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Effects of Reaction pH on Properties and Performance of Urea-Formaldehyde Resins

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Keywords
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Molar ratio
Molecular weight
^{13}C NMR spectra
Bond strength
Formaldehyde emission

Summary

Urea formaldehyde resins were formulated with combination variables of three reaction pH (1.0, 4.8, and 8.0) and four molar ratios of formaldehyde to urea (2.5, 3.0, 3.5, and 4.0). The resins were prepared by placing all formaldehyde and water in reaction kettle and pH was adjusted with sulfuric acid and sodium hydroxide, respectively. Urea was added in 15 equal parts at 1-minute intervals.

The proportion of high molecular weight products in the resin increased substantially as the reaction pH decreased. Furthermore, the F/U molar interacted with reaction pH to effect resin molecular weight. At acidic pH, the high molecular weight products increased as F/U ratio decresed; while, at alkaline pH, little difference was evident between the high or low molecular weight products at various F/U ratios. The formation of a high percentage of uron derivatives under strong acidic conditions also indicated these resins differed considerable from conventional UF resins formulated in the past.

Panels bonded with resins catalyzed at strong acidic conditions resulted in lowest formaldehyde emission but slightly lower bonding strength. Of the three pH conditions evaluated in the study, both weak and strong acid catalysts systems are not commonly used in conventional UF resin formulation. Based on the bond strength and formaldehyde emission data, however, the weak acid catalysts seems to provide the best compromise between the strong acid and the conventional alkaline-acid catalyst system currently used for formulating UF resin wood adhesives.

Introduction

Low cost and proven performance have made urea-formaldehyde resins (UF) the most important of wood adhesives for interior applications. Up to the middle of the 1960's, most of these resins were formulated using two stage reactions. Initially, the resin was reacted with an alkaline catalyst to initiate the addition reaction and, at the appropriate reaction time, the resin solution was converted to the acid side to promote condensation reactions. These formulations have long been used successfully for UF resins in F/U ratio between 1.45 to 1.65 (Rayner 1965).

However, during the late 60's and early 70's, both a) the formaldehyde emission from particleboard, and b) weakening glue bond caused by the hydrolytic degradation of UF polymers have increasingly become a problem of major concern in the industry. New resins with much lower formaldehyde emission were formulated mainly by decreasing F/U ratio (i.e. down to 1.1 to 1.2). Lower F/U ratios, while yielding substantially lower formaldehyde emission, resulted in longer cure time and lower IB strength due to insufficient formaldehyde to complete the condensation reaction. Thus, a new resin formulation (greatly different from two-stage alkaline-acid catalysts system) was introduced. A significant development was the formulation of UF resins under weakly acidic catalysts without first using an alkaline catalyst (Lambuth 1987). The weak acidic catalyst was thought to promote higher degrees of condensation and to reduce formaldehyde emission of the resin without changing the working conditions of the resins. More recently, UF resins catalyzed by strong acidic conditions have been introduced to form extremely stable UF prepolymers (Williams 1983). These developments have greatly expanded the range of potential effects in UF resin formulation. The objective of this study is to evaluate these new developments and to examine the effects of wide ranges of pH on properties and performance of UF resins.

Procedure

Resin preparation

All UF resins were prepared in the laboratory. Each resin preparation was replicated one time. To prepare each resin, all formaldehyde and water were placed in a reaction kettle and pH was adjusted with sulfuric acid and sodium hydroxide, respectively.

Urea was added in 15 equal parts at 1-minute intervals. To initiate the reaction, the mixture was heated and maintained at 50 °C for the first 30 minutes; thereafter, temperature was increased to 80 °C with the exception of the resin made at strong acidic condition that was reacted at 60 °C. When the viscosity reached Gardner-Holt viscosity A, the reaction was stopped by rapidly cooling the mixture to 25 °C. Gel time, pH, solid content, specific gravity, and free formaldehyde content were determined. The variables for resin preparation were:

1. Reaction pH
   a. Strong acid – pH 1.0
   b. Weak acid – pH 4.8
   c. Alkaline-acid – pH 8.0 for 30 minutes and then adjusted to 5.0.
2. Molar ratio of formaldehyde to urea (F/U)
   a. 2.5
   b. 3.0
   c. 3.5
   d. 4.0

Gel-permeation chromatography

A Water associates GPC with four Shodex GPC-AD-802S columns was used with dimethylforamide solvent at flow rate of 1 mL/minute. This gel is a polystyrene-divinyl benzene copolymer that has an exclusion limit of 8,000 (polystyrene molecular weight). Sample injection volume was 100uL at concentration of 1 percent (wt/v).

NMR measurement

Each resin was diluted with 2- to 3-volumes of deuterium oxide and a ^{13}C-NMR spectrum was obtained using a FX-100 spectrometer (Japan Electron Optics Lab. Co.) at a frequency of 25.0 MHz. A 7.0-sec pulse delay time and a °45 pulse were used with the gated decoupling to remove N.O.E. Chemical shifts were determined using internal methanol at 50.0 ppm. Quantitative analyses were based on the signal intensities.

Free formaldehyde determination

A slightly modified sodium sulfite method was used for determination of free formaldehyde in the resins. Fifty mL of a 1-molar solution of sodium sulfite and three drops of thymophthalein indicator solution were placed in a 250 mL Erlenmeyer flask and carefully neutralized by titration within hydrochloric acid until the blue color of the indicator disappeared. An accurately measured, neutralized resin sample was then added to the sodium sulfite solution and the temperature was kept at 4 °C to minimize hydrolysis of the resin. The resulting mixture was titrated with the 0.1 N HCL to complete decoloration. The percent of free formaldehyde was determined as:

$$\%\ \text{HCHO} = \frac{(\text{acid titer})\ (\text{normality of acid})\ (3.003)}{\text{weight of sample}}$$

Formaldehyde emission measurement

The determination of formaldehyde absorbed in distilled water is based on the specific reaction of formaldehyde with chromotropic acid-sulfuric acid solution, forming a purple mono-cationic chromogen. The absorption of the purple solution was read using a spectrophotometer at 580 nm. The test was performed in accordance with NPA 2-hour desicator test.

Glue bond performance

All panels were prepared in the laboratory with dried southern pine wood particles. The wood particles were obtained at a particleboard plant in Louisiana and used without additional preparation. The sieve analysis of particles showed:

+4 mesh:	1.2%
−4 mesh, +8 mesh:	20.5%
−8 mesh, +20 mesh:	55.9%
−20 mesh, +32 mesh:	12.1%
−32 mesh, +48 mesh:	4.9%
−48 mesh:	5.4%

The resins were adjusted to F/U ratio of 1.1/1 by adding urea one night before blending. Resin was applied to the wood particles by sprayer in a rotating drum with air-atomizing nozzles. The general conditions for board manufacture were:

Panel size:	20 × 24 inches
Particle moisture content:	4.5%
Resin content:	4.5%
Hot-press temperature:	375 °F
Hot-press time:	4 minutes

Bending strength (MOR and MOE) and internal bond (IB) were performed in accordance with ASTM standards for evaluating the properties of wood-base fiber and particle panel materials (D-1037–72).

Results and Discussion

Resin properties

Average physical and chemical properties of UF resins as affected by reaction pH and molar ratio of F/U are summarized as follows:

Reaction pH	F/U ratio	Solid content %	Viscosity cps	Specific gravity	Free HCHO %
1.0	2.5		(gelled)		
	3.0	49	80	1.255	6.35
	3.5	45	30	1.250	6.60
	4.0	43	25	1.250	7.05
4.8	2.5	54	110	1.257	6.31
	3.0	51	65	1.255	6.46
	3.5	48	40	1.255	6.57
	4.0	46	30	1.258	6.86
8.0–5.0	2.5	55	45	1.255	5.11
	3.0	51	35	1.246	5.70
	3.5	48	25	1.250	5.80
	4.0	46	25	1.245	6.28

In general, the solids content and viscosity of the resin decreased as the F/U molar ratio increased. Differences in resin specific gravity were not significant. The high free-formaldehyde content for these resins was expected due to the high F/U molar ratio in the resin preparation. When compared among the same reaction pH conditions, the free-formaldehyde increased as the F/U ratio increased. It is noted also that, within the same F/U ratio, the free-formaldehyde decreased as the reaction pH increased. This result agreed with the general belief that the addition of formaldehyde is enhanced and the methylol compounds obtained are relatively stable under alkaline conditions as compared to that of acidic conditions.

Most UF resins were cured with the addition of catalysts such as NH_4Cl. The gel time was measured after the addition of two levels of NH_4Cl catalyst and the results are summarized as follows:

		1% NH_4CL		0.25% NH_4CL	
Reaction pH	Molar ratio	pH	Gel time min.	pH	Gel time min.
1.0	3.0	4.30	1.45	4.55	1.80
	3.5	4.35	1.28	4.20	1.55
	4.0	4.50	1.20	4.35	1.38
4.8	2.5	4.55	0.75	4.20	0.90
	3.0	4.35	0.70	4.05	0.87
	3.5	4.05	0.52	3.95	0.60
	4.0	3.95	0.42	3.95	0.55
8.0–5.0	2.5	4.50	0.81	3.95	0.97
	3.0	4.45	0.80	4.15	0.96
	3.5	4.30	0.70	4.10	0.85
	4.0	4.15	0.60	3.90	0.65

The resins catalyzed with strong acids (pH 1.0) resulted in gel times almost twice as long as those catalyzed with weak acids (pH 4.8) or alkaline conditions (pH 8.0). When compared at the same reaction pH, the gel time decreased as the F/U ratio increased. It should also be noted that the gel time decreased slightly as the level of NH_4CL addition increased as well.

Effect of reaction pH on resin structure

The effect of reaction pH on resin structure was investigated by ^{13}C-NMR spectroscopy. ^{13}C-NMR spectra of resins prepared at various pH conditions at formaldehyde to urea ratios of 3 : 1 are shown in Figure 1. Each signal observed in the ^{13}C-NMR spectrum could be assigned according to chemical shifts reported earlier (Tomita and Hatano 1978; Slonim *et al.* 1977; Ebdon and Heaton 1977). In the ^{13}C-NMR spectra of resins synthesized under strong acid conditions of pH 1.0, the signals attributed to the carbonyl carbons of uron derivatives were evident at

Table 1. ^{13}C-NMR analysis of urea resin sample

	Reaction pH						
	pH 1			pH 4.8		pH 8 → 5.0	
Structure	A		C	E	G		K
Total methylene	0.63 (20.4)	0.65 (17.7)	0.56 (13.2)	0.53 (16.9)	0.66 (15.8)	0.41 (12.7)	0.36 (8.2)
$-NH\underline{CH_2}NH-$	0.10	0.07	0.05	0.09	0.12	0.14	0.09
$-N(CH_2-)CH_2-)_2NH-$	0.30	0.32	0.29	0.32	0.37	0.18	0.14
$-N(CH_2-)CH_2N(CH_2-)-$	0.23	0.26	0.22	0.12	0.17	0.09	0.13
Total methylol	0.93 (30.0)	0.90 (24.8)	0.94 (22.3)	0.87 (28.3)	0.67 (16.1)	1.14 (35.2)	1.29 (29.8)
$-NH\underline{CH_2}OH$	0.19	0.19	0.20	0.31	0.25	0.50	0.49
$-NHCH_2OCH_2OH$	0.14	0.13	0.10	–	–		
$-N(\underline{CH_2}-)CH_2OH$	0.39	0.32	0.35	0.56	0.42	0.64	0.80
$-N(\underline{CH_2}-)CH_2OCH_2OH$	0.21	0.26	0.29	–	–		
Total methylated methylol	0.10 (3.2)	0.11 (3.1)	0.1 (2.3)	0.05 (1.5)	0	0	0
$-NH\underline{CH_2}OCH_3$	0.10	0.11	0.10	0.03	–	–	
$-N(CH_2-)CH_2OCH_2$	–	–	–	0.02			
Total dimethylene ether	0.52 (17.0)	0.48 (13.3)	0.48 (11.3)	0.44 (14.0)	0.70 (16.3)	0.91 (28.1)	1.02 (23.5)
$-NHCH_2OCH_2NH-$	0.13	0.18	0.16	0.14	0.31	0.50	0.49
$-N(CH_2-)CH_2OCH_2=$	0.39	0.30	0.32	0.30	0.39	0.41	0.53
Total free formaldehyde	0.92 (30.0)	1.50 (41.2)	2.15 (50.9)	1.22 (39.3)	2.14 (51.3)	0.77 (23.9)	1.69 (38.8)
$HOCH_2OH$	0.43	0.53	0.80	0.45	0.68	0.25	0.53
$HOCH_2O\underline{CH_2}OH$ $=NCH_2O\underline{CH_2}OH$	0.43	0.73	.05	0.62	1.10	0.41	0.87
$HO\underline{CH_2}OCH_3$ $-CH_2O\underline{CH_2}OCH_3$	0.06	0.24	0.30	0.15	0.36	0.11	0.29
Total carbonyl carbon	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$=NCON=$	0.75	0.82	0.85	1.00	1.00	1.00	1.00
URON	0.25	0.18	0.15		–	–	
$H_2NCONHCH_2OH$	–				–	–	
H_2NCONH_2	–	–					
Total formaldehyde	3.1 (100)	3.6 (100)	4.2 (100)	3.1 (100)	4.1 (100)	3.2 (100)	4.3 (100)
Combined formaldehyde	2.18 (70.3)	2.15 (58.8)	2.1 (49.7)	2.1 (60.7)	2.4 (48.9)	2.4 (76.1)	2.7 (61.2)

Note: Amount of formaldehyde is based on the molar ratio to urea residue (F/U). The value in parentheses is percentage (%) to total formaldehyde.

155–156 ppm as well as those of urea residues at about 160 ppm.

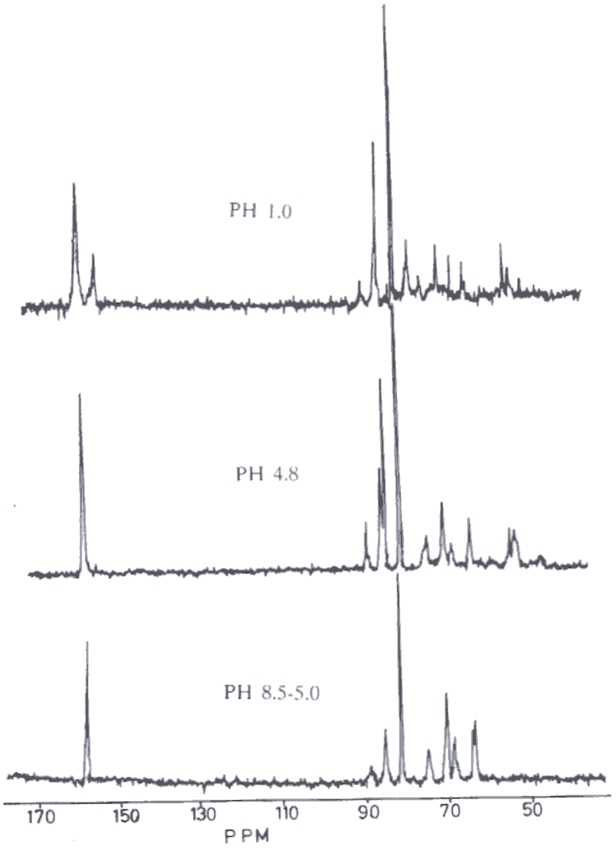

Fig. 1. ^{13}C-NMR spectra of UF resins reacted at various pH conditions at F/U ratio of 3/1.

The results of quantitative measurements on seven resins are summarized in Table 1. The high free formaldehyde content in all resins, caused by the high molar ratio of F/U, was confirmed also with free-formaldehyde determination by sodium sulfite method. When compared among resins made with the same molar ratios, the free formaldehyde content decreased with increased reaction pH implying that combined formaldehyde increased with increased reaction pH. A large amount of hemiformal methylol group was evident in resins prepared with higher free-formaldehyde. Methylene linkages between urea residues increased as the pH was lowered, while dimethylene ether linkages increased with increased reaction pH.

At the strongly acidic condition of pH 1.0, however, the greater part of dimethylene ether group was confirmed to be involved in the formation of uron rings. For example, in the resin with a F/U molar ratio of 3 : 1, the formation of uron ring amounted to 25% of the total urea. Since two methylene carbons are joined with a carbonyl carbon in the formation of the uron ring, the result indicated that the quantity of methylene carbon incorporated in uron was F/U = 0.5. On the other hand, the quantity of dimethylene ether as determined in Table 1 was F/U = 0.52, which was only slightly higher than the value of 0.5. Since the carbonyl carbon in the uron ring could not be detected in resins made at higher pH, the formation of uron derivatives was indicative of reactions made under strong acid conditions.

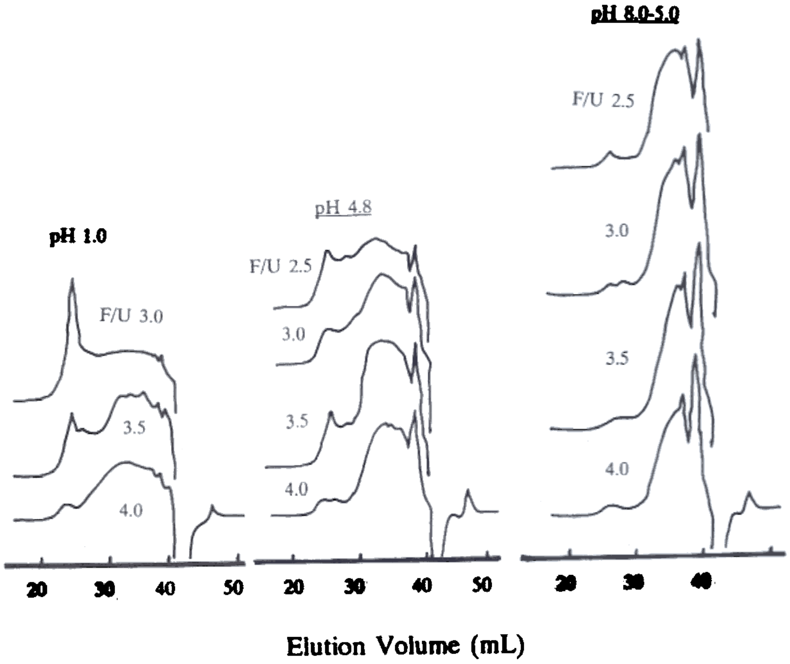

Fig. 2. GPC chromatograms of UF resins reacted at different pH and F/U ratios.

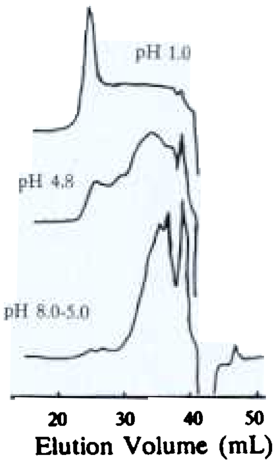

Fig. 3. GPC chromatogram of UF resins reacted at different pH conditions at F/U ratio of 3/1.

Gel permeation chromatography

Figure 2 shows the GPC chromatograms of UF resins reacted at different pH and F/U ratios. The significant effect of reaction pH on molecular weight distribution is illustrated in Figure 3. The large fraction of sample eluted between 21 and 29 mL (upper chromatogram) indicated that strong acidic conditions favored condensation. On the other hand, the strong signal between 30 and 39 mL (lower chromatogram) showed that alkaline conditions enhanced methylol formation. The high methylol content in resins made under alkaline conditions as compared to acidic conditions was also detected by ^{13}C-NMR analysis (Table 1). In general, GPC can be divided into two groups of peaks. The peaks between 39 and 40 mL elution volume are those of urea or mono-methylol urea, the first negative peak between 41 and 43 mL is due to formaldehyde and water in the sample. These identifications were made by comparing GPC chromatograms of UF resins before and after addition of urea, formaldehyde, and water to the sample. Other peaks evident at early stages of reaction (i.e., those between elution volumes 30 and 39 mL) may be dimers, trimers and tetramers of polymethylol urea as indicated by previous workers (Dankelman *et al.* 1976; Dunky and Lederer 1982; Matsuzaki *et al.* 1980; Tsuge 1980). These peaks can be integrated together (group A) as an estimate of the amount of low molecular weight products. The peaks at low elution volumes (i.e., 21 to 29 mL) can be integrated together (group B) to represent a measure of the high molecular weight products obtained from condensation reactions.

The composition of low and high molecular weight products are summarized as follows:

Resin	pH	F/U ratio	Low molecular weight products	High molecular weight products
			%	%
A	1.0	3.0	54.7	45.3
B	1.0	3.5	78.2	21.8
C	1.0	4.0	88.8	11.2
D	4.8	2.5	70.5	29.5
E	4.8	3.0	79.8	20.2
F	4.8	3.5	88.2	11.8
G	4.8	4.0	92.3	7.7
H	8.0–5.0	2.5	94.8	5.2
I	8.0–5.0	3.0	96.2	3.8
J	8.0–5.0	3.5	97.0	3.0
K	8.0–5.0	4.0	96.1	3.9

The proportion of high molecular weight products increased substantially as the reaction pH decreased. Furthermore, the F/U molar ratios interacted with reaction pH to effect resin molecular weight. At acidic pH the high molecular weight products increased as F/U ratio decreased; while, at alkaline pH, little difference was evident between the high or low molecular weight products at various F/U ratios. It should be noted, however, the molecular weight buildup was so fast for the resin made with a F/U ratio of 2.5 at strong acidic condition (i.e., pH 1) that an insoluble gel formed early so control of the reaction was not practical.

Mechanical properties and formaldehyde emission

Average mechanical properties and the formaldehyde release of the particleboards are summarized as follows:

Resin	pH	F/U Ratio	Internal Bond Strength	Bending Strength MOR	Bending Strength MOE	Formaldehyde Emission
		psi	MPa	MPa	MPa	ppm
A	1.0	3.0	0.56	11.56	2459	1.4
B	1.0	3.5	0.57	11.93	2344	2.1
C	1.0	4.0	0.55	11.52	2241	2.3
D	4.8	2.5	0.70	11.72	2523	1.6
E	4.8	3.0	0.69	12.20	2772	2.0
F	4.8	3.5	0.71	12.67	2613	2.5
G	4.8	4.0	0.71	12.05	2606	3.0
H	8.0–5.0	2.5	0.74	12.60	2689	1.9
I	8.0–5.0	3.0	0.67	12.58	2779	2.3
J	8.0–5.0	3.5	0.62	12.11	2579	3.4
K	8.0–5.0	4.0	0.68	12.51	2717	3.8

Panels bonded with resins catalyzed at strong acid conditions (A–C) resulted in consistently lower internal bond strength and bending strength. On the other hand, resins catalyzed with weak acid (D–G) and alkaline (H–K) conditions produced panels with slightly higher formaldehyde emission. When compared among the resins catalyzed with weak acid and alkaline conditions, little difference was evident in the mechanical properties. However, alkaline catalyzed resins resulted in consistently higher formaldehyde emission than that of weakly acidic conditions.

One of the interesting results of the study was the formation of a high percentage of uron derivatives under strong acidic conditions. The formation of these cyclic derivatives was not detected in resins made using either weak acid or alkaline conditions. The results indicated that resins formulated under strong acidic conditions differed considerably from conventional UF resins formulated in the past. Experiences with UF resins used in the textile and paper industries has indicated that cyclic compounds are desirable compounds as cross-linking agents (Meyer 1979). This study also showed the resins catalyzed under strong acidic conditions resulted in lowest formaldehyde emission. The result is particularly significant since the formaldehyde release from the glued wood products is the most pressing environmental problem concerning the wood industry. It should be mentioned, however, the bonding strength was slightly lower using resins synthesized under strong acidic conditions. Furthermore, it was also noted that the resins catalyzed at strong acidic conditions resulted in cure rates, as measured by gel time, almost twice as long as those of resins catalyzed with weakly acidic or alkaline conditions. The slower cure rate was not expected because the strong acid was known to favor condensation as shown in GPC data. The result suggests that curing agents other than conventional NH_4Cl, such as mixed catalysts, should be evaluated in order to improve the cure rate. Development of highly reactive catalyst system would be important economically and practically for the UF resins.

Of the three pH conditions evaluated in the study, both weak and strong acid catalysts systems are not commonly used in present UF resin formulation. Based on the bond strength and formaldehyde emission data, however, the weak acid catalysis seems to provide the best compromise between the strong acid and the conventional alkaline-acid catalyst system currently used for formulating UF resin wood adhesives.

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