

Novel Oxidatively Drying Urea Resin. I. Drying Properties of Urea Resins Prepared from *N,N'*-Bis(methoxymethyl) Urea and Alcohols Containing Allyl Ether Groups

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Synopsis

A new type of urea resin prepared by copolycondensating *N,N'*-bis(methoxymethyl) urea with an alcohol containing allyl ether groups have been studied and found to have adequate drying properties when used for surface coating purposes. The drying behavior of the resins can be controlled by conventional drier metals, cobalt being an efficient catalyst. Calcium was found to have a synergetic effect with cobalt on drying, zinc and lead had no synergetic effect, and manganese and sodium hydroxide acted as drying inhibitors. Increasing the amount of allylic alcohol in the monomer mixture and higher molecular weight led to the formation of a faster drying resin. The molecular weight distribution of the resins was found to have an effect on the surface coating properties. It was found that for resins having an equal drying rate those with a broader molecular weight distribution had higher solution viscosities. Resins with a narrow molecular weight distribution were also found to be advantageous when formulating coating compositions containing a minimum concentration of solvents.

INTRODUCTION

Air-Drying Amino Resins Containing Allyl Ether Groups

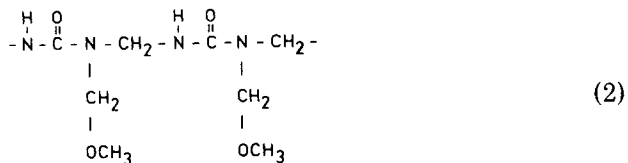
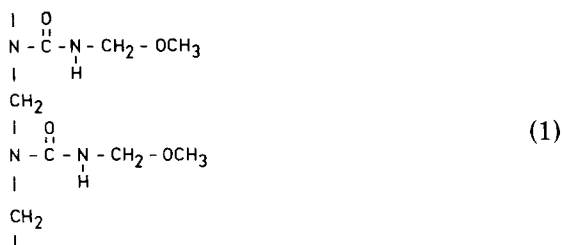
Allyl ether groups containing amino resins have been investigated as oxidatively drying binders in surface coating formulations. Most of the work has been done to develop aminotriazine-formaldehyde resins made air-drying by etherifying methylol groups containing condensates with allyl alcohol¹⁻⁴ or with a higher boiling allyl ether alcohol.^{5,6} The drying and hardening properties of these resins have generally been found to be poor.^{7,8} Better results have been obtained when using the resins in mixtures with alkyds¹ or unsaturated polyesters.⁹

Allylated urea resins have been proposed to be used in stoving finishes^{10,11} or in compositions cured by peroxides.^{12,13} Widmer and Zuppinger⁴ have treated allylated urea-formaldehyde resins as an oxidatively drying binder. The properties of the resins were, however, found to be poor: the films dried rapidly free of tackiness but remained soft and were not water resistant. Also Brookes et al.¹⁴ have shown urea-formaldehyde resins containing allyl ether groups when used as binders in autoxidatively drying formulations to dry too slowly. In addition, the slow hardening films were found to be brittle. The surface-coating properties of these allylated resins were essentially improved by copolymerization

with an unsaturated compound. The relatively large amounts of ethylenic comonomers used in the modifications could mean also that the physical drying mechanism after evaporation of solvents has been of great importance in the film formation behavior of these resins. Yukhnovskii and Semova¹⁵ tested urea-formaldehyde precondensates modified with allyl alcohol as an oxidatively drying film former. The cured films had poor water resistance. Better results were achieved when the resins were partly etherified with butanol before the treatment with allyl alcohol. These air-drying amino resins mixed with certain plasticizers are claimed to dry into hard, elastic, oil- and water-resistant films within 24 h. Chernaya and Kovtun¹⁶ investigated the air-drying behavior of allyl ethers of certain polyhydric alcohols. These allylated derivatives were also used in the modification of urea resins. The coating properties of these products are not described in detail.

Polycondensation of *N,N'*-Bis(alkoxymethyl) Ureas

The capability of dialkylethers of dimethylolurea to form homopolycondensates upon heating with or without acidic catalysts is well known.¹⁷⁻²² Structures of these polymers have been discussed in a few papers.^{23,24} and in one of the most thorough investigations²⁵ polymers based on *N,N'*-bis(methoxymethyl) urea (BMMU) are presented as consisting of one of the following units:



N,N'-bis(alkoxymethyl) ureas have also been used to prepare copolymers. Compounds like amino alcohols,²⁶ monohydric alcohols,^{27,28} or polyols²⁹⁻³¹ have been used as comonomers. Petersen^{32,33} has treated thoroughly the reactions of etherified methylolated derivatives of ureas with different nucleophiles. In these studies the condensations of *N,N'*-bis(alkoxymethyl) ureas have not been dealt with especially from a polymerization point of view.

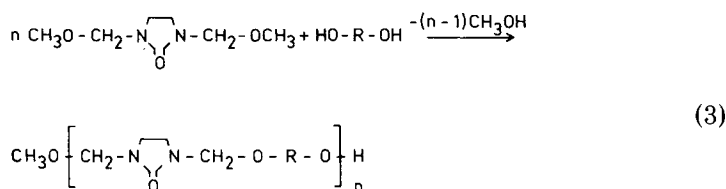
Allylated urea resins free from harmful unreacted formaldehyde and with good film-forming properties can be prepared by copolycondensating an *N,N'*-bis(alkoxymethyl) urea with an allylic alcohol.³⁴ In this paper these new type of air-drying urea resins and their drying properties are described.

PREPARATION OF AIR-DRYING AMINO RESINS FROM *N,N'*-BIS(ALKOXYMETHYL)UREAS

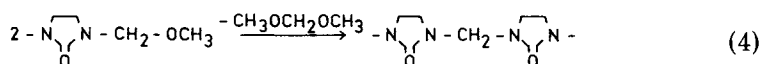
Preliminary Experiments with Linear Amino Resins

The air-drying characteristics of polyesters containing allyl ether groups have been found to be dependent on the average number of allyl ether groups per molecule, i.e., the functionality of the resin and the proportion by weight of allyl ether groups.³⁵ To outline the corresponding relationship between the molecular architecture and drying properties of allylated amino resins, some preliminary tests were carried out. The aim of these experiments was to get a rough idea whether it is generally possible to synthesize an allylated amino resin with reasonable drying properties.

To simplify the interpretation of test results and to avoid the possible gelation of the polymerizing mixtures, amino resins having a linear chain structure were used as a model. The resins were prepared by polycondensating a bifunctional urea derivative, *N,N'*-bis(methoxymethyl)ethylene urea (BMMEU), with diethyleneglycol (DEG) and trimethylolethane monoallyl ether (TMEA) or pentaerythritol diallyl ether (PEDA). The polymerizations were catalysed with a low concentration of *p*-toluene sulfonic acid (PTSA) (0.2% by weight of monomer mixtures). The condensations proceeded via liberation of methanol:



At higher concentrations of PTSA (2% by weight), BMMEU reacted also with itself:



The drying properties of the polymers were tested. The drying rate was found to be strongly dependent on the average molecular weight and the allyl ether functionality of the resin (Table I). On the assumption that a drying time of 4–5 h can be considered short enough for a binder to be used in trade sales surface coatings, an allylated amino resin prepared using this technique can fill this requirement.

Resins from BMMU

The development of the allylated urea resins was continued by studying the copolycondensation of the economically more feasible *N,N'*-bis(alkoxymethyl) ureas. Monohydric alcohols were used as modifying comonomers. The actual extension of the polymeric chains resulted now from homopolymerization of

TABLE I
 Properties of Linear Amino Resins

BMMEU	Monomer composition of resins (mol)			\bar{M}_n^a	Drying time ^b (h)
	PEDA	TMEMA	DEG		
0.2	—	0.16	0.04	552	72
0.2	—	0.16	0.04	1596	21.5
0.2	0.16	—	0.04	1318	14
0.2	0.16	—	0.04	1470	4.8
0.2	0.16	—	0.04	1602	4

^a By vapor pressure osmometer.

^b 0.2% Co as drier by weight of resin.

N,N'-bis(alkoxymethyl) urea and the desired surface-coating properties of the resins were based on the modification via transesterification of the unreacted alkoxy groups by comonomers.

In this study BMMU was used as a urea derivative due to its low melting point and because the methanol formed in the condensation is easily removed as a volatile compound from the polymerizing mixture. Trimethylolpropane diallyl ether (TMPDA) was used as an allyl ether component, because it is the cheapest commercially available high boiling allyl ether derivative. The resins were further modified with 2-ethylhexanol (2EH) for better water resistance.

Drying Characteristics of Autoxidative BMMU Resins

The significance of chemical changes in the film formation of the resins was studied with polycondensates prepared by replacing the allyl ether reagent partly or totally with the analogical saturated compound. The drying times and the hardness measurements (Table II) showed that the allyl ether functionality of the resins is essential and the physical drying of the films can be regarded as negligible.

Figure 1 illustrates the effect of the main variables of the structure of resins on drying rate. The air-drying properties are improved when the allyl ether functionality of the resins is increased either because of a larger amount of allylic compound included in the monomer mixture or as a result of an increase in the average molecular weight.

Cobalt is known to have catalytic activity in the autoxidation of allyl ether groups.³⁶ Lead, manganese,³⁷ and alkalis like sodium hydroxide³⁸ behave as inhibitors. The effect of different drier metals on the drying properties of a typical allylated BMMU-based resin is shown in Figure 2 and Table III. Cobalt

 TABLE II
 Significance of Chemical Drying in Film Formation

Monomer composition of resins (mol)				\bar{M}_n^a	Drying time ^b (h)	Koenig hardness of 7-day-old lacquer films (s)
BMMU	GDAE	GDPE	2EH			
1.19	0.307	—	0.41	826	12.5	57
1.19	0.154	0.154	0.41	762	25	27
1.19	—	0.307	0.41	673	26.5	8

^a By vapor pressure osmometer.

^b 0.1% Co as drier by weight of resin.

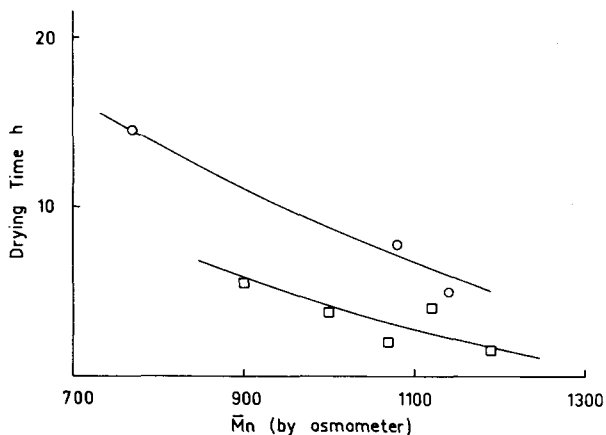


Fig. 1. The effect of amount of allyl ether compound in monomer mixture and molecular weight of resin on drying time. Resins modified with TMPDA and 2EH, total amount of modifying monomers being 31 wt % of monomer mixtures. (O) TMPDA content 14.4 wt %; (□) TMPDA content 20.6 wt %, as calculated by the total weight of monomer mixture. Drier: 0.1 wt % Co as naphthenate by weight of resin.

is seen to accelerate the drying rate efficiently. The rate of drying could be increased further by the synergetic effect of calcium, although this element did not have any catalytic activity as such. Zinc or lead did not have synergism with cobalt, but neither were they inhibitors like manganese and sodium hydroxide.

Effect of the Molecular Weight Distribution on the Properties of the Resins

The polymerizations of BMMU were found to be very sensitive to the presence of bi- or multifunctional compounds having active hydrogen atoms capable to react with *N*-alkoxy groups. Polyhydric alcohols and urea, e.g., caused a rapid gel formation when added to reaction mixtures. With regard to the drying

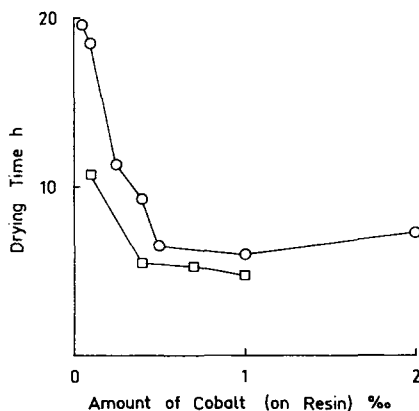


Fig. 2. Effect of drier concentration on drying. Resin: TMPDA/BMMU = 0.312 and 2EH/BMMU = 0.199 w/w, osmometric molecular weight $\bar{M}_n = 910$. (O) Only Cobalt as drier; (□) 0.2% Ca added.

TABLE III
Effect of Various Additives Used with Cobalt on Drying Times^a

Co (% by weight of resin)	Additive (% by weight of resin)	Drying time (h)
0.1	—	6.0
0.1	Ca/0.045	5.9
0.1	Ca/0.2	4.8
0.1	Zn/0.05	6.3
0.1	Zn/0.2	6.3
0.1	Pb/0.05	6.0
0.1	Pb/0.2	5.5
0.1	Mn/0.05	21.5
0.1	NaOH/0.064	7.8
0.1	NaOH/0.128	14.0
0	Ca/0.2	>24

^a Monomer composition of the resin: TMPDA/BMMU = 0.312, 2EH/BMMU = 0.199. Osmometric molecular weight 910.

properties, the degree of polymerization of the resins should be as high as possible. In practice, however, the increasing melt viscosity of a resin becomes a limiting factor at a certain stage of the polymerization, since the faster the molecular weight distribution broadens the sooner the polymerization must be stopped because of the increasing danger of gelation. Also there will be an increased need to use solvents in surface-coating formulations based on a resin with a broad molecular weight distribution. To evaluate the significance of the increase in polydispersity caused by possible impurities in resin raw materials, a few resins were prepared adding small amounts of urea in the polymerization mixtures to broaden the molecular weight distributions.

The effect of urea on the polydispersity and the solution viscosity of a resin

TABLE IV
Apparent Molecular Weights and Solution Viscosities of Resins^a Made from Monomer Mixtures Containing Urea as Impurity

Resin	Urea in monomer mixture (mol %) ^b	\overline{M}_n^c	$\frac{\overline{M}_w^c}{\overline{M}_n}$	Solution viscosity (mL/g)
1	0	1440	7.36	0.605
2	0	860	3.96	0.402
3	0	730	3.20	0.300
4	0	490	2.60	0.172
5	2	1510	853	0.910
6	2	670	5.65	0.525
7	2	410	2.74	0.406
8	4	1040	34.3	0.743
9	4	570	5.43	0.458
10	4	500	2.80	0.300
11	6	1370	24700	1.330
12	6	1240	21.9	0.792
13	6	440	4.03	0.390
14	6	290	2.63	0.223

^a Monomer composition: TMPDA/BMMU = 0.395 w/w, 2EH/BMMU = 0.305 w/w.

^b By moles of BMMU in monomer mixtures.

^c Determined by GPC.

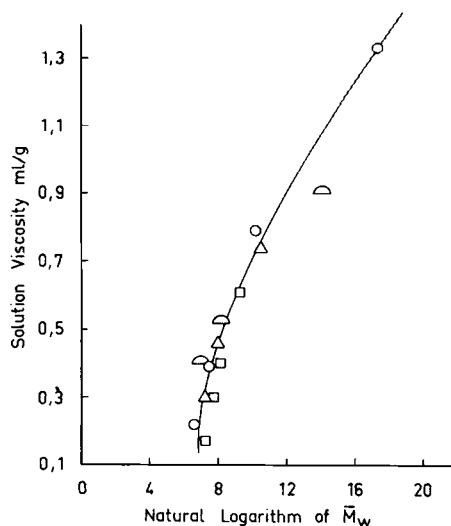


Fig. 3. Correlation between solution viscosities and apparent weight average molecular weights of resins from Table IV. Urea added to monomer mixtures (mol %): (\square) 0; (\circ) 2; (Δ) 4; (\diamond) 6.

is presented in Table IV. To emphasize pollutional aspects, an unconventional way of expressing solution viscosities, which describes the amount of solvent needed in formulating a resin into a paint, has been used. The viscosity measurements correlated very well with the weight average molecular weights regardless of the large differences in the polydispersities of the resins (Fig. 3).

A change in the polydispersity had also effect on the drying rate and the thinnability of the standardized ethanolic solution of the resin (Table V). When

TABLE V
Some Properties of Resins^a Made from Monomer Mixtures Containing Urea as Impurity

Resin	Urea in monomer mixture (mol %) ^b	Thinnability (%)	Solution viscosity (mL/g)	Drying time (h) ^c
15	0	45.1	0.280	12.2
16	0	42.4	0.347	10.2
17	0	37.7	0.490	6.2
18	0	33.8	0.872	3.5
19	2	49.5	0.173	19.0
20	2	43.4	0.323	12.5
21	2	38.5	0.482	8.3
22	2	35	0.643	6.0
23	4	47.1	0.331	12.0
24	4	42.7	0.420	9.0
25	4	38.1	0.753	6.0
26	4	35.5	1.018	5.3
27	8	49.1	0.318	11.0
28	8	45.9	0.451	9.3
29	8	43	0.573	8.8
30	8	40.4	0.855	8.0

^a Modification of resin: TMPDA/BMMU = 0.395 w/w, 2EH/BMMU = 0.305 w/w.

^b By moles of BMMU in monomer mixtures.

^c 0.15% Co as drier by weight of resin.

molecular weight distributions were broadened as a result of an increasing amounts of urea being added to polymerization mixtures, the drying rates of the resins with an equal solution viscosity lengthened (Fig. 4). An increase in the solution viscosity due to the broadening of the molecular weight distribution cannot thus be compensated by lowering the degree of the polymerization without having a decrease in the drying rate of the resin at the same time. Too large a polydispersity can also mean that the continuation of the polymerization in order to prepare a resin with sufficient drying properties is not possible, because of the gelation of the reaction mixture before the adequate degree of polymerization is reached. The hydrophilicity of the products as measured by the thinnability of ethanolic solutions with water was one of the important properties investigated because of the desired applications of the resins in water based formulations. The possibility of using water as a thinner leads to a reduction in the total amount of solvents required in coating formulations. Figure 5 shows the solution viscosity of a resin with a constant thinnability with water to increase rapidly when the molecular weight distribution broadens. Thus a broad molecular weight distribution is a disadvantage also when the amount of solvent needed to formulate a resin into a coating composition is considered to be of importance.

EXPERIMENTAL

Linear Amino Resins

The resins were prepared as follows. A batch of 80 g of the monomer mixture was weighed in a 250 mL three-necked flask fitted with a stirrer, an outlet for the distillate, and a nitrogen inlet tube. The mixture was heated up to 363 K, and 0.16 g of PTSA was added to the monomer melt. The polymerization was carried out at the beginning under atmospheric pressure by blanketing the reaction mixture with a low stream of nitrogen. After 0.5 h the pressure was lowered down to 1300 Pa to facilitate the removal of the distillate and the polycondensation proceeded until the proper degree of polymerization was achieved.

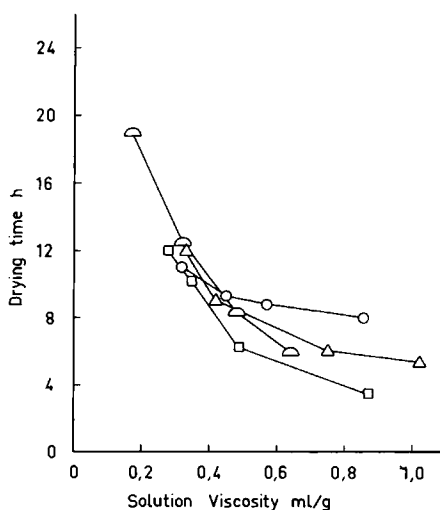


Fig. 4. Drying time vs. solution viscosity. Values from Table V. Urea added to monomer mixtures (mol %): (□) 0; (◐) 2; (△) 4; (○) 8.

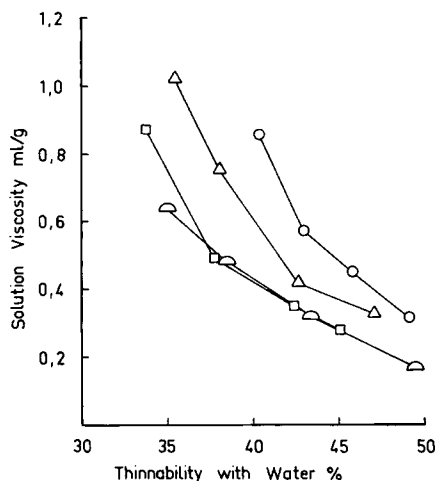


Fig. 5. Solution viscosity versus thinnability with water. Values from Table V. Urea added to monomer mixtures (mol %): (\square) 0; (\ominus) 2; (Δ) 4; (\circ) 8.

BMMU Resins

A batch of 1000 g of the monomer mixture was placed in a 2-L wide-neck flask fitted with an anchor stirrer, an inlet tube for nitrogen, and a condenser as an outlet for the distillate. The mixture was heated up to 373 K to form a clear homogenous solution. 1 g of maleic acid was now added slowly to the mixture to start the reactions. The polymerization was carried out at normal pressure under a nitrogen blanket. The progress of a polymerization was monitored by visual estimation of the melt viscosity or by determining the thinnabilities of small resin samples taken out of the reaction mixture at constant intervals.

Osmometry

A Hewlett-Packard vapor pressure osmometer model 302 B was used to measure the number-average molecular weights. Determinations were carried out at an operation temperature of 303 K. Methanol was used as a solvent and polypropyleneglycols (from Waters Associates, Inc., U.S.A.) as molecular weight reference standards.

Gel Permeation Chromatography

A Hewlett-Packard model 1010 A Liquid Chromatograph fitted with four pairs of Styragel columns of 30,000-Å, 1000-Å, 100-Å, and 60-Å pore size (Waters Associates, Inc., U.S.A.) was used for the analysis of the molecular weight distributions. The diameter of the columns was 9.5 mm ($\frac{3}{8}$ in.), the total length being 7.3 m (24 ft). Redistilled tetrahydrofuran was used as an eluant in running the chromatograms at a flow rate of 3 mL/min and at the temperature of 295 K. The detector was Multiref 901 differential refractometer (Optilab AB, Sweden) operating at 296 K.

Data acquisition and the numerical calculations to normalize, calibrate, and integrate the chromatograms and to compute the molecular weight averages were performed on line using a Hewlett-Packard 3352 Data System. Calibration was

carried out with polystyrene and polypropyleneglycol standards (Waters Associates, Inc., U.S.A.). No chromatogram corrections for the changes in the refractive index or the shape of the molecules versus molecular weight were made. To get some idea about the accuracy of the molecular weight determinations with the GPC system, a few resins were analyzed for their number-average molecular weights by both GPC and vapor pressure osmometry. The comparison of the results are in Table VI.

Tests of Coating Films

Drying Time

Resins were tested as siccated 60 wt % solutions in ethanol. The films were applied with an I.C.I. Automatic Film Applicator (Sheen Instruments, Ltd., England) to get a wet film thickness of 100 μm . Measurements were made in a controlled atmosphere of 294 K and 50% relative humidity using the ICI Drying Time Recorder device (Sheen Instruments Ltd., England). The resin films were regarded as being dry when sand spread on films could be removed by light brushing.

Hardness

Measurements were obtained according to DIN 53157 using the pendulum hardness rocker made by Erichsen GMBH and Co. KG (W. Germany). The films were prepared as described above.

Thinnability with Water

A 5-g sample of resin was dissolved in 5 mL of absolute ethanol and titrated with water to the cloud point. The thinnability of the resin was expressed as the concentration of water in wt % in the water-ethanol solvent at the cloud point.

Solution Viscosities

Resin was dissolved in absolute ethanol to make a concentrated solution. The solution was then reduced with ethanol to the viscosity as near to 500 cP as possible, estimated visually. The real viscosity was then measured using a Brookfield viscometer (Brookfield Engineering Laboratories, Inc., U.S.A.) with the small sample adapter and a constant spindle speed of 12 rpm. If the reading

TABLE VI
Comparison of GPC and Vapor Pressure Osmometry (VPO) in Determining Number-Average Molecular Weights of a BMMU-Based Aminoresin^a

Resin	\bar{M}_n	
	GPC	VPO
1	1440	1280
2	860	830
3	730	640
4	490	580

^a Resin composition: TMPDA/BMMU = 0.395 w/w, 2EH/BMMU = 0.305 w/w.

differed from 500 cP, as was usually the case, the final concentration of the solution corresponding the viscosity of 500 cP was predicted using the following model:

$$C_2 = 6.8139 \cdot \ln(500) + 23.9486 - 6.8139 \cdot \ln(Y) - 23.9486 + C_1$$

where

C_2 = the predicted concentration of the solution at the viscosity of 500 cP in wt %

C_1 = the concentration of the test solution in wt %

Y = the measured viscosity of the test solution

The mathematical expression was created by fitting a logarithmic model to the viscosity concentration data measured using solutions of a typical air-drying urea resin (Table VII). The viscosities were expressed as concentrations of solutions at the viscosity of 500 cP in the units of mL of ethanol/g of resin.

Reagents

N,N'-bis(methoxymethyl) urea (BMMU). Dimethylolurea (DMU) was prepared by reacting urea with aqueous formaldehyde (38 wt %) overnight at 290 K and at pH = 7.0. The mole ratio of urea to formaldehyde was 2.19. The reaction mixture was buffered using 0.6% $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ calculated from the weight of formaldehyde solution. The filtered and dried DMU was then etherified with methanol using 5.9 mol of methanol for 1 mol of DMU. The reaction was carried out at ambient temperature (296 K) for 2 h at the pH of 3.0. The melting point of the crystallized product was 371–373 K. The value given in the literature³⁹ is 374 K.

N,N'-bis(methoxymethyl) ethylene urea (BMMEU): The method used for the preparation was essentially that of Hoover and Vaala.⁴⁰ The product was purified by vacuum distillation. The distillate boiling at 380 K at 400 Pa was used in the polymerizations.

Pentaerythritol diallylether (PEDA): The preparation was done according to Zimmermann and Dathe.⁴¹ The fraction boiling between 428 and 432 K at 1333 Pa was used in the experiments. The equivalent weight based on the hydroxyl group concentration was found to be 107 g/eq (theor. 108 g/eq) as determined with the method of Stetzler and Smullin.⁴²

Trimethylolethane monoallylether (TMEMA): The compound was synthesized according to Zimmermann and Dathe⁴¹ and purified by vacuum dis-

TABLE VII
Solution Viscosities of a Typical Resin^a

Concentration of ethanolic resin solution (wt %)	Viscosity (cP)
70.1	967
60.4	163
50.3	56

^a Resin: TMPDA/BMMU = 0.319 w/w, 2EH/BMMU = 0.089 w/w, polymerized to correspond the thinnability with water of 49.7%.

tillation. The product boiling between 393 . . . 399 K at 400 Pa was used in the preparations of the resins. The hydroxyl group concentration was found to be 75.7 g/eq (theor. 80 g/eq) according to the method of Stetzler and Smullin.⁴²

Glycerol α,α' -diallylether (GDAE): The synthesis was carried out according to Mleziva et al.⁴³ The fraction boiling from 365 to 369 K at 533–667 Pa was collected.

Glycerol α,α' -dipropylether (GDPE): The compound was prepared analogous to GDAE. The purified product boiled between 353 and 359.5 K at 533–667 Pa.

Trimethylolpropane Diallylether (TMPDA): The chemical was purchased from Perstorp AB, Sweden, and used without further purification.

2-Ethylhexanol (2EH), urea, and diethylene glycol (DEG): Supplied by E. Merck, Darmstadt, were of analytical grade and used as such.

Siccatives: The following driers were used:

Cobalt: 10 wt % solution as naphthenate (Servo bv-delden, Netherlands);

Calcium: 4 wt % solution as naphthenate (Servo bv-delden, Netherlands);

Zinc: Zinc octoate (Chemische Werke München, Otto Bärlocher GmbH);

Manganese: 6 wt % solution as naphthenate (Akzo Chemie, Netherlands);

Lead: 30 wt % solution as naphthenate (Servo bv-delden, Netherlands).

CONCLUSIONS

Air-drying urea resins with good drying properties can be prepared by polycondensating *N,N'*-bis(methoxymethyl) urea with an alcohol containing allyl ether groups. The drying behavior of the resins can be controlled by the concentration of the allyl ether compound in the monomer mixtures, by the average molecular weight of the product and by using conventional siccatives. The polydispersity of the polymers is of importance in view of the surface-coating properties. When resins with an equal drying rate are compared, the one with a broader molecular weight distribution has a higher solution viscosity. A broad molecular weight distribution was revealed to be a disadvantage, also, when the resin is used as a base for surface-coating formulations with minimum concentration of solvents.

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