

Preparation of *sec*-Butanol-Modified Melamine-Formaldehyde Resin Varnish

YOSHIAKI MOTOYAMA and KEIICHI UCHIDA, *Research Laboratory, Totsuka Factory, Nippon Oils & Fats Co., Ltd., Totsuka-ku, Yokohama, Japan*

Synopsis

sec-Butanol was employed to prepare etherified methylol-melamine resins to be used in the coatings industry as crosslinking agents. Difficulties associated with slow rate of etherification as compared to the rate of polycondensation of methylol-melamine were overcome by finding the determining factors which controlled the two competitive reactions independently. Attempts were made to interpret the effects of various factors from a mechanistic point of view.

Introduction

The melamine resins which are widely used in the coatings industry as crosslinking agents are the so-called oligomers of methylol-melamine properly etherified with such alcohols as *n*- or isobutanol. Etherification of the methylol group is necessary to make the product resins compatible with other film-forming polymers (oligomers), and to give sufficient storage stability. It is well known that the compatibility depends also on the degree of polycondensation. In general the higher the degree of polycondensation, the poorer the compatibility.

The two reactions, polycondensation and etherification, proceed under similar conditions, and thus it becomes increasingly difficult to prepare sufficiently etherified melamine-formaldehyde resins of sufficiently low degree of polycondensation as the alcohol becomes less reactive.

Mineral spirits tolerance (MST) (see Experimental Section) and viscosity of resin solutions (50-60%) are universally employed as rough measures of the extent of etherification and the degree of polycondensation, respectively. The MST of the *n*- or isobutanol-modified resin solutions must be over ca. 3 and the viscosity less than ca. 50 poises for the product to be useful for the coatings industry.

The purpose of this work was to prepare *sec*-butanol-modified melamine-formaldehyde resins with a MST over ca. 5 and a viscosity less than ca. 5 poises. The experimental work aimed at determining the factors involved so that the two competitive reactions can be controlled independently is described, and the results are interpreted from a mechanistic viewpoint. A typical preparative method based on these results is also presented.

Experimental

A three-necked flask fitted with a stirrer and a condenser was charged with formaldehyde (as 37% formalin, or as a mixture of paraformaldehyde, water, and methanol) and *sec*-butanol, and was made alkaline with concentrated sodium hydroxide solution to pH 8–9. The solution was then heated to its boiling temperature (90–92°C.) and was kept at this temperature for 60 min. before melamine was added; after another 60 min. the solution was acidified with formic acid to pH 4.0–5.4. The solution was kept refluxing for a specified period, and the excess reactants were then removed by distillation under reduced pressure until a solids content of about 65% was obtained. *sec*-Butanol was finally added to adjust the solids content to 50%.

The mineral spirits tolerance (MST) of the product resin solutions were calculated from the equation:

$$\text{MST} = \frac{\text{volume (ml.) of mineral spirits required to make solution turbid}}{\text{weight (g.) of resin solution}}$$

The viscosity of the resin solutions was determined at 20°C. with a Brookfield viscometer.

Results and Discussion

There are a number of reports concerning the kinetics and mechanisms of the addition stage in the melamine–formaldehyde reaction,^{1,2} of the polycondensation stage of methylol–melamine,^{3,4} and of the polycondensation of butylated methylol–melamine.^{5,6} To our knowledge, there is only one paper on the attempted preparation of *sec*-butanol-modified melamine–formaldehyde resin.⁷ It is, however, doubtful whether the resin prepared by the procedure described in this paper is of any practical use in the coatings industry because of its poor storage stability and poor compatibility; both of which suggest that the etherification has not proceeded sufficiently (MST less than 1.5).⁸

Inoue and Kawai⁹ studied the reaction of trimethylolmelamine in the presence of methanol. The most plausible mechanisms suggested for the two competing reactions are shown in eqs. (1) and (2) for etherification and polycondensation, respectively:



Here MCH_2OH stands for the methylol group of monomeric or polycondensed trimethylol–melamine and MH for the free NH — group carried by a melamine nucleus. A pH of 5.5–6.0 was found best for obtaining a resin with a high degree of etherification. Below pH 5.8 only the polycondensation was accelerated, whereas the etherification was only slightly affected.

Since the addition reaction between melamine and formaldehyde under our reaction conditions has reached its equilibrium position by the time the

system is acidified (as confirmed by following the change in unreacted formaldehyde concentration as a function of time⁸), the main reactions that proceed as the system is acidified are polycondensation and etherification. The equilibrium of the addition stage will not be affected greatly by the change in acidity.²

Let us suppose that the overall processes of these two reactions were mechanistically similar to those proposed by Inoue and Kawai,⁹ and let us suppose further that they are S_N2 processes. It would follow that the most plausible mechanisms in the acidic medium are the initial protonation (rapid) on the oxygen atom of a methylol group [eq. (4)], which is followed by the rate-determining displacement of water molecule by the nucleophiles, *sec*-BuOH or the free NH— group [eqs. (5) and (6)].



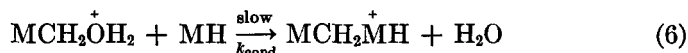
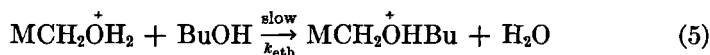
with

$$K_{\text{eq}}^1 = [\text{MCH}_2\text{OH}]/[\text{MH}][\text{CH}_2\text{O}]$$



with

$$K_{\text{eq}}^2 = [\text{MCH}_2\overset{+}{\text{O}}\text{H}_2][\text{HCOO}^-]/[\text{MCH}_2\text{OH}][\text{HCOOH}]$$



The rate expressions for this model are given by eq. (9) for the etherification

$$V_{\text{eth}} = k_{\text{eth}}K_{\text{eq}}^2[\text{MCH}_2\text{OH}][\text{sec-BuOH}](\text{[HCOOH]}/\text{[HCOO}^-]) \quad (9)$$

and by eq. (10) for the polycondensation.

$$V_{\text{cond}} = K_{\text{cond}}K_{\text{eq}}^2[\text{MCH}_2\text{OH}][\text{MH}](\text{[HCOOH]}/\text{[HCOO}^-]) \quad (10)$$

Here K_{eq}^1 and K_{eq}^2 are the equilibrium constants for eqs. (3) and (4), respectively; k_{eth} and k_{cond} are the specific rate constants for the rate-determining steps, eqs. (5) and (6).

From eqs. (3), (9), and (10), one obtains the relationship,

$$V_{\text{eth}}/V_{\text{cond}} = (k_{\text{eth}}/k_{\text{cond}})K_{\text{eq}}^1[\text{sec-BuOH}][\text{[CH}_2\text{O]}/\text{[MCH}_2\text{OH]}] \quad (11)$$

where $[\text{MCH}_2\text{OH}]$ can be regarded as independent of the formaldehyde/melamine ratio, at least as a first approximation, since the range of this ratio studied is narrow (5.0–6.0), that is,

$$V_{\text{eth}}/V_{\text{cond}} \propto [\text{sec-BuOH}][\text{CH}_2\text{O}] \quad (12)$$

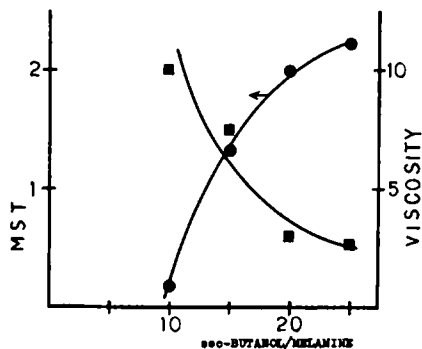


Fig. 1. Plots of (●) MST and (■) viscosity in poises as a function of *sec*-butanol, melamine ratio; reaction time, 150 min.; formaldehyde/melamine, 6 (formalin, H₂O/melamine = 14.5); pH 4.3.

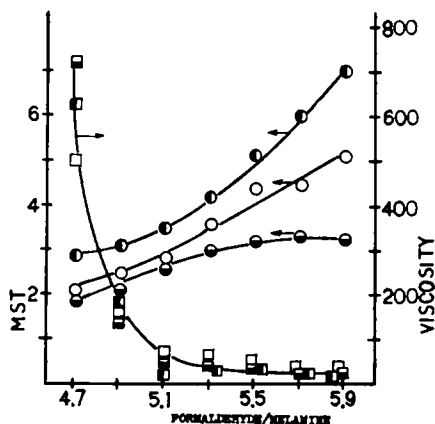


Fig. 2. Plots of (●, ○, □) MST and (■, □, □) viscosity in poises as a function of formaldehyde/melamine ratio: (●, ■) water/melamine 13.3 (formalin); (○, □) water/melamine 8.9 (80% paraformaldehyde); (○, □) water/melamine 13.3 (80% paraformaldehyde). Reaction time, 120 min.; *sec*-butanol/melamine, 20; H₂O/melamine, 8.9 or 13.3; pH 4.3.

This final approximation suggests that the larger the product, [*sec*-BuOH]-[CH₂O], the greater the extent of etherification and the lower the degree of polycondensation.

In deriving eq. (12), distribution of the reactivities of various methylol groups and free NH—groups, and the possible gradual changes of their reactivities with the degree of polycondensation are not considered. Yet it is of interest to find out to what extent eq. (12) would hold by determining the molecular weights of product resins and the number of moles of *sec*-butanol reacted.¹⁰ In the course of this study the authors, however, did not determine these characteristics; instead only the MST and the viscosity of concentrated resin solutions were determined as rough measures of the extent of etherification and the degree of polycondensation, respectively.

TABLE I
 Effects of Methanol and Water^a

H ₂ O/melamine (mole ratio)	CH ₃ OH/ melamine (mole ratio)	pH	Clear point ^b	MST
14.5	0	5.2	15 min.	1.7, 1.6
	0	4.2	15 min.	2.0, 1.9
	1.7	5.2	15 min.	1.0, 1.2
	1.7	4.2	15 min.	2.0, 2.0
	3.4	5.2	15 min.	1.5, 1.6
	3.4	4.2	15 min.	1.5, 1.5
6.5	0	5.2	>24 hr.	°
	0	4.2	15 min.	5.2, 5.0
	1.7	5.2	15 min.	2.6, 2.6
	1.7	4.2	15 min.	5.9, 5.8
	3.4	5.2	15 min.	2.3, 2.2
	3.4	4.2	15 min.	5.9, 5.6
2.5	0	5.2	>24 hr.	°
	0	4.2	>24 hr.	°
	1.7	5.2	12 hr.	6.9, 6.2
	1.7	4.2	40 min.	18, 15
	3.4	5.2	7 hr.	4.1, 4.6
	3.4	4.2	5 hr.	3.2, 3.1

^a *sec*-BuOH/melamine = 20. The solution is refluxed for 3 hr. after it is acidified. When it took more than 3 hr. for the solution to become clear, it was kept refluxing for 10 min. over the clear point.

^b Time required to obtain a clear solution after the system is acidified.

^c Reaction discontinued.

If this contention is accepted, it can be seen from Figures 1 and 2 that eq. (12) appears to hold at least qualitatively. The MST or the extent of etherification increases, while the viscosity or the degree of polycondensation decreases if [*sec*-BuOH] is increased at constant [CH₂O]. Exactly the same trend appears if [CH₂O] is increased with [*sec*-BuOH] constant.

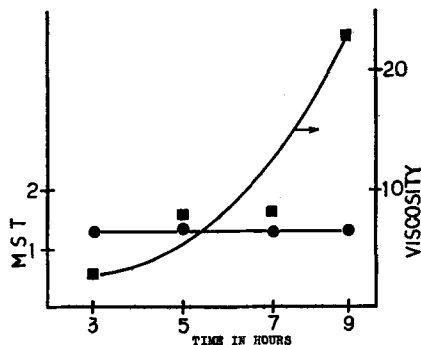


Fig. 3. Plots of (●) MST and (■) viscosity in poises as a function of reaction time (refluxing period since the system is acidified until heating is arrested); *sec*-butanol/melamine, 20; formaldehyde/melamine, 5.5 (formalin, H₂O/melamine = 14.5); pH 5.3.

The effects of methanol present in the system on the MST are probably to be attributed to its much higher reactivity compared with that of *sec*-butanol. It is reported that methanol reacts with methylol-melamine even in slightly basic medium.¹¹

Let us now recall that in deriving eq. (12) the possible reversibilities of the steps (5) and (6) were not taken into account. As shown in Figure 2 and Table I, the effects of water are such that the etherification reaction in the reverse direction is promoted while the polycondensation is not. The effects of reaction time as shown in Figure 3 are also in accord with this assumption. The etherification reaction has reached its equilibrium within 3 hr.; thereafter only the polycondensation appears to proceed.

Preparative Method for *sec*-Butanol-Modified Methylol-Melamine Resin with MST 9

From the work described in the previous part, it has become clear that the two reactions, polycondensation and etherification, can be controlled either independently of each other or in the opposite directions, by four factors as summarized in the following. (1) Water present in the system does not affect the polycondensation reaction but reduces the extent of etherification. (2) Prolonged reaction time does not affect the extent of etherification but promotes the polycondensation reaction. (3) An increase in the formaldehyde/melamine charge ratio results in a decrease in the degree of polycondensation and an increase in the extent of etherification. (4) An increase in the *sec*-BuOH/melamine charge ratio also results in a decrease in the degree of polycondensation and an increase in the extent of etherification.

The preparative method employed as described in the Experimental Section was so designed as to make the interpretation of data clear-cut. The mixtures of melamine, formaldehyde, water, and *sec*-butanol were refluxed under basic conditions long enough for the addition stage [eq. (3)] to reach an equilibrium point before the mixtures were acidified in order to start the polycondensation and etherification. If the mixtures were acidified right from the start, all the three reactions would have proceeded in parallel, making the interpretation of data difficult.

For the practical purpose of preparation, however, it is probably wise to start the reaction in slightly acidic condition (pH 6-7) before the reaction mixture is made more acidic (pH 4-4.5). In general, the MST is higher and the viscosity lower if the reactions are initiated in this way.⁸ A suggested practical method of preparing a resin with MST 9 and viscosity 2-3 poises is as follows.

A mixture of *sec*-butanol (1480 g., 20 moles), 80% paraformaldehyde (218 g., 5.8 moles), and water (0-40 g., as required to make methylol-melamine soluble) is heated to boiling and acidified if necessary with formic acid to pH 6. Melamine (126 g., 1 mole) is then added, acidified to pH 4.2-4.4 with formic acid after a few minutes, and kept refluxing. A clear solution should be obtained 1-2 hr. after the addition of melamine. The

azeotropic mixture may now be removed from the system. The temperature of the azeotrope rises gradually from 90°C., and when it reaches 100°C. heating is discontinued. The product is filtered while it is still hot and *sec*-butanol is added until the solids content reaches 60%. The MST is around 9 and the viscosity 2-3 poises.

References

1. M. Okano and Y. Ogata, *J. Am. Chem. Soc.*, **74**, 5728 (1952).
2. M. Gorden, A. Haliwell, and T. Wilson, *J. Appl. Polymer Sci.*, **10**, 1153 (1966).
3. I. Koeda, *Kogyo Kagaku Zasshi*, **60**, 1567 (1957).
4. N. Yoshimi, M. Yamao, T. Kawakita, and M. Tanaka, *Kogyo Kagaku Zasshi*, **66**, 279 (1963).
5. J. H. Lady, R. E. Adams, and I. Kesse, *J. Appl. Polymer Sci.*, **3**, 65 (1960).
6. T. Ishikawa, K. Akiyama, and T. Wada, *Colour Material*, **34**, 171 (1960).
7. R. Seabone, *J. Oil Colour Chemists Assoc.*, **38**, 345 (1955).
8. Y. Motoyama, unpublished results.
9. M. Inoue and M. Kawai, *Nagoyashi Kogyo Kenkyujo Hokoku*, **14**, 25 (1966).
10. T. Miyauchi, *Kobunshi Kagaku*, **20**, 42 (1963).
11. I. Koeda, *Nippon Kagaku Zasshi*, **75**, 1266 (1954).

Résumé

Le butanol secondaire a été employé pour préparer des résines méthylolmélamine suffisamment éthérisées afin d'être utilisées pour l'industrie de revêtement comme agent de pontage. Des difficultés associées à des vitesses lentes d'éthérisation comparées à la vitesse de poly-condensation du méthylol-mélamine ont été surmontées en déterminant les facteurs qui contrôlent les deux réactions compétitives indépendantes. Des essais ont été faits pour interpréter des effets des divers facteurs d'un point de vue mécanistique.

Zusammenfassung

Sek-Butanol wurde zur Darstellung genügend stark verätherter Methylol-Melaminharze verwendet, die als Vernetzungsmittel für industrielle Überzüge in Frage kommen. Die durch die im Vergleich zur Geschwindigkeit der Methylol-Melaminpolykondensation geringe Verätherungsgeschwindigkeit bedingten Schwierigkeiten konnten durch Auffindung der für die unabhängige Kontrolle der beiden kompetitiven Reaktionen bestimmenden Faktoren überwunden werden. Eine Interpretation der Einflüsse verschiedener Faktoren von einem mechanistischen Gesichtspunkt aus wurde versucht.

Received October 7, 1966

Revised November 22, 1966

Prod. No. 1534