

# Novel Oxidatively Drying Urea Resin. II. Surface Coating Properties of *N,N'*-Bis(methoxymethyl) Urea-Based Air-Drying Resins

HANNU TOIVONEN, *Kemira Oy, Espoo research Centre, SF 02270 Espoo 27, Finland*

## Synopsis

The surface coating properties of the air-drying urea resins prepared by polycondensating *N,N'*-bis(methoxymethyl) urea (BMMU) with trimethylolpropane diallylether (TMPDA) and 2-ethylhexanol (2EH) were studied. It was found that the thinnability of the ethanolic resin solutions with water decreased with increasing molecular weight and the degree of modification of the resins with TMPDA and 2EH. The viscosity of the ethanolic resin solutions increased with the molecular weight but was independent on the resin's degree of modification. The drying performance was improved with increasing molecular weight and decreasing modification with 2EH. The hardness of the paint films was proportional to the modification of the resins with TMPDA and the molecular weight. 2EH led to the plasticization of the coatings. The water resistance of the paint films was improved with increasing modification with 2EH and molecular weight of the resin. The analysis of the elastic properties of the hardened films was not possible due to the scatter of the experimental data. The comparison of the amino resin paints to some commercial paint products indicated that BMMU-based resins having good drying performance and adequate water resistance at the same time can be prepared. Neutral ethanolic and aqueous ethanolic resin solutions were found to have a good storage stability as determined by following the viscosities of the solutions and the hydrolysis resistance of the resins.

## INTRODUCTION

In the preceding paper,<sup>1</sup> the properties of the allylated amino resins presented in the literature were treated. The film-forming properties of these autooxidatively drying resins have generally been reported to be poor. We also discussed an unconventional method of preparing alkylated urea resins using *N,N'*-bis(alkoxymethyl) ureas as a raw material and showed that allylated resins with good drying properties can be produced with an analog procedure by copolycondensating *N,N'*-bis(methoxymethyl) urea (BMMU) with an alcohol containing allyl ether groups. In this report these new type of air-drying urea resins are presented in further detail.

## EFFECT OF MONOMERIC COMPOSITION AND MOLECULAR WEIGHT ON PROPERTIES OF BMMU-BASED RESINS

### Experimental Design, Testing and Treating of Results

A series of BMMU-based resins modified with trimethylolpropane diallylether (TMPDA) and 2-ethylhexanol (2EH) was prepared by varying the ratios of the modifying monomers to BMMU and the molecular weights of the resins. The experimentation was started by following 2<sup>3</sup>-factorial design (Table I). When

TABLE I  
Coding of Variables

Variable	Symbol	Levels			
		+1		-1	
		(w/w)	(eq/eq) <sup>a</sup>	(w/w)	eq/eq) <sup>a</sup>
TMPDA/BMMU	X1	0.629	0.20	0.315	0.10
2EH/BMMU	X2	0.709	0.40	0.177	0.10
$\bar{M}_n$	X3	1100		500	

<sup>a</sup> Calc.: hydroxyl groups (mol)/methoxyl groups (mol).

the linear models were found insufficient, the design was expanded to a Box design<sup>2</sup> (Table II). Because of too large steps between the lower and upper levels of X2 and X3 chosen for the factorial design at the beginning, some modifications in the star point levels had to be made. The lower level of X2 was raised to move the real value of the variable above zero. Poor drying of the resins with a low molecular weight and a high 2EH content led to the changes also in the treatments of 15 and 16. The levels of X1 and X2 could be fixed exactly in every experiment to correspond the designed values whereas the real value of X3 could not be controlled in advance. To get the values of X3 nearer to the design, some of the polymerizations were repeated. Due to the replicates of the experiments, the information from the region of the experimentation increased to such an extent that some of the center points in the box design were dropped out.

The resins were analyzed for their number average molecular weights, thinabilities with water, solution viscosities, and drying rates (Table III). The surface coating properties of the resins were tested as paint films (Table IV). Resins no. 5 and no. 11 were omitted from the paint tests because of their poor drying properties.

TABLE II  
Experimental Design and Realized Experiments

Resin	Coded design <sup>a</sup>			Real values of X3	
	X1	X2	X3	Designed	Measured
1	+1	+1	+1	500	800
2	+1	+1	+1	500	723
3	-1	-1	+1	1100	1035
4	-1	-1	+1	1100	1533
5	-1	+1	-1	500	492
6	-1	+1	+1	1100	1078
7	+1	-1	-1	500	904
8	+1	-1	+1	1100	1526
9	+1	+1	-1	500	421
10	+1	+1	+1	1100	1060
11	-1.68	0	0	900	1019
12	-1.68	0	0	900	1625
13	+1.68	0	0	900	790
14	0	-1.23 (-1.68)	0	900	1061
15	0	+1.00 (+1.68)	0	900	1098
16	0	0	-1.00 (-1.68)	600	625
17	0	0	+1.68	1387	1418
18	0	0	0	900	632
19	0	0	0	900	1019

<sup>a</sup> When the level used differs from the Box design for three variables with six center points<sup>2</sup>, the value according to Box is given in parenthesis.

TABLE III  
Properties of Resins

Resin	Thinnability with water (%)	Solution viscosity (mL/g)	Drying time (h)
1	54.1	0.245	15.5
2	50.4	0.406	11.5
3	47.0	0.488	6.5
4	42.0	0.542	3.5
5	39.0	0.047	>20
6	20.6	0.400	19
7	38.5	0.321	8
8	33.0	0.575	5
9	23.9	0.207	17
10	14.6	0.348	8
11	39.0	0.274	>20
12	33.9	0.428	11
13	39.0	0.127	15.5
14	45.5	0.429	5
15	12.3	0.508	7.5
16	40.0	0.165	19.5
17	25.3	0.422	6.5
18	40.4	0.126	17.5
19	28.1	0.330	9

The results were treated by fitting quadratic models to the experimental data by regression analysis using a computer and a stepwise multiple linear regression program. Only statistically significant variables were included in the final regression solutions (Table V).

TABLE IV  
Properties of BMMU-Based Air-Drying Urea Resin Paints

Resin	Koenig hardness (s)			Bend test (mm)	Water resistance (min)
	1 day	14 days	28 days <sup>a</sup>		
1	22	35	51	6	27
2	48	50	64	11	12
3	47	72	89	1	16
4	76	81	103	>32	16
5 <sup>b</sup>	—	—	—	—	—
6	30	48	57	1	>1200 <sup>c</sup>
7	46	78	95	4	24
8	91	123	150	28	108
9	28	45	53	5	216
10	62	72	96	6	>300 <sup>c</sup>
11 <sup>b</sup>	—	—	—	—	—
12	38	49	62	3	>380 <sup>c</sup>
13	57	66	73	20	60
14	71	85	103	29	8
15	52	65	88	6	326
16	38	51	52	9	155
17	69	82	89	16	257
18	46	51	68	10	150
19	66	84	90	>32	200

<sup>a</sup> The age of paint film.

<sup>b</sup> The drying of resin was not sufficient.

<sup>c</sup> No visible changes on films were observed.

TABLE V  
Results of Stepwise Multiple Linear Regressions

Dependent variable	CL <sup>a</sup>	C <sub>MC</sub> <sup>b</sup>	Regression equation <sup>c</sup>
Thinnability with water	0.99	0.9491	$0.8378E02 - 0.1190E03 \cdot X1 - 0.4574E - 01 \cdot X2 \cdot X3 + 0.1018E03 \cdot X1^2$
Solution viscosity	0.99	0.6839	$-0.5363E - 01 + 0.3858E - 03 \cdot X3$
	0.95	0.7732	$-0.4948 + 0.1283E - 02 \cdot X3 - 0.4150E - 06 \cdot X3^2$
Drying time of resin	0.99	0.4567	$0.2272E02 - 0.1135E - 01 \cdot X3$
	0.95	0.7923	$0.5312E02 - 0.7565E - 01 \cdot X3 + 0.1049E - 01 \cdot X2 \cdot X3 + 0.2742E - 04 \cdot X3^2$
Koenig hardness (28 days)	0.99	0.8502	$37.401992 - 84.458845 \cdot X1 \cdot X2 + 0.127418 \cdot X1 \cdot X3$
Bend test	0.95	0.542	$3.207653 - 0.016597 \cdot X2 \cdot X3 + 0.029620 \cdot X1 \cdot X3$
Water resistance	0.99	0.8647	$-46.613840 + 0.486598 \cdot X2 \cdot X3$

<sup>a</sup> Confidence level.

<sup>b</sup> Coefficient of multiple correlation.

<sup>c</sup> Calculations are based on the real values of the variables, X1 and X2 are in w/w units.

### Results and Discussion

The resins were colorless and almost odorless viscous liquids or solid materials depending on the monomeric composition and molecular weight. The resins dissolved in most polar solvents such as alcohols, esters, and ketones, as well as in aromatic hydrocarbons. Solutions prepared using a water soluble solvent like ethanol could be thinned further with water.

The thinnability of an ethanolic resin solution with water indicates the maximum concentration of water that can be included as a cheap and nontoxic cosolvent in the paint formulations. The regression model of thinnability was in good agreement with the experimental data. Increasing the amounts of a hydrophobic side chains forming monomer 2EH or TMPDA lowered the thinnability of the resin (Fig. 1). The increase of the molecular weight had a parallel effect.

The viscosity of a resin solution determines mostly the amount of solvent needed in paint formulations. To emphasize this, the solution viscosities were described unconventionally as a volume of solvent per unit weight of resin needed to produce a resin solution of a constant viscosity. For a viscosity reference, a typical value for a brushable paint, 700 cP, was chosen. In the regression analysis only molecular weight had statistical significance. According to the model, increasing molecular weight increases the solution viscosity regardless of the modification of the resin.

The drying performance of the resins was improved with increasing molecular weight (Fig. 2). Modification with 2EH slowed down the drying rate. This is clearly a consequence of the plasticization effect of the modification leading to the decrease in the physical drying of the films. The amount of the allyl ether alcohol in the monomer mixtures was not found to have any effect on the drying properties of the products. In the preceding paper<sup>1</sup> we showed, however, that a larger concentration of the allyl ether component in a polymerization mixture

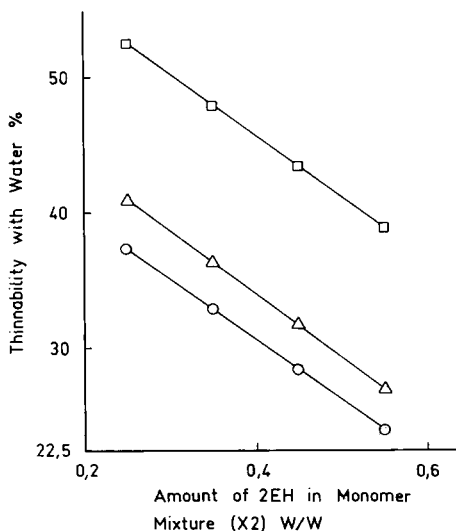


Fig. 1. Effect of 2EH (X2) and TMPDA (X1) concentration in monomer mixture on thinnability of resin solutions with water at constant molecular weight of X3 = 1000 according to regression model. X1 (w/w): (□) 0.2; (Δ) 0.4; (○) 0.6.

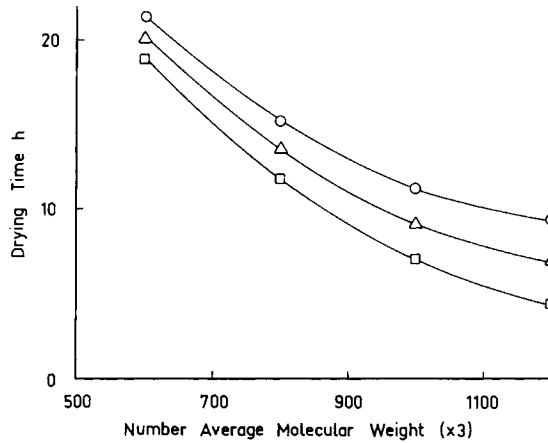


Fig. 2. Effect of molecular weight (X3) and 2EH concentration in monomer mixture (X2) on drying time according to regression model ( $CL = 0.95$ ). X2 (w/w): (□) 0.2; (Δ) 0.4; (○) 0.6.

leads to the formation of a faster drying resin. The difference between these observations can probably be explained by the poor fit of the regression equation to the experimental data in this study.

The hardness of the paint films increased substantially on ageing (Table IV). The measurements obtained from 4-week-old films were analyzed by regression analysis. Hardness was found to increase with molecular weight. TMPDA was the more significant modifying monomer (Fig. 3), leading to the formation of harder films when present in larger proportions in the monomer mixtures. 2EH acted as a plasticizer softening the films.

Large differences were found in the water resistances of the paint films. Some films swelled and blistered heavily after a few minutes in the test while some test panels stayed unchanged for hours. The regression analysis showed improved water resistance with increasing molecular weight and concentration of 2EH.

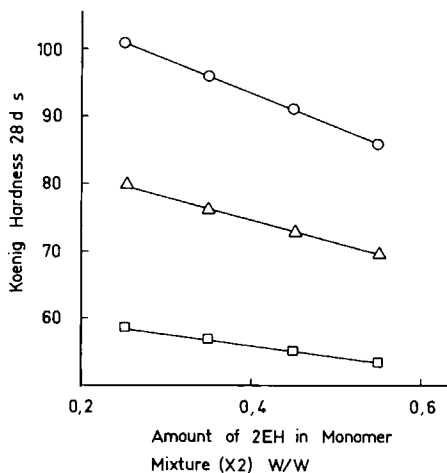


Fig. 3. Effect of 2EH (X2) and TMPDA (X1) concentration in monomer mixture on Koenig hardness of paint films at constant molecular weight of X3 = 1000 according to regression model. X1 (w/w): (□) 0.2; (Δ) 0.4; (○) 0.6.

The regression model describing the bend test results accounted for only so small a part of the variance that the interpretation of the measurements was not really meaningful. All the paint films had a high gloss.

### COMPARISON OF BMMU-RESIN BASED PAINTS TO SOME COMMERCIAL PRODUCTS

Using the regression models, monomer compositions and degrees of polymerizations for resins having good drying properties, adequate thinnability with water and water resistance were searched. Water resistances were determined now using a more advanced test method according to SIS 839118, which better describes the resistance of a paint film to water under real conditions. Paint films on wooden panels were exposed to water for 1 h, 6 h, and 24 h and the possible deterioration of the films was evaluated using a scale from 1 (heavy deterioration) to 5 (no changes). The product having test results of 5 (1 h), 5 (6 h), 5 (24 h) fulfills the very high requirements for indoor use but for the most purposes also the result of 4,4,4 is generally regarded to be adequate. A commercial-solvent-based general purpose gloss tall oil alkyd paint (MIRANOL), a semigloss interior paint based on an acrylic dispersion fortified with an alkyd resin (REMONTTI-ÄSSÄ) and a semigloss interior block resistant acrylic dispersion paint (KAUNIS KOTI) were used as references.

As seen from Table VI, amino resin paints having both good water resistance and drying properties could be prepared (paints I and II). Increasing the thinnability of a resin to the level of 40% enabled paint brushes to be washed in soap and water instead of solvents. The water resistance of such paints was decreased but still were on adequate level for indoor use (paints III and IV). The predictions for the drying times of the resins used in the paints III and IV as calculated using the regression model had a good correspondence to the measured values.

### STABILITY OF RESINS IN SOLUTIONS

#### Introduction

Etherified amino resins comprise functional groups capable of decomposition via solvolysis in aqueous or alcoholic coating formulations. The hydrolysis of a *N*-alkoxymethyl group can proceed in acidic solutions<sup>3</sup>:

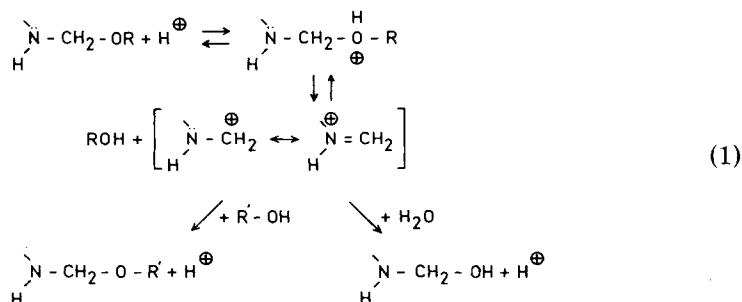


TABLE VI  
Comparison of BMMU-Resin Based Paints to Some Commercial Paint Products

Paint	$\bar{M}_n^b$	Thinnability with water (%)	TMPDA/BMMU (w/w)	2EH/BMMU (w/w)	Drying time (h)		Water resistance <sup>d</sup>		
					Predicted <sup>c</sup>	Measured	1 h	6 h	24 h
Miranol <sup>a</sup>	—	—	—	—	—	5.3	5	5	5
Kaunis Koti <sup>a</sup>	—	—	—	—	—	1	5	4	4
Remontti-Ässä <sup>a</sup>	—	—	—	—	—	0.8	4	4	4
BMMU resin I	—	22.7	0.419	0.431	—	6	5	5	5
BMMU resin II	—	24.5	0.419	0.431	—	9	5	5	5
BMMU resin III	1091	39.5	0.330	0.230	5.9	5.5	4	4	4
BMMU resin IV	1071	39.6	0.321	0.199	5.8	5.3	4	4	4

<sup>a</sup> Manufacturer: Tikkurilan Väritehtaat Oy, PL 53, 01301 VANTAA 30, Finland.

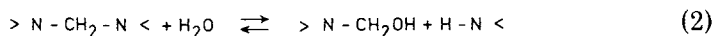
<sup>b</sup> Osmometric molecular weight.

<sup>c</sup> Calculated using the regression model of drying time (Table V,  $CL = 0.95$ ).

<sup>d</sup> According to SIS 839118.



The reactions lead to the formation of methylol groups, or the alkoxy side chains in the resin molecules are exchanged for the alcohol present in the solvnet mixture. The methylol groups are labile and can be decomposed further with the liberation of formaldehyde.<sup>4</sup> If the nitrogen atom in an *N*-alkoxymethyl group carries a proton, as is the case with the amino resins treated in this study, the hydrolysis can also proceed in alkaline media according to another mechanism.<sup>5</sup> Also the polymeric backbone itself can be attacked by the solvolytic action<sup>6</sup>:



### Stability Measurements

The solvolytic resistance of BMMU-based resins was evaluated by following the viscosity changes in ethanolic and aqueous ethanolic solutions at room temperature. Maleic acid used as a catalyst in the polymeriations lowered the pH values of the resin solutions. The viscosities of these solutions were observed to decrease markedly during the first 2 weeks, while the neutralized samples stayed essentially unchanged (Fig. 4).

The stability of *N*-alkoxymethyl groups was also studied more carefully by measuring the changes in the extent of reaction of the modifying alcohol in resin solutions on ageing for a longer test period. To avoid analytical difficulties, a resin modified only with 2EH was examined. The concentration of 2EH in the ethanolic and aqueous ethanolic solutions was determined by a novel liquid chromatographic method,<sup>7</sup> which enabled the accurate measurements of small 2EH concentrations without a risk of further decomposition of the resin during

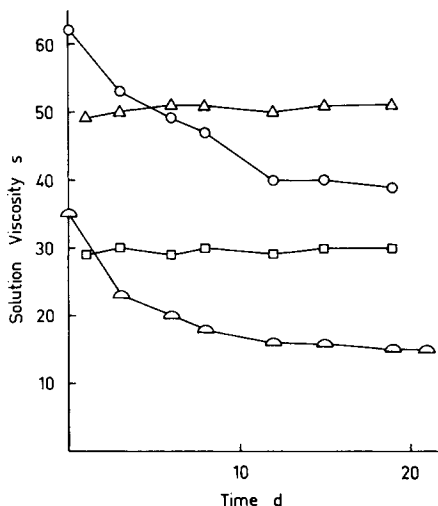


Fig. 4. Stability of resin solutions at ambient temperature of 296 K. Changes in viscosities measured as falling times of a steel ball in solutions using Höppler viscometer. (O) 52 wt% resin in ethanol, pH = 2.9; (∩) former solution diluted with water (70:17.5 v/v), pH = 3.5; (Δ) 52 wt % resin in ethanol, pH = 7.0; (□) former solution diluted with water (70:17.5 v/v), pH = 7.0. Resin composition: TMPDA/BMMU = 0.572 w/w, 2EH/BMMU = 0, osmometric molecular weight  $\bar{M}_n$  = 620.

the analysis. During the test period of over 8 months, no essential decrease in the conversion of the modifying 2EH could be detected in any of the solutions (Table VII).

The test results indicate the importance of controlling the pH level of the resin solutions in order to achieve a good self-life. Neutralized ethanolic or aqueous ethanolic solutions of the BMMU-based esterified urea resins can be regarded to have adequate stability for surface coating purposes.

## EXPERIMENTAL

The preparation of the resins, thinnability measurements, and osmometric determinations of the number average molecular weights were carried out as described previously.<sup>1</sup>

### Solution Viscosity

Measurements were done as described earlier<sup>1</sup> except the viscosity of 700 cP was now used as a reference.

### Drying Time

The drying times of the resins were determined as in the previous paper.<sup>1</sup> Cobalt as naphthenat (Servo bv-delden, Netherlands), 0.1% calculated on the weight of the resin, was used as a drier.

## Paint Film Performance Tests

### *Preparation of Paints*

The resins were used as neutralized ethanolic solutions thinned down to a viscosity of 700 cP. The pigment (Finntitan RR, Kemira Oy, Vuorikemia, Finland) was dispersed in the resin solution in a ball mill for 20 h using 44% of

TABLE VII  
Stability of Neutralized Resin<sup>a</sup> Solutions at 303 K. Changes in Concentration of Free Comonomer in 50 wt % Resin Solutions in Different Solvent Composition

Age of solutions (days)	Solvent composition: water/ethanol (w/w)							
	0.56		0.28		0.11		0	
	2EH <sup>b</sup> (wt %)	C <sup>c</sup> (%)	2EH (wt %)	C (%)	2EH (wt %)	C (%)	2EH (wt %)	C (%)
0	0.228	98.6	0.224	98.6	0.228	98.6	0.223	98.7
1	0.232	98.6	0.231	98.6	0.229	98.6	0.231	98.6
4	0.230	98.6	0.230	98.6	0.230	98.6	0.230	98.6
11	0.242	98.5	0.243	98.5	0.249	98.5	0.268	98.4
18	0.244	98.5	0.247	98.5	0.246	98.5	0.250	98.5
54	0.235	98.6	0.236	98.6	0.240	98.6	0.239	98.6
257	0.292	98.2	0.320	98.1	0.288	98.3	0.316	98.1

<sup>a</sup> Resin: TMPDA/BMMU = 0, 2EH/BMMU = 0.343 w/w, polymerized to the thinnability with water of 36.6%.

<sup>b</sup> Concentration of 2EH in resin solution.

<sup>c</sup> Conversion of 2EH in resin calculated on the basis of solution composition.

the resin from the final formulation. The dispersion was mixed with the rest of the binder solution to adjust the ratio of pigment to resin to 0.70. 0.056% cobalt as naphtenate (Servo bv-delden, Netherlands) on the weight of the resin was added as a drier and the paint was allowed to stand for 1 day before application.

#### *Preparation and Aging of Test Panels*

The coating films for the tests were applied using an I.C.I. Automatic Film Applicator (Sheen Instruments Ltd., England). The test panels were stored in the controlled atmosphere of 294 K and 50% relative humidity.

#### *Hardness*

The measurements were accomplished according to DIN 53157 using the pendulum hardness rocker made by Erichsen GMBH and Co. KG (W. Germany). Four test panels were prepared from each paint and the final hardness value was read from the graphical representation of hardness vs. film thickness to correspond the dry film thickness of 30  $\mu\text{m}$ .

#### *Flexibility*

The flexibility of the paint films was assessed by the bend test described in SIS 184174. The age of the films was 7 days. Thicknesses of dry films were about 20  $\mu\text{m}$ .

#### *Water Resistance*

The paints were applied on glass plates. The dry film thicknesses were about 30  $\mu\text{m}$ . After having aged a film 30 days, a petri dish filled with distilled water was placed upside down on the panel and changes in the appearance of the paint films were followed. The time which elapsed until the appearance of the first blisters was regarded as a measure of the water resistance of the film.

The tests according to SIS 839118 were carried out using particle board coated with birch veneer as test panel material. Two coats of paints were applied on panels and the tests were carried out after a drying period of 28 days.

#### **Reagents**

*N,N'*-bis(methoxymethyl) urea (BMMU) was prepared, as described in the previous paper.<sup>1</sup>

*Trimethylolpropane diallylether* (TMPDA) was of technical grade (Perstorp AB, Sweden) and was used as such. The equivalent weight based on the hydroxyl group concentration was found to be 232.8 g/eq as determined by the method of Stetzler and Smullin.<sup>9</sup> The allyl group content of the product was 8.94 mmol/g determined by a iodometric titration.<sup>10</sup>

*2-Ethylhexanol* (2EH) was purchased from E. Merck, Darmstadt. The equivalent weight of the product was found to be 131.1 g/eq as calculated from the hydroxyl group concentration determined by the method of Stetzler and Smullin.<sup>9</sup>

*Maleic Acid and Sodium Hydroxide.* Supplied by E. Merck, Darmstadt, were of analytical grade and used as such.

## CONCLUSIONS

According to the regression models the following relationships between the properties of the BMMU-based resins and the degree of modification with 2EH and TMPDA and the molecular weight of the products were found:

a. The thinnability of an ethanolic resin solution with water decreases with the increasing degree of modification and the molecular weight of the resin.

b. The viscosity of an ethanolic resin solution depends only on the resin's molecular weight and increases with molecular weight.

c. The drying performance of a resin is improved when the molecular weight increases or the modification with 2EH is reduced.

d. The hardness of a paint film depends on the type of modification and the molecular weight of the resin. A large amount of TMPDA in the monomer mixture or a high molecular weight leads to a hard paint film. The modification of the resin with 2EH softens the coating films.

e. The water resistance of the paint films was directly proportional to the amount of 2EH in the resin and the molecular weight.

Too large a scatter of the bend test results made the analysis of the elastic properties of the paint films impossible. The comparison of a few paints to some commercial products indicated that amino resins having good drying performance and adequate water resistance can be prepared. The stability of the resins in neutral ethanolic or aqueous ethanolic solutions was found to be adequate for surface-coating purposes.

The author would like to thank Marja Saarinen for technical assistance.

## References

1. H. Toivonen, *J. Appl. Polym. Sci.*, **26**, 4021 (1981).
2. V. Chew, Ed., *Experimental Designs in Industry: A Symposium held November 5-9, 1956 at North Carolina State College*, Wiley and Chapman-Hall, New York, and London, 1958, p. 188.
3. H. Petersen, *Text. Res. J.*, **38**, 156 (1968).
4. J. I. De Jong and J. De Jonge, *Recueil*, **71**, 661 (1952).
5. J. Ugelstad and J. De Jonge, *Acta Chem. Scand.*, **10**, 1475 (1956).
6. J. J. De Jong and J. De Jonge, *Recueil*, **72**, 202 (1953).
7. B. Björkqvist and H. Toivonen, *J. Chromatogr.*, **153**, 265 (1978).
8. H. Kadowaki, *Bull. Chem. Soc. Jpn.*, **11**, 248 (1936).
9. R. S. Stetzler and C. F. Smullin, *Anal. Chem.*, **34**, 194 (1962).
10. A. I. Vogel, *Elementary Practical Organic Chemistry. 3. Quantitative Organic Analysis*, 6th ed., Longmans, London, 1970, p. 767.

Received November 13, 1980

Accepted April 22, 1981