible that the reactivity of the tertiary hydrogen atoms is governed in part by the nature of the carboxylate groups. The replacement of carboxyl hydrogens with the amide and/or ammonium groups may favor the formation of hydroperoxides, which in turn readily decompose to bring about chain scission.

Unfortunately, no attempt was made to investigate the fundamental aspects of the observed viscosity behavior. However, the experiments reported were helpful in devising methods for the preparation of improved lithographic plate coating solutions.

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Solubility of Acidic Gases in Aqueous Monoethanolamine

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The solubility behavior of acidic gases in aqueous monoethanolamine (MEA) solution is of particular interest in the proper design and operation of amine-type units for the removal of hydrogen sulfide and carbon dioxide from gaseous systems.

Determinations of the solubility of carbon dioxide in aqueous monoethanolamine solutions have been made by several investigators. Mason and Dodge (*4*) studied the solubility of carbon dioxide in 0.5, 2.0, 5.0, 9.5, and 12.5*N* solutions at temperatures of 0°, 25°, 50°, and 75°C. and at partial pressures of carbon dioxide ranging from about 20 to 750 mm. Reed and Wood (*7*) published a small-scale plot showing the solubility of carbon dioxide in 2.5*N* (15.3 weight %) MEA solutions at temperatures of 100°, 120°, and 140°C., and carbon dioxide partial pressures from 20 to 250 p.s.i.a. These authors did not claim high accuracy for their measurements. Similar data are given by Reed (*6*). Lyudkovskaya and Leibush (*3*) studied the solubility of carbon dioxide in 0.5, 2, and 5*N* MEA solutions at temperatures of 25°, 50°, and 75°C. and carbon dioxide partial pressures from 2.5 to 40 atm. Muhlbauer and Monaghan (*5*) recently reported data on the solubility of carbon dioxide in 2.5*N* MEA solutions at 25° and 100°C. and partial pressures of about 1 to 1000 mm.

Riegger, Tartar, and Lingafelter (*8*) measured the solubility of hydrogen sulfide in 0.6, 1.0, 1.5, 2.0, 3.0, and 5.0 molal solutions of MEA at temperatures of 25°, 45°, and 60°C. and at partial pressures of hydrogen sulfide from 25 to 700 mm. Leibush and Shneerson (*2*) reported the solubility of hydrogen sulfide in 0.93 and 2.5*N* solutions of MEA at temperatures of 15°, 25°, and 50°C. and over a partial pressure range of about 0.01 to 250 mm. Reed (*6*) included a small-scale plot showing the solubility of hydrogen sulfide at 100° and 120°C., with experimental points covering a partial pressure range of about 22 to 53 p.s.i.a. Muhlbauer and Monaghan (*5*) reported values at 25° and 100°C. for partial pressures of about 1 to 950 mm. Atwood, Arnold, and Kindrick (*1*) computed activity coefficients for the system hydrogen sulfide–MEA–water. Limited data at 25°C. on the solubility of mixtures of carbon dioxide and hydrogen sulfide in 15.3 weight % MEA have been obtained by Leibush and Shneerson (*2*). In their experiment, the hydrogen sulfide concentration was held constant at either 0.145 or 0.265 mole per mole of amine while the carbon dioxide concentration was varied from 0.025 to 0.416 mole per mole of amine. Muhlbauer and Monaghan (*5*) published data on the simultaneous solubility of hydrogen sulfide and carbon dioxide in 15.3 weight % MEA at temperatures of 25° and 100°C. Their data were obtained at hydrogen sulfide partial pressures ranging from 1 to 964 mm. and at carbon dioxide pressures from 1 to 1290 mm.

There are considerable differences in the reported values for the solubilities of hydrogen sulfide and carbon dioxide. Data in the low partial pressure, high temperature region are very meager. The data on mixtures of the two acidic gases are also limited in scope and temperature range covered.