

Here Is

An Ion Exchange Casting Resin . . .

that allows greater flexibility in application than conventional strongly acid ion exchange resins as its form is not limited to beads and films. Greater resistance to cracking and disintegration on drying and rewetting is another advantage

A strongly acid ion exchange resin which could be cast in pieces 12 inches or more maximum dimension has been prepared by the condensation of *p*-phenolsulfonic acid with formaldehyde. Shrinking, swelling, and cracking have been greatly reduced. The method seems preferable to sulfonation of a casting made from unsulfonated resin. Resins have been prepared previously by this method but not in large pieces (1-5).

Procedure

Using a 12-liter flask, 1458 grams (18 moles) of formalin are added dropwise to a mixture of 8440 grams (30 moles) of 65% *p*-phenolsulfonic acid (Koppers or Monsanto) and 1440 grams of water and stirred rapidly. The precipitate formed is removed by filtration through a Hormann filter using a D-O pad; 92.7% is recovered as filtrate. The solution is bodied by heating overnight (about 16 hours) at 70° C. (The exothermic reaction, once started, requires the removal of heat by a cold finger inserted in the mixture in addition to a reflux condenser. After a short period, temperature of 70° C. is maintained by external heating.) Then 259 grams (92.7% of 3 moles) of aniline are added. Water is removed by distillation under reduced pressure until the weight is 7941 grams corresponding to 70.0% solids. The final ratio is 1:0.55 when aniline is considered a reactant.

The casting solution is prepared by adding 3300 grams of formalin to 10,000 grams of first-stage resin, or a final ratio of 1:1.6. This solution in a ceramic mold is immersed in mineral oil at 70° C. for 8 hours. This corresponds to about 6 hours at 70° C. for the resin

Table I. Concentrating the First Stage Resin by Distillation Shows Improvement

All samples cured 72 hours at 90° C.

Ratio; Phenol- sulfonic acid/ Form- aldehyde	Modulus of Rupture, ^a P.S.I.	Total Exchange Capacity, ^b Meq./G
Unconcentrated Resin		
1:1.0	Disintegrated on washing	2.2
1:1.4	534	1.6
1:1.8	712	0.84
1:2.2	519	0.62
70% First Stage Resin		
1:1.0	Disintegrated on washing	2.5
1:1.4	206	2.1
1:1.8	1240	1.2
1:2.2	1330	0.84

^a Determined with Dillon tester on 4-inch span of 7/16 inch diameter cross section.

^b Based on dry resin. Water content determined azeotropically.

solution as 2 hours are required to bring it to oven temperature in the poorly conducting ceramic mold. The cooled casting washed free of sulfates, treated with 10% hydrochloric acid, and washed free of chlorides with deionized water is ready for use.

Results and Discussion

The precipitate formed during condensation, once removed, did not form again. The amount varied between 2 and 4%. As the phenolsulfonic acid contained up to 3% phenol, the precipitate is probably a highly condensed product of phenol and formaldehyde formed before the phenolsulfonic acid reacted. Dilution with water until the batch corresponded to one made with 55% acid is necessary to obtain a reasonable filtration rate.

The time required to body the resin solution varied with the ratio and the

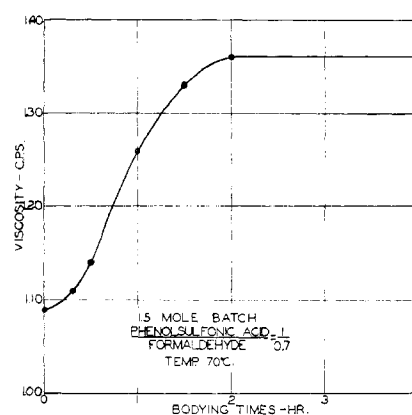


Figure 1. Viscosity change during bodying

The time required varies with ratio and batch size

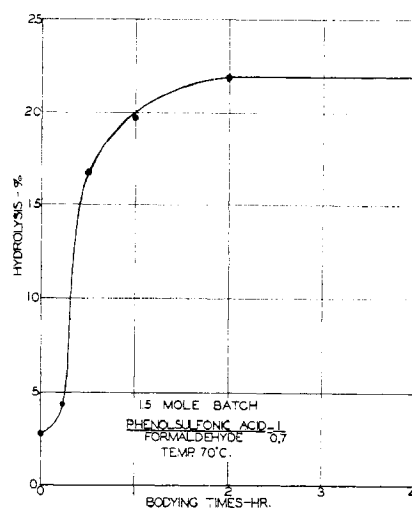


Figure 2. Hydrolysis during bodying is related in some way to presence of formaldehyde

batch size. On a 1.5-mole scale, a constant viscosity is reached between 2 and 4 hours (Figure 1) so 4 hours seemed safe. Larger batches up to 30 moles required much longer times.

Removal of sulfonic acid groups by hydrolysis during the preparation (Figure

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Table II. Emulsifiers

70% first-stage resin; final ratio 1:1.6; cured 72 hours at 70° C.; amount of emulsifier equivalent to 1% total mixture weight. Variation in amounts of emulsifier showed little or no improvement over 1%

Emulsifier	Source	Modulus, P.S.I.	
		Rupture	Elasticity
Amine 220	Union Carbide Chemicals Co.	1630	48,000
Aquarex D	E. I. du Pont de Nemours & Co.	721	40,000
Nonic 218	Sharples Chemicals, Inc.	1360	34,000 ^a
Nonic 261		1450	40,000
Santomer No. 3	Monsanto Chemical Co.	910	44,000
Tergitol NPX	Union Carbide Chemicals Co.	1100	43,000
Tween 80	Atlas Powder Co.	1300 ^b	41,000
2-Amino-2-methyl 1,3-propanediol	Commercial Solvents Corp.	1260	43,000 ^c
2-Amino-2-methyl 1-propanol		1180	42,000
Arquad 2C	Armour Chemical Division	1240 ^b	40,000
Arquad S		1180 ^d	49,000
Surface active agent BPE	American Cyanamid Co.	1420 ^b	46,000
Oronite N I-W	Oronite Chemical Co.	1400	53,000

^a Exchange capacity, 2.0 meq./gram. ^b 25% defective samples. ^c Exchange capacity, 1.8 meq./gram. ^d 20% defective samples.

2) make a three-dimensional polymer possible. This hydrolysis is in some way related to the presence of formaldehyde as with an equivalent amount of water and no formaldehyde, only 1.4% hydrolysis occurred in 6 hours. Hydrolysis can be reduced with sulfuric acid, but these differences are small and disadvantages of considerable sulfuric acid make it undesirable.

In the early work, curing after the addition of more formalin invariably

resulted in the formation of cracks, blisters, or deformation due to irregular swelling. Cures from 60 to 90° C., ratios of 1.0 to 2.2, and drying times up to 72 hours all give low flexural strengths of 500 to 700 pounds per square inch. Blistering is suppressed somewhat by equalizing the osmotic pressure inside the samples with baths of first 5% and then 1% sulfuric acid before washing.

Considerable improvement is obtained by concentrating the first-stage resin by vacuum distillation. Use of 70% first stage resin seemed to be the best compromise between strength and viscosity. This improvement is given in Table I.

As some nonhomogeneity developed during curing, emulsifiers are added and resulted in an improvement (Table II).

Hollow truncated cones 2.5 inches in diameter, 5 inches high, and 0.5 inch wall thickness made from some of these mixtures showed good stability under water but developed cracks on drying slightly in air.

The best castings are made from resins containing amines which probably formed resins with the formaldehydes. The stabilizing effect of 0.1 mole of various amines is shown in Table III. Emulsifiers are not used with the amines.

Lower ratios and milder cures are possible when amines are used (Table IV). However, a ratio of 1:1.6 and a cure of 6 to 8 hours at 70° C. are usually used. Castings including a small tank 11 × 3 × 6 inches and 0.5 inch wall thickness proved to be stable when exposed in air for 1 hour or more.

Beads of resin are made by pouring a 1:1.4 ratio mixture into rapidly stirred mineral oil at 70° C. The 70° C. temperature and stirring are continued until the beads are cured. These beads are completely stable to complete drying and rewetting.

Literature Cited

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Table III. The Stabilizing Effect of Various Amines

(In all cases the ratio of phenolsulfonic acid to formaldehyde is 1:1.6. Cured 24 hours at 85° C.)

Amine	Mole Amine ^a / Mole Phenol-sulfonic Acid	Modulus, P.S.I.	
		Rupture	Elasticity
Aniline	0.10	1940	46,000
<i>o</i> -Toluidine	0.10	1990	42,000
<i>p</i> -Toluidine	0.10	2110	48,000
α -Naphthylamine	0.05	1340	43,000
7-Aminonaphthalene-1,3-disulfonic acid	0.033	1170	41,000
Dimethylaniline ^b	0.05	1480	35,000
<i>o</i> -Phenylenediamine	0.05	1390	48,000
<i>m</i> -Phenylenediamine	0.05	1010	40,000
<i>p</i> -Phenylenediamine	0.05	1590	40,000
Tris (hydroxymethyl) amino-methane	0.10	1200	41,000
Morpholine	0.10	1400	36,000
Ethylenediamine	0.10	1170	39,000
2-Aminopyridine	0.10	2000	50,000

^a When feasible 0.10 mole of amine per mole *p*-phenolsulfonic acid is used. In many cases this solution is too viscous so the amount is reduced to 0.05 mole or less.

^b 80% defective samples.

Table IV. Milder Cure Conditions Are Possible with Amines

Ratio ^a	Cure Time, Hr.	Modulus, P.S.I.		Exchange Capacity, ^b Meq./G.
		Rupture	Elasticity	
1:1.6	2	1720	23,000	1.5
	4	1810	35,000	
	6	1990	37,000	
	8	2110	42,000	
	24	2460	50,000	
1:1.5	2	1360	28,000	1.7
	4	1760	30,000	
	6	1840	27,000	
	8	2060	35,000	
	24	1910	41,000	
1:1.4 ^c	2	1280	19,000	1.8
	4	1550	29,000	
	6	1380	30,000	
	8	1510	30,000	
	24	1450	40,000	
1:1.3	2	1490	21,000	
	4	1680	28,000	
	6	1450	27,000	
	8	1140	31,000	
	24	1170	36,000	

^a Ratios calculated as moles *p*-phenolsulfonic acid plus moles aniline to moles formaldehyde.

^b Based on dry resin. ^c All but 2- and 8-hour cures had 16.7% defective samples.