

# Amic Acids of Alphamethyl Styrene and Maleic-Anhydride Copolymer as a Dispersing Agent

M. A. SHENOY, KUSUM S. JOSHI

University Department of Chemical Technology, Matunga, Mumbai-19, India

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**ABSTRACT:** Alphamethyl styrene (AMS) and maleic anhydride (MAAn) were copolymerized in 2-butanone using benzoyl peroxide as initiator. Low molecular weight (8000) of alphamethyl styrene-maleic anhydride copolymer was prepared using AMS dimer as a chain-transfer agent. This copolymer was then treated with two different amines, such as dibutylamine and diethanolamine, having different hydrophilicity, to obtain the corresponding amic acids. Application of these amic acids as a dispersing agent to disperse titanium dioxide ( $\text{TiO}_2$ ) in water was studied. The Daniel Flow point method was used to assess the dispersing ability of these amic acids, and diethanolamic acid was found to show the better dispersing property. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 424–428, 2000

**Key words:** alphamethyl styrene; copolymer; maleic anhydride; amic acids; 2-butanone; benzoyl peroxide; dimer; chain-transfer agent; amine; dibutylamine; diethanolamine; hydrophilicity

## INTRODUCTION

The term “dispersion” is used to refer to the process of incorporating a powder into a liquid medium so that final product consists of fine particles distributed throughout the medium.

Many industries involve the process of dispersing solid particles in liquids, such as paint, pigment, resin, textile, paper, and agriculture.<sup>1,2</sup> Therefore, the dispersing process has attracted a wide range of interests in both theoretical studies and practical applications.<sup>3,4</sup>

In order to acquire stable dispersion, a dispersant is usually added to help suspend solid particles in liquid. If the dispersion has not been stabilized, flocculation may occur as a result of clumping together of the particles. The main function of the dispersant is to provide the particles with electrostatic barriers<sup>5</sup> or with steric hindrance<sup>6</sup> to produce a barrier to prevent flocculation.

Surfactants and polymers are usually used as dispersants.<sup>7,8</sup> Due to the ability to provide a high density of charges and an efficient steric hindrance, polymers are widely used as dispersants in various industries. Polymeric dispersants can reduce interactions between particles much more effectively than conventional dispersant can. Particles may be prevented from coming together and flocculating due to the presence of adsorbed layers of polymeric dispersant. The physical interactions of the adsorbed molecules as the particles approach each other act as a barrier to flocculation.

The basic performance of a dispersing agent is greatly affected by its chemical composition.<sup>9</sup> To maximize the electrostatic repulsion between particles, a high concentration of ionic groupings such as carboxylic acid or sulphonic acid is usually introduced in to the polymeric system. Sodium salts of polyacrylic acids and styrene-maleic anhydride copolymer have been widely used as dispersant for inorganic pigments such as titanium dioxide ( $\text{TiO}_2$ ).

Also, performance of a dispersant is affected by its molecular weight and its dispersity.<sup>9</sup> Alpha-

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Correspondence to: M. A. Shenoy.

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methyl styrene and maleic-anhydride were copolymerized in presence of alphas-methyl styrene dimer as a chain-transfer agent to obtain low molecular weight copolymer with low dispersity. This copolymer was then reacted with different amines to obtain amic acids of the copolymer. Dibutylamine and diethanolamine were used to open the anhydride ring. The dispersing abilities of these amic acids for dispersing titanium dioxide in water were studied and correlated with their structures.

## EXPERIMENTAL

### Materials

Alphas-methyl styrene (AMS) (M/s Herdillia Chemicals Ltd.), Maleic-anhydride (MAn) (s.d Fine Chemicals), benzoyl peroxide (s.d Fine Chemicals), 2-butanone (s.d Fine Chemicals), petroleum ether (s.d Fine Chemicals), dibutylamine (s.d Fine Chemicals), diethanolamine (s.d Fine Chemicals), and acetone (s.d Fine Chemicals) used were of analytical grade and used as received. Titanium dioxide (TiO<sub>2</sub>) (SCM Chemicals, USA) used as received. The water used in the experiments was distilled and deionized.

### Synthesis and Characterization of the Copolymer

Copolymerization of AMS and MAn was carried out in a four-necked glass reactor, equipped with a stirring arrangement at the center to agitate the reaction mixture. The reactor was also equipped with nitrogen purger and the water condenser.

The reaction kettle was charged with 23.6 g of AMS (0.2 mole), 19.6 g of MAn (0.2 mole), and 40 g of 2-butanone containing 0.3% w/w of the benzoyl peroxide as an initiator and alphas-methyl styrene dimer (0.6 g) as a chain-transfer agent. Then contents of the flask were flushed with oxygen-free nitrogen for half an hour and the copolymerization was carried out in nitrogenous atmosphere.

Reaction temperature was increased slowly to 60°C and maintained at this temperature with the help of a thermostat. After completion of the reaction, the copolymer was precipitated out by pouring the reaction mixture in petroleum ether with constant stirring. The copolymer was then filtered and thoroughly washed with distilled water to remove traces of unreacted maleic anhy-

dride and solvent. Finally, it was filtered and dried in the oven at 80°C for 12 h.

### Synthesis of Sodium Salts of Amic Acids

In a three-necked flask, 20 g of the AMS-MAn copolymer in 100 g of 2-butanone was heated to 50°C and then the appropriate amount of dibutylamine or diethanolamine was added. The reaction was continued until almost half the acid groups were converted to amide groups. Then sodium hydroxide solution was added to the reaction mixture to obtain the sodium salt of the amic acids. Copolymers were then precipitated in acetone, filtered, and washed. Finally, they were dried at 70°C for 24 h.

### Evaluation of the Dispersing Ability of the Amic Acids

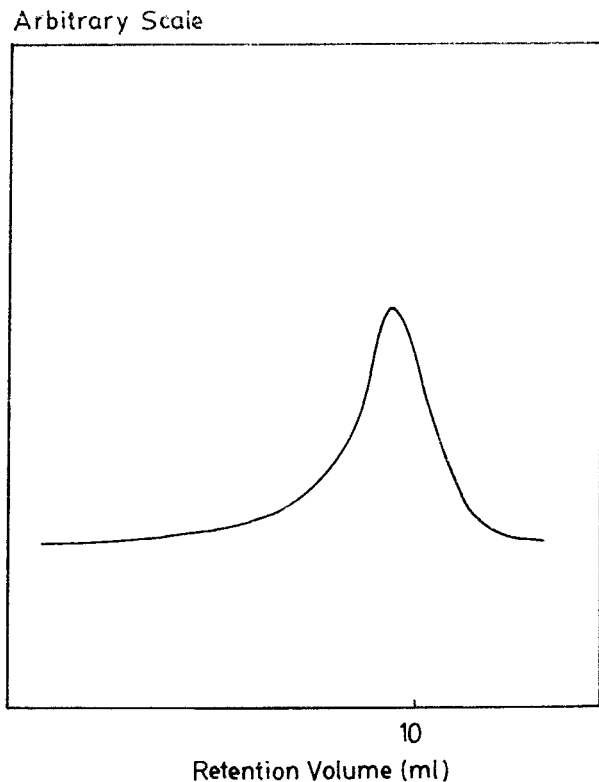
The Daniel Flow point method was used for assessing the dispersing efficiency of the amic acids of the AMS-MAn copolymer.

Various concentrations—viz. 0.5–5%—of sodium salts of amic acids were prepared in distilled water. These aqueous solutions of amic acids were then taken in a burette and added to 20 g of TiO<sub>2</sub> dropwise with constant stirring and rubbing with a glass rod until a heavy and smooth paste was obtained. Then some more aqueous solution of amic acid was added gradually to the paste until the mass achieves a consistency at which it could be stirred without significant resistance. A characteristic end point was reached when a thin and even film material remained on the glass rod and the last drop fell at an interval of 1–2 s. These drops appear to break with an elastic snap back.

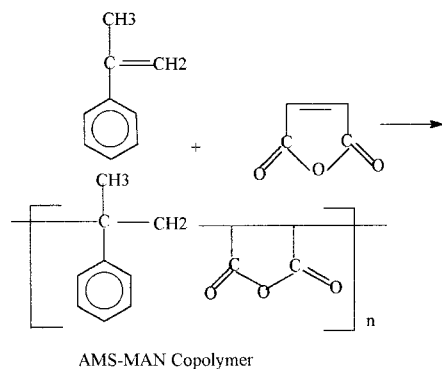
Then a graph of the amount of each aqueous solution of amic acid required to reach the above end point against the concentration of the dispersing agent was plotted to give a “U”-shaped curve, having a minimum that corresponds to the optimum composition for efficient dispersion.

The molecular weights of the copolymer was determined using gel permeation chromatography (GPC), on a Jasco Intelligent Series GPC, with an RI detector 930. The measurements were carried out at 30°C using tetrahydrofuran as a mobile phase. Figure 1 shows the gel permeation chromatograph of the AMS-MAn copolymer. The instrument was calibrated using polystyrene standards. Analysis was carried out at constant flow rate of 1 mL/min.

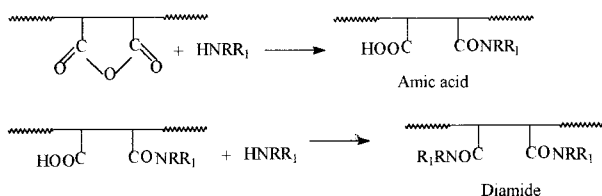
The reactions can be represented as follows:



**Figure 1** Gel permeation chromatography of the AMS-MAN copolymer.

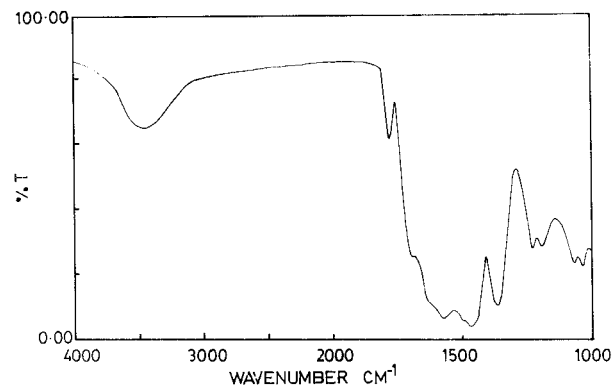


#### Amidification of AMS-MAN Copolymer.



## RESULTS AND DISCUSSION

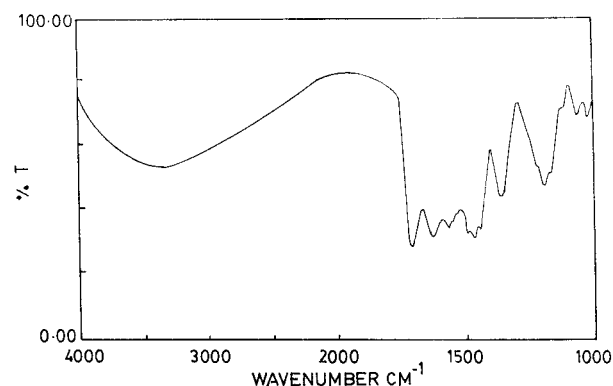
In the present study the AMS-MAN copolymer was synthesized in 2-butanone using the chain-



**Figure 2** IR spectrum of dibutylamide of the AMS-MAN copolymer.

transfer agent. This technique yielded an alternate copolymer with MW 8000 and polydispersity 1.497 as determined by GPC. The alternate copolymer was obtained due to very low monomer reactivity ratios. A copolymer with the above features was found to be effective for dispersing  $\text{TiO}_2$  in aqueous solution. This low molecular weight copolymer was then used to prepare derivatives of alkylamines, i.e., amic acids that can be used as dispersants. Dibutylamine and diethanolamine was used to open the anhydride ring of the maleic anhydride in the copolymer. These two amines were selected in such a way that both of them have almost same carbon chain lengths but different hydrophobicity.

IR spectra show (Figures 2 and 3) N—H stretching bands at 3439.8 and 3416.2  $\text{cm}^{-1}$  for dibutylamic acid and diethanolamic acid, respectively. Also, C=O stretching bands were found at 1572.5 and 1632.1  $\text{cm}^{-1}$  for dibutylamic acid and diethanolamic acid, respectively.



**Figure 3** IR spectrum of diethanolamide of the AMS-MAN copolymer.

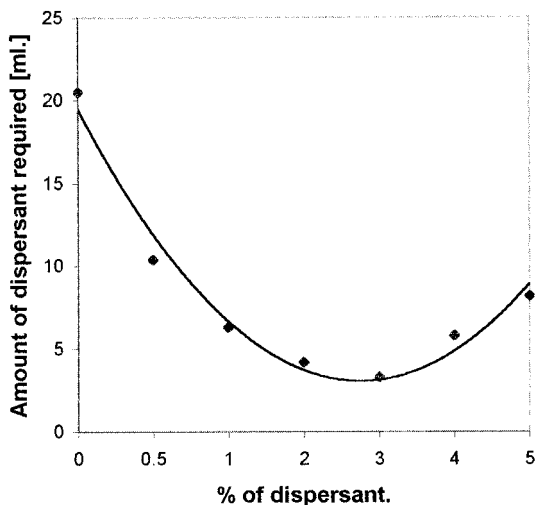


Figure 4 Daniel Flow for dibutylamic acid.

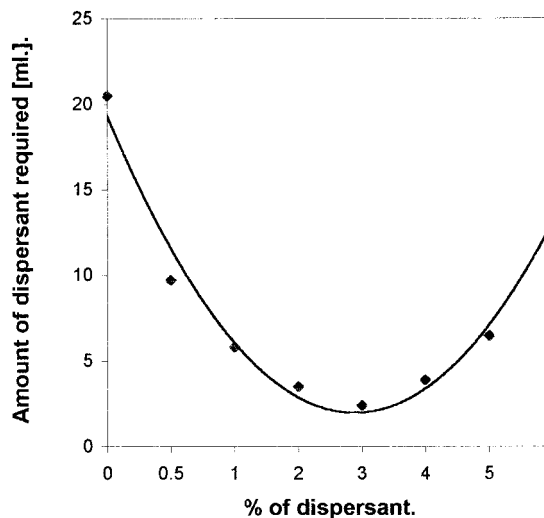


Figure 5 Daniel Flow for diethanolamic acid.

As discussed in the experimental section, sodium salts of these amic acids were used as dispersing medium (binder in this system) to disperse the 20 g of TiO<sub>2</sub>. Different concentrations of amic acids from 0.5 to 5% were prepared in distilled water. Since in the present system an inorganic pigment with a slightly reactive surface (TiO<sub>2</sub>) was used, it was possible to form an ion-pair bond between a charged site on the particle surface and an oppositely charged atom or functional group on the dispersant, i.e., carboxylic acid groups of the amic acids. This ion-pair bond helped the dispersant to anchor on the pigment surface effectively, and further, they were prevented from coming close to each other by electrical repulsion as well as steric hindrance.

As shown in Figures 4 and 5, the amount of aqueous solution (acting as binder in this system) required to disperse the pigment in absence of dispersant was as high as 20.5 mL, which drops down to 10.4 mL in the presence of 0.5% dibutylamic acid and to 9.7 mL in the presence of diethanolamic acid. As the concentration of dispersant increased, the amount of binder required to disperse the pigment decreased. Then it passed through a minimum viscosity point, after which the demand for binder increased and a minimum was obtained at the concentration of 3% of the dispersant, and this was the optimum concentration.

For both the amic acids, the optimum dispersant concentration was found to be 3%. However, as shown in Figure 6, in the case of diethanolamic acid it was observed that the amount of binder

required for the same amount of pigment was less than that of dibutyl amic acid, suggesting that diethanol amic acid has better dispersing efficiency. This behavior is attributed to the more hydrophilic nature of the diethanolamic acid. These diethanolamic acids get adsorbed on the pigment surface by anchoring through the carboxyl group and the overall surface of the pigment particle can be visualized as hydrophilic in nature due to presence of hydroxyl group directing outside the surface. Thus the overall pigment surface becomes hydrophilic in nature and hence it is easier to disperse such a pigment particle in a hydrophilic aqueous medium, whereas in the case

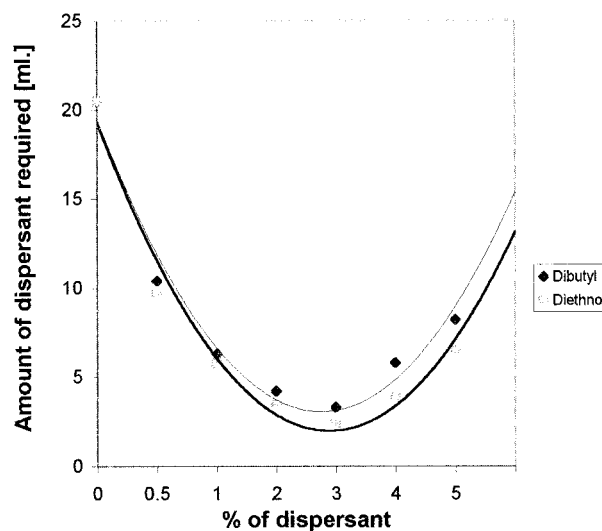


Figure 6 Daniel Flow for different amic acids.

of dibutylamic acids the overall pigment could be hydrophobic in nature due to the presence of the butyl group directed outside the pigment surface and hence less effective.

## CONCLUSION

The AMS-MAn copolymer of low molecular weight and low dispersity could be used to prepare amic acids by reacting with alkylamines. These amic acids were found to be effective for dispersing  $\text{TiO}_2$  in aqueous solutions. Dibutylamine and diethanolamine both were effective dispersants, but diethanolamine was found to be a better dispersing agent due to its better hydrophilicity.

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