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**EUROPEAN PATENT APPLICATION**

21 Application number: 84100380.9

51 Int. Cl.<sup>3</sup>: **C 08 G 18/54**  
**C 08 G 8/36**

22 Date of filing: 16.01.84

30 Priority: 17.01.83 US 458283

43 Date of publication of application:  
22.08.84 Bulletin 84/34

84 Designated Contracting States:  
DE FR GB IT

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54 **Phenolic polyols and rigid cellular compositions derived therefrom.**

57 Modified benzyl ether-containing resole polyols derived from phenol, paraformaldehyde and an aliphatic hydroxyl compound are prepared using a metal derivative as a catalyst. These polyols react with organic polyisocyanates to yield closed cell, low friability, low combustibility, rigid polyurethane foams without the need for post curing at elevated temperature. They are also useful in the preparation of modified rigid polyisocyanurate foams.

PHENOLIC POLYOLS AND RIGID CELLULAR  
COMPOSITIONS DERIVED THEREFROM

This invention relates to phenol/aldehyde-based  
5 polyols and to rigid cellular compositions derived from  
these polyols. Specifically it deals with modified benzylic  
ether-containing resole polyols and the rapid curing, low  
combustibility, low friability, closed cell, rigid cellular  
plastic compositions obtained by reaction of the polyols  
10 with polyisocyanates.

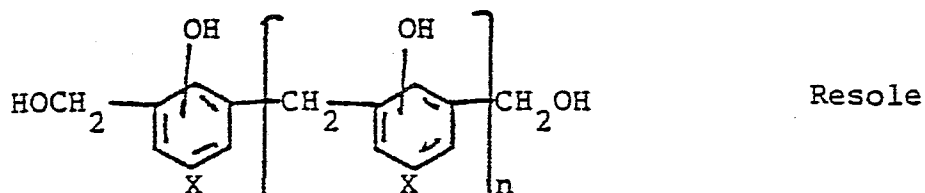
Simple phenolic foams obtained by the thermal and  
acid catalyzed polymerization of resole resins or of novolac  
resins with added aldehydic compounds are old in the art.  
Such foams are noted particularly for their excellent fire  
15 resistance. However, they also possess the properties of  
punking, extreme friability, and being opened-cell which  
make them ill-suited for insulation or any use where the  
foam must be handled or support weight. There is a long-  
established desire to use such phenolic resins in cellular  
20 polyurethane or polyisocyanurate formations with the hope of  
improving strength, insulation, and punking properties while  
retaining the inherent low combustibility of phenolic foams.

In the art of phenol/aldehyde condensates, it is  
known that the properties and structures of the products

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vary, primarily dependent on the phenol/aldehyde mole ratio and the type of catalysis used for the condensation. Alkaline catalysis (alkaline hydroxide, organic amines) with aldehyde in excess results in products known as "resoles"

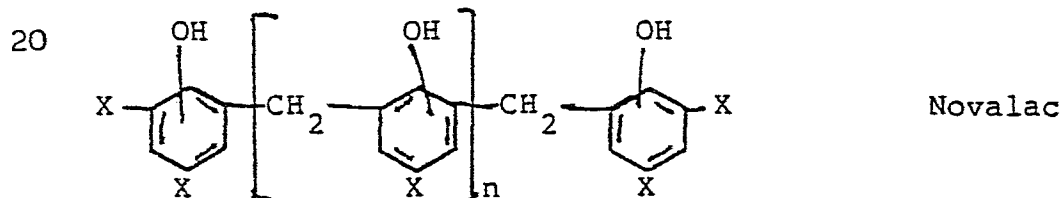
5 having the following idealized formula:



where X is H or  $-\text{CH}_2\text{OH}$  and  $n = 0, 1, 2, 3$ , or higher.

10 The hydroxymethyl ring substituents of the above "resole" are highly reactive toward unsubstituted ortho or para phenolic ring positions. Thus, such condensates can be easily cross-linked to form infusible solids by heating or acidifying. Acid catalysis is not normally used in the  
15 preparation of resoles since cross-linking leading to gelation can easily occur.

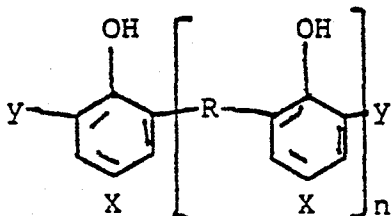
When the phenol is used in molar excess, the product has little or no hydroxymethyl substitution as shown in the following idealized formula:



where X is hydrogen and  $n = 0, 1, 2, 3$ , or higher.

Such products are called "novolacs" and, lacking the reactive hydroxymethyl substituent, can be prepared under acid catalysis to benefit from a faster rate of formation. In all phenol/aldehyde condensates (novolacs and  
 5 resoles) small quantities of starting materials and intermediates are present.

A British study (Fraser, et al, J. Appl. Chem. 7 689 (1957) showed that electropositive divalent metal ions which also catalyze the phenol/aldehyde condensation, cause  
 10 (1) the substitution on the phenol ring to occur predominantly in the ortho rather than the para position and  
 (2) results in the formation of a high percentage of benzylic ether linkage in addition to some methylene linkages between phenol rings. This is illustrated in the  
 15 following formula:



high ortho  
 benzylic ether-  
 containing resin

20

where R is  $-\text{CH}_2\text{OCH}_2-$  or a mixture of  $-\text{CH}_2\text{OCH}_2-$  and  $-\text{CH}_2-$

X is H

Y is H or  $-\text{CH}_2\text{OH}$

and  $n = 1, 2, 3$ , or higher.

The differences between these three types of phenol/aldehyde condensates is demonstrated in their conversion to highly cross-linked infusible phenolic polymers. Resoles, containing an abundance of reactive hydroxymethyl groups and available unsubstituted ring positions, react when heated alone. Novolac, having no significant amount of hydroxymethyl groups, must be heated with an aldehyde source (hexamethylene tetraamine or paraformaldehyde) to undergo cross-linking reaction. The benzylic ether-containing resin will cross-link at a slow rate as the benzylic ether linkage decomposes (at 150°C and higher temperature) to form methylene bridges and liberate formaldehyde which serves to cross-link the resin. Thus, the structural differences between novolacs, resoles, and benzyl ether-containing resins are reflected in and explain the known differences in chemical behavior of these different phenol/aldehyde condensates.

The use of benzylic ether-containing resins in the preparation of polyurethanes has been disclosed in Japanese Patent 1973-43,097 (to Hatashi Chemical Industries) and U. S. Patent 3,948,824 (to Robins). The benzylic ether resoles used by Robins were prepared according to U. S. 3,485,797. While these patents represented novel improvements over the then existing art, the polyurethane foams obtained by the teaching of these patents have been found

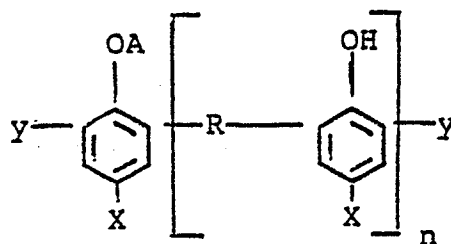
5 both in our laboratories and by others to be deficient in one or more properties (see Example 2 hereinafter; U. S. 4,293,658; and Schafer, et al, J. Cellular Plastics 1978 p. 147). The polyurethane foams obtained were slow to cure and friable. To achieve desirable strength and friability properties required post-curing of the foams at elevated temperatures.

In Great Britain 2,033,413, modified resoles are etherified with aliphatic polyols (under acid conditions) and the products are used to prepare polyurethane or polyisocyanurate foams. However, these phenol-formaldehyde derived resins yielded polyurethanes with poor inherent flammability properties. To obtain suitable flame retardant foams required the use of chlorophenol as the phenolic reactant and/or added phosphate-type flame retardant in the foam formulation.

A seemingly related group of patents have recently issued to Vasishth et al and been assigned to Cor Tech Research Ltd. (U. S. 4,235,989; 4,219,634; 4,184,032; 4,140,845). Although the patents disclose and teach the preparation of benzyl ether-containing resins in the presence of methanol, the processes and products differ from the present invention in several important respects. The patents teach the use of aqueous formaldehyde plus added water such that the condensation is carried out in an

aqueous system until the resin precipitates as a second phase. Second, the reaction is carried out at a lower temperature, from 90°C to "approximately 100°C" (reflux). Finally, infrared and NMR spectroscopy reported in the 5 patents did not reveal any "reacted" methanol and the resins were not used as "polyols" in polyurethane formation.

This invention is a class of modified benzyl ether-containing resole polyols obtained by a process 10 comprising reacting at 100°C to 130°C (a) a phenol which is free of ortho substituents, (b) a molar excess relative to the phenol of a nonaqueous aldehyde having the formula  $RCHO$  where R is hydrogen, an alkyl group of 1 to 6 carbon atoms, or a halogenated alkyl group of 1 to 3 carbon atoms, and (c) 15 less than fifty mole percent relative to the phenol of an aliphatic hydroxyl compound having a functionality of 1 to 4, 1 to 12 carbon atoms, and 0 to 5 ether oxygen atoms in the presence of a catalytic amount of a metal derivative selected from the group consisting of (i) carboxylate salts 20 of divalent ions of Mn, Zn, Cd, Mg, Co, Ni, Fe, Pb, Ca, Ba, and (di  $C_1-C_5$  alkyltin) where the carboxylate ions each contains 1 to 20 carbon atoms, and (ii)  $(C_nH_{2n+1})_4TiO_4$  where n is an integer of 3 to 8. These polyols are believed to have the following formula:



where n is 1, 2, 3, or a higher integer;

x is H, halogen,  $C_1-C_{12}$  alkyl or a mixture thereof;

y is a mixture of hydrogen and  $-CH_2OA$  ;

5 A is a mixture of hydrogen and a radical or mixture of radicals resulting from removal of a hydroxyl group from an aliphatic hydroxyl compound or mixture of compounds having 1 to 4 hydroxyl groups, 1 to 12 carbon atoms and 0 to 5 ether oxygen atoms;

10 R is  $-CH_2OCH_2-$  or a mixture of  $-CH_2OCH_2-$  and  $-CH_2-$  with the ratio of  $-CH_2OCH_2-$  groups to  $-CH_2-$  groups being greater than 1; and

wherein the amount of substituent radical A is at least 5 mole percent but less than 35 mole percent of the phenol rings present.

15 The polyols are especially suited for reaction with organic polyisocyanates to yield low combustibility, low friability, closed-cell, rigid cellular plastics. The polyurethane foams are rapid curing and do not require post curing to achieve excellent physical properties.

The modified benzyl ether-containing resole polyols of this invention are prepared by the metal salt or

titanate ester catalyzed reaction of a phenol with a molar excess of a nonaqueous aldehyde and a modifying amount of a mono- or polyhydroxyl compound.

The general procedure for the production of these  
5 polyols is to charge the phenol, nonaqueous aldehyde, catalyst, and modifying hydroxyl compound to a stirred reactor fitted with a condenser system which is suitable for either reflux or distillate removal. The stirred mixture is heated rapidly to about 100°C to 105°C at which point a  
10 slight exotherm occurs. The mixture is maintained at 110°C to 115°C for several hours under slow reflux. The reaction temperature is then increased to approximately 120°C and the distillate (essentially water) removed. After the desired amount of water, which is indicative of the desired degree  
15 of phenol/aldehyde/hydroxyl compound condensation, is collected, the mixture is cooled to about 60°C and stripped at reduced pressure to further reduce the water content to less than three, preferably less than one weight percent of the polyol. No effort is made to neutralize or remove residual  
20 catalyst which remains in the product.

The desired phenol/aldehyde condensate is one possessing hydroxymethyl substituents and, therefore, use of a molar excess of aldehyde is indicated. The useful mole ratio is from 1.1 mole to 2.25 moles of aldehyde per mole of  
25 phenol. When the mole ratio falls below 0.9, the condensate

becomes more "novolac" in structure (lacking hydroxymethyl substituents) and as the mole ratio approaches three, more para substitution and/or cross-linking occurs. The preferred mole ratios of aldehyde to phenol range from 1.2 to 5 1.8.

The amount of modifying hydroxyl compound used is governed by the amount required to achieve improvement in the normal high friability and opened cell structure of phenolic foams and limited by the amount which would obviate 10 the fire resistance of the phenolic structure. Below about one mole percent of hydroxyl compound based on the amount of phenol used, the hydroxyl compound is ineffective in improving strength and friability properties. Above 50 mole percent on the same basis, the hydroxyl compound causes the 15 loss of the inherent fire retardancy of the phenolic structure. Thus, a useful range of hydroxyl compound is 1 to 50 mole percent of the phenol compound used. The preferred range is 10 to 25 mole percent.

Metal derivatives are effective as catalysts at 20 concentration of 0.01 to 0.10 weight percent metal based on the total charge. The preferred catalyst level is 0.04 to 0.07 weight percent metal.

No solvent is needed for this reaction. Although certain solvents can be used as entrainment agents to 25 facilitate the removal of water, we have found this to be

unnecessary. Water is easily removed essentially as it forms simply by maintaining the reaction mixture at or above a temperature of 120°C.

Phenols which are suitable for use in the preparation of these products are those which are unsubstituted in the ortho positions but which may be substituted in the meta or para positions with halogen,  $C_1$  to  $C_{12}$  alkyl, or halogen-substituted alkyl of 1 to 6 carbon atoms. Examples of such phenols are phenol, p-cresol, p-tertiarybutylphenol, p-chlorophenol, p-bromophenol, p-trifluoromethylphenol, p-(2,3-dibromopropyl)phenol; 3,5-xyleneol; 3,5-dichlorophenol, p-dodecylphenol, p-trichloromethylphenol, p-nonylphenol, as well as mixtures of any of the foregoing. The preferred phenolic reactant is phenol itself or phenol mixed with a minor amount of the aforementioned substituted phenols.

Aldehydes which are suitable for use in the preparation of the polyols of this invention are aliphatic or halogenated aliphatic aldehydes having the formula  $RCHO$  where R is hydrogen or alkyl of 1 to 6 carbon atoms, optionally halogenated. Examples of such aldehydes are formaldehyde, acetaldehyde, pivaldehyde, hexanal, chloral, and 2,3-dibromopropanal. The preferred aldehyde is formaldehyde. Preferably the aldehyde is used in a nonaqueous state such as paraformaldehyde, trioxane, paraldehyde, or chloral.

The modifying hydroxyl compound suitable for use in the preparation of the polyols of this invention are aliphatic monols, diols, triols, or tetrols having 1 to 12 carbon atoms and 0 to 5 ether oxygen atoms or mixtures thereof. Examples of such hydroxyl compounds are methanol, ethanol, butanol, ethylene glycol, diethylene glycol, propylene glycol, trimethylene glycol, 1,4-butanediol, 2,3-butanediol, 1,3-butanediol, 1,12-dodecanediol, 1,2,5-hexanetriol, trimethylolpropane, pentaerythritol, tripropylene glycol, tetrapropylene glycol, hexaethylene glycol. The preferred class of hydroxyl compounds are the diols, especially 1,4-butanediol and diethylene glycol.

The catalyst used in the preparation of the modified benzylic ether-containing resole polyols of this invention is selected from derivatives of certain metals. These are the  $C_1-C_{20}$  carboxylic acid salts of the group of divalent metal ions consisting of those of Mg, Ca, Mn, Fe, Co, Ni, Zn, Cd, Ba, and Pb (with or without added PbO);  $C_1-C_{20}$  carboxylic acid salts of divalent (dialkyltin) where the alkyl groups each contain 1 to 5 carbon atoms; and alkyl (3 to 8 carbon atoms) ortho titanates. Examples of suitable catalysts include lead naphthenate (with or without added PbO), zinc neodecanoate, cobalt naphthenate, tetrabutyl titanate, tetraoctyl titanate, manganese valerate, ferrous lactate, cadmium acetate, zinc benzoate, zinc acetate,

dibutyltin dilaurate, dimethyltin diacetate, lead butyrate.

The preferred catalysts are zinc neodecanoate, lead naphthenate, and dibutyltin dilaurate. The catalyst used in the polyol preparation is not removed or neutralized and remains  
5 in the product.

The modified benzyl ether-containing resole polyols prepared with the above indicated preferred materials have viscosities of less than 1,500,000 cps at 25°C and generally in the range of 5000 to 650,000 cps at 25°C.  
10 The hydroxyl number values of the products, determined by the phenyl isocyanate method, generally range from 375 to 675, mostly in the 500 to 600 range.

The rigid cellular compositions derived from these novel polyols are made by state of the art techniques and  
15 are "phenolic" containing polymers with superior properties requiring no special treatment or equipment for their manufacture. Thus like any ordinary polyol, they can be reacted with organic polyisocyanates in the presence of the usual urethane catalysts using water or volatile organic  
20 blowing agents along with surfactants, plasticizers, fillers, or other additives. Reaction is achieved by intensely mixing the ingredients for a brief period and allowing the mixture to react. The products cure rapidly at room temperature without application of heat. Similarly the  
25 polyols can be used in the manufacture of urethane-modified

polyisocyanurate foams by using a large molar excess ("high index") of polyisocyanate, a blowing agent, a surfactant, and an isocyanurate catalyst such as potassium acetate or tris(dimethylaminopropyl)hexahydrotriazine.

- 5           Suitable polyisocyanates for manufacture of these novel rigid cellular plastics are any organic di- or higher functionality isocyanate which is reactive with Zerewitinoff type hydrogen atoms. Examples of such isocyanates are hexamethylene diisocyanate, 1,3- or 1,4-cyclohexane diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexane isocyanate, 2,2'-, 2,4'-, or 4,4'-dicyclohexylmethane diisocyanate, 1,3- or 1,4-bis(isocyanatomethyl)cyclohexane, m- or p-xylylene diisocyanate, 2,4- or 2,6-toluene diisocyanate, 2- or 4-methyl-1,3-cyclohexane diisocyanate, 1,3,5-tris(6-isocyanatohexyl)isocyanurate, N,N',N"-tris(6-isocyanatohexyl)biuret, 2,2'-, 2,4'- or 4,4'-diphenylmethane diisocyanate, 2,2'-, 2,4'- or 4,4'-diphenyl diisocyanate, 3,3'-dimethyl-2,2'-, 2,4'- or 4,4'-diphenylmethane diisocyanate, bis(4-isocyanatophenyl) ether or sulfide, polyphenyl
- 10
- 15
- 20 polymethylene polyisocyanate, or mixtures of any of the aforementioned isocyanates. Aromatic polyisocyanates are preferred and in particular the mixture of diphenylmethane diisocyanate isomers with polyphenyl polymethylene polyisocyanates ("crude MDI") is the isocyanate of choice.

The catalysts used for polyurethane formation are

those known in the art and consist of tertiary amines, metal salts, or mixtures thereof. Examples of such suitable catalytic compounds are triethylamine, dimethylaminoethanol, N,N,N',N'-tetraethylethylenediamine, N,N,N',N'-tetramethyl-1,3-butanediamine, bis(dimethylaminoethyl)ether, N,N-dimethyl-3-dimethylaminopropionamide, 1,4-diazo[2.2.2]-bicyclooctane, N-methyl- or ethylmorpholine, stannous oleate, stannous 2-ethylhexanoate, dibutyltin dilaurate, dibutyltin dilauryl mercaptide, dibutyltin diacetate, lead naphthenate, zinc stearate, or mixtures thereof. Amine catalysts are preferred and the most preferred catalyst is diazabicyclooctane.

Blowing agents suitable for use in the preparation of these polyurethanes foams are water (which reacts with the isocyanate to form carbon dioxide) and volatile low boiling organic compounds. Examples of such compounds are alkanes such as pentane or hexane, oxygenated compounds such as methyl formate, halogenated aliphatic compounds such as fluorotrichloromethane or methylene dichloride. The preferred blowing agents are water, methylene dichloride, fluorotrichloromethane (Refrigerant 11), or mixtures thereof.

Suitable surfactants to serve as emulsifying agents or cell stabilizers in the manufacture of these

polyurethane foams are alkylarylsulfonates such as sodium didecylbenzenesulfonate, alkali metal or ammonium salts of alcohol sulfates such as potassium lauryl sulfate or ammonium salt of sulfated castor oil, oxyethylated fatty  
5 alcohols or acids such as oxyethylated tetradecanol containing 63 percent oxyethylene by weight, or silicone surfactants such as polyalkylsiloxane-polyoxyalkylene block copolymers. The preferred surfactants are the silicone surfactants.

10 Plasticizers such as tris(chloroethyl) phosphate or didecylphthalate may be incorporated into the foam if desired.

Chain extenders such as low molecular weight diols may be used in quantity of less than 10 percent by weight of  
15 the polyol. Such low molecular weight diols can also serve to reduce the polyol viscosity for use in machine foaming.

The foams obtained by the practice of this invention are rapid curing, rigid, closed-cell polyurethanes which show good strength and flammability properties.

The following examples show the preferred embodiments of this invention in greater detail. In the examples, all parts given are by weight unless otherwise specified. The test results reported are based on the following ASTM

5 tests:

Tumb. Friab. = tumbling friability test (C421)

Butler Chimney = combustion test (D3014)

K Factor = thermal insulation test (C518)

10% Comp. Strength = force for 10% compression (D1621)

NBS Smoke = maximum smoke density (E662)

Materials used in foam formulations were:

DC-193 - a polyoxyalkylene-polydialkyl-siloxane block copolymer sold by Dow Corning Company

F-11A - stabilized fluorotrichloromethane  
- a refrigerant sold by DuPont Company

PAPI 135 - a polymethylene polyphenylene polyisocyanate/diphenylmethane diisocyanate mixture (functionality of 2.7) sold by Upjohn Company

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DABCO R8020 - a tertiary amine catalyst consisting of 20 percent diazabicyclooctane and 80 percent dimethylaminoethanol sold by Air Products and Chemicals Company, Houdry Division

5

POLYCAT 8 - N,N-dimethylcyclohexylamine sold by Abbott Laboratories, Chemicals Division

10 LUPRANATE M20 - a polymethylene polyphenylene polyisocyanate/diphenylmethane diisocyanate mixture (functionality of 2.7) sold by BASF Wyandotte Corporation

Example 1

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Phenol (634.24 parts), 91 percent paraformaldehyde (364.5 parts), 30 parts of 1,4-butanediol, 0.39 parts of PbO, and 0.88 parts of lead naphthenate solution (24 percent Pb) were charged to a reactor fitted with a mechanical stirrer, thermometer, and a reflux condenser/takeoff assembly. The stirred mixture was heated at 110°C to 116°C for 2 hours with total reflux and then the distillate was taken off while the mixture was heated to 126°C to 128°C.

When the major portion of the water of reaction had been removed at atmospheric pressure, the pressure was reduced to remove residual water. The stripped resin polyol had a hydroxyl number of 575 mg KOH/g and a water content of 0.5 percent.

15

Comparative Example A

Following the process of U. S. 3,485,797 - Example 1, a state of the art benzylic ether-containing resole polyol was prepared. The charge of reactants was the same as in the above Example 1 except that no butanediol was charged. The preparation was carried out in the same equipment used in Example 1, and the reaction conditions were the same. The stripped resin polyol obtained had a hydroxyl number of 593 and a water content of 1.1 percent.

The products of the two prior examples were compared in polyurethane behavior by conventional hand foaming methods. This comparison is summarized in Table I which shows the formulation used and the properties of the foams obtained. It is readily apparent that the foam prepared from the polyol of the present invention (Foam 1) is superior to those (Foams A1 and A2) prepared from a polyol of the prior art in friability, flammability, and insulating (closed-cell) properties.

TABLE I

Foam No.	A1	A2	1
Polyol of Comp. Ex. A, pbw	100	100	—
15 Polyol of Example 1, pbw	—	—	100
DC-193, pbw	3.4	3.4	3.0
F-11A, pbw	51.4	51.4	42.5
DABCO R8020, pbw	0.25	0.20	0.30
PAPI 135 (120 Index), pbw	169	169	174.5
20 Properties of Foam:			
Density, pcf	1.55	1.69	1.86
Tumb. Friability, % wt.chg.	-87.5	-100	-7.9
Butler Chimney Test, % weight retained	62.4	51.8	80.6
25 K-factor, initial	0.168	0.176	0.129

U.S. 4,519,010  
0116308  
Examples 3 and 4

The preparation of benzylic ether resole polyols modified with different levels of 1,4-butanediol and using a different catalyst (zinc neodecanoate -16 percent Zn) is  
5 summarized in Table II. The reaction conditions used in these preparations are otherwise the same as described in Example 1. Table II also shows the properties of the polyurethane foam derived from the polyols. It can be readily seen that in comparison with Example 1, the use of higher  
10 quantities of butanediol is also effective in reducing friability and improving insulating properties. Note that at the higher level of butanediol (32 mole percent of the phenol) the fire retardance is less than at lower levels.

TABLE II

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Example	3	4
Polyol Preparation Charge (pbw):		
Phenol	650	650
5 Paraformaldehyde (91%)	356	356
Zinc Neodecanoate (16% Zn)	4.0	4.0
1,4 Butanediol	100	200
Polyol Properties:		
Hydroxyl number	523	534
10 Water content, %	1.45	1.6
Foam Formulation (parts/hundred parts polyol):		
DC-193	3.0	3.0
DABCO R8020	0.5	0.5
F-11A	33.2	32.7
15 PAPI 135 (120 Index)	177.1	183.0
Foam Properties:		
Density, pcf	2.13	1.91
Tumb. Friab., % wt. chg.	-1.25	-0.87
Butler Chimney Test, 20 % wt. retained	81	66
K-Factor, initial	0.114	0.123

Example 5-11

The usefulness of this invention over a wide range of formaldehyde-phenol ratios is demonstrated in the series

of experiments summarized in Table III. A mixture of phenol (83.0 mole percent) and p-nonylphenol (2.7 mole percent) containing 1,4-butanediol (14.3 mole percent) was reacted in the presence of lead naphthenate catalyst in the manner  
5 described above with varied quantities of paraformaldehyde. The properties of the polyols and the polyurethane foams derived therefrom are shown. Throughout the range of formaldehyde-phenol ratios tested, the use of butanediol as a reactant resulted in polyols which yielded polyurethane  
10 foams with excellent strength, insulating (low K-factor), and flamability properties. The latter values are slightly reduced due to the nonylphenol used in making the polyol.

TABLE III

Example	5	6	7	8	9	10	11
Formaldehyde-Phenol Mole Ratio	0.90	1.10	1.33	1.55	1.73	2.00	2.25
Polyol Properties:							
Viscosity, cps x 10 <sup>-3</sup>	59.6	410	390	250	293	20.8	60.8
Hydroxyl number	542	504	476	491	526	537	610
Water content, %	0.11	0.63	0.24	0.39	0.44	0.20	0.12
Foam Formulation: (pbw)							
Polyol	100	100*	100	100	100	100	100
DC-193	1.0	3.0	1.0	1.0	3.0	1.50	3.0
F-11	40.5	39.6	40.2	39.7	40.8	37.6	46.9
DABCO R8020	1.0	0.5	0.7	0.5	0.5	0.5	0.5
PAPI 135, Index	100	100	100	100	100	80	100
Foam Properties:							
Density, pcf	1.66**	1.79	1.81	1.82	1.76	1.97	1.78
Tumb. Friab., % weight change	-8.7	-7.81	-3.0	-5.9	-2.59	-5.99	-3.8
Butler Chimney, % weight retained	73.2	67.0	60.8	62.8	63.7	69.5	60.3
NBS Smoke, D <sub>m</sub>	65	122	102	93	101	85	--
K-Factor, initial	0.122	0.126	0.122	0.125	0.130	0.112	0.127
10% Compression Strength, psi	33.0	32.2	33.7	32.4	33.3	32.3	31.4

\*Formulation contains 6 parts added propylene glycol.

\*\*This foam required post-curing at 100°C for one hour to achieve the properties shown.

Examples 12-19

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To demonstrate the variety of low molecular weight hydroxyl compounds which can be used to modify benzylic-ether containing resole polyols, the procedure of Example 15 was repeated with different added hydroxyl compounds and varied catalysts as shown in Table IV. The added hydroxyl compounds were used in an amount ranging from 9.7 mole percent (triethylene glycol) to 19.0 mole percent (1,2-propanediol) based on the phenol used. Each of these 10 modifiers yield a resole polyol having an acceptable viscosity and hydroxy number. Each resole polyol was used (Table V) to prepare a polyurethane foam with good friability, flamability, and insulating properties.

TABLE IV

Example	12	13	14	15	16	17	18	19
Phenol/formaldehyde charge,* (pbw)	90.8	90.9	90.8	90.8	90.8	90.2	90.2	90.2
Hydroxyl compound added, (pbw)								
1,4-Butanediol	9.0				9.0			
Triethylene glycol		9.0						
1,5-Pentanediol			9.0					
1,2-Propanediol				9.0				
Neopentyl glycol						9.4		
Trimethylolpropane							9.4	
Pentaerythritol								9.4
Catalyst used, (pbw)								
Lead Naphthenate (24% Pb)	0.24							
Zinc Neodecanoate (16% Zn)		0.12	0.18	0.18				
Dibutyltin dilaurate					0.24	0.38	0.38	0.38
Polyol Properties:								
Viscosity, cps x 10 <sup>-3</sup>	158	150	500	17.5	8.4	43.7	180	412
Hydroxyl number	503	518	512	636	478	495	507	538
Water content, %	0.78	1.74	1.78	1.90	0.12	0.17	0.27	0.56

\*A phenol-paraformaldehyde (91%) mixture in a ratio of 1.6 moles formaldehyde per mole phenol.

TABLE V

Example	12	13	14	15	16	17	18	19
Foam Formulation: (pbw)								
Polyol	100	100	100	100	100	100	100*	100*
DC-193	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
F-11A	27.7	21.7	29.2	35.7	45.2	45.8	45.7	47.1
DABCO R8020	0.5	0.5	0.5	0.5	0.2	0.5	0.5	0.5
PAPI 135, Index	120	120	100	100	120	120	120	120
Foam Properties:								
Density, pcf	2.27	2.25	2.02	1.63	1.52	1.56	1.53	1.47
Tumb. Friab., % weight charge	-4.0	-4.9	-8.2	-9.6	-4.6	-4.4	-3.9	-13.6
Butler Chimney, % weight retained	85.9	84.9	80.1	66.4	73.0	75.2	69.9	53.8
K-Factor, initial	0.129	0.135	0.125	0.143	0.139	0.138	0.139	0.148
10% Compression Strength, psi	53.2	--	17.6	10.3	21.9	25.3	26.1	12.0

\*In addition, formulation contained 6 parts of propylene glycol.

The use of monohydroxyl compounds is shown in

Examples 20 and 21, summarized in Table VI. The procedures and apparatus used were the same as that described in

- 5 Example 1 except for the differences in reactants charged which is shown in the table. It should be noted that while the methanol charged in Example 20 is much higher (45 mole percent) than that used with other hydroxyl compounds, the effective concentration in the liquid reaction mixture is
- 10 much smaller due to the volatility of the methanol.

Analysis of such products (NMR and infrared spectroscopy) showed that only about one-fourth of the charged methanol reacted with the phenol/aldehyde condensate.

TABLE VI

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Example

20

21

## Polyol Preparation: (pbw)

	Phenol	58.63	58.63
	Paraformaldehyde (91%)	32.11	32.11
5	Methanol	9.02	
	1-Butanol		9.02
	Dibutyltindilaurate	0.24	0.24

## Polyol Properties:

10	Hydroxyl number	415	396
	Viscosity, cps x 10 <sup>-3</sup>	96.8	52.5
	Water content, %	0.54	0.57

## Foam formulation: (pbw)

15	Polyol	100	100
	DC-193	3.0	3.0
	F-11A	39.1	37.9
	POLYCAT 8	1.0	0.5
	LUPRANATE M20 (120 Index)	129.6	124.6

## Foam Properties:

20	Density, pcf	1.99	1.84
	Tunb. Friab., % wt. chg.	-7.9	-20.1
	Butler Chimney, % wt. retained	77.9	62.9
	K-Factor, initial	0.126	0.143
	10% Comp. Strength, psi	37.4	31.9

Examples 22-26

25           The use of varied quantities of substituted-phenols is demonstrated in Examples 22 through 26 which are summarized in Table VII. The procedure followed is the same as that used in Example 1 except for differences in charge

30 given in the Table.

TABLE VII

Example	22	23	24	25	26
Polyol Preparation: (pbw)					
Phenol	56.6	52.6	47.6	49.4	50.7
p-Nonylphenol	2.0	6.0	12.4		
p-Butylphenol				8.9	
p-Cresol					6.5
Paraformaldehyde (91%)	32.1	32.1	31.1	32.1	33.1
1,4-Butanediol	9.0	9.0	8.7	9.2	9.3
Lead naphthenate (24% Pb)	0.24	0.24			
Dibutyltin dilaurate			0.23	0.36	0.37
Polyol Properties:					
Viscosity, cps x 10 <sup>-3</sup>	216	95.2	57.6	12.2	7.0
Hydroxyl number	530	525	465	509	549
Water content, %	0.54	1.07	0.07	0.30	0.48
Foam Formulation: (pbw)					
Polyol	100	100	100	100	100
Propylene glycol	6.0	6.0	-	-	-
DC-193	9.0	9.0	3.0	3.0	3.0
DABCO R8020	0.5	0.5	0.5	0.5	0.5
F-11A	47.7	44.2	44.8	45.8	46.9
PAPI 135, index	120	120	120	120	120
Foam Properties:					
Density, pcf	1.75	1.73	1.63	1.45	1.40
Tumb. Friab., % weight change	-3.9	-1.7	-7.5	-3.3	-2.6
Butler Chimney, % weight retained	64.5	68.4	48.7	58.5	53.7
K-Factor, initial	0.131	0.129	0.138	0.148	0.146
10% Compression Strength, psi	30.3	34.2	23.4	23.9	20.9

Examples 27-33

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The use of various catalysts for the preparation of the modified resole polyols of this invention are shown in Examples 27 through 33 which are summarized in Table VIII. Also shown are the properties of the polyurethane foams obtained from these polyols in the manner previously described using crude MDI (PAPS 135) at an index of 120.

TABLE VIII

Examples	27	28	29	30	31	32	33
Polyol Preparation: (wt. % of charge)							
Phenol	58.7	54.5	58.6	54.1	54.5	54.5	54.5
p-Nonylphenol	-	4.1	-	4.1	4.1	4.1	4.1
1,4-Butanediol	9.0	9.0	9.0	9.0	9.0	9.0	9.0
Paraformaldehyde (91%)	32.1	32.1	32.1	31.9	32.1	32.1	32.1
Zinc neodecanoate (16% Zn)	0.045						
Lead naphthenate (24% Pb)		0.24					
Dibutyltin dilaurate			0.24				
Cobalt naphthenate (6% Co)				0.96	0.24	0.24	0.24
Tetraethyl titanate							
Tetraisopropyl titanate							
Tetraoctyl titanate							
Polyol Properties:							
Viscosity, cps x 10 <sup>-3</sup>	28	587	12	12	7	7	6
Hydroxyl number	559	507	504	560	417	454	428
Water content, %	1.8	0.28	0.22	0.32	0.22	0.63	0.48
Foam Properties:							
Density, pcf	2.53	1.73	1.52	1.68	-	1.42	1.41
Temp. Friab., % weight change	-2.7	-4.5	-6.0	-2.5	-10.4	-19.5	-25.5
Butler Chimney, % weight retained	78.5	68.4	87.8	67.3	58.7	70.6	67.1
K-Factor, initial	0.127	0.119	0.146	0.144	0.146	0.141	0.142
10% Compression Strength, psi	61.6	32.3	22.6	27.5	24.5	25.2	22.6

Analytical Comparison with Prior Art Products

In Example 2, the performance comparison was made between the product of this invention and that of U. S.

5 3,485,797. Since the latter product is made without added diol, a product produced by the process of this invention was carefully examined to determine the fate of diol used in the manufacture.

Phenol, paraformaldehyde (1.6 moles  $\text{CH}_2\text{O}$ /mole of  
10 phenol), and 1,4-butanediol (16 mole percent of phenol) were reacted in the presence of 0.24 percent of lead naphthenate solution (24 percent Pb) by heating the mixture at 110°C to 117°C for 3 hours under total reflux and then withdrawing the distillate. Over a 3 hour and 35 minute period while  
15 the temperature of this reaction mixture rose to 129°C, a total of 185.5 g of water was collected. Over the next 30 minutes, the pressure was reduced to strip off residual volatiles from the product. The final conditions were a product temperature of 95°C and a pressure of <1 mm Hg. The  
20 weight of strippings collected was 59.2 g and the product weighted 1427.7 g. Thus, 1667.4 g out of a total charge of 1668 g was recovered in the three fractions.

Examination of the three fractions by a gas-liquid chromatographic procedure which had a butanediol detection  
25 limit of 0.02 percent (using spiked standards) showed no free butanediol in any of the fractions. Thus, all of the

33

butanediol had reacted. Proton NMR spectra of a number of 0116308  
similarly produced resole polyols (using varied catalysts)  
showed clearly the presence of reacted butanediol moiety.  
Other structural features of the modified resole polyols  
5 shown by proton and  $^{13}\text{C}$  NMR spectroscopy were predominant  
dibenzyl ether bridging compared to methylene bridging, low  
methyloxy phenol (mono cyclic) content, and predominantly  
ortho ring substitution.

#### Comparative Example B

10           Following the procedures of Example 1 and  
Example 3 of Great Britain 2,033,413, two phenolic resin  
polyols were prepared.

          The first of these was the reaction of a 1.7 mole  
ratio of paraformaldehyde and phenol in the presence of a  
15 molar quantity (based on phenol) of diethylene glycol using  
potassium hydroxide catalysis followed by further reaction  
under acid conditions. The second preparation was a repeat  
of the first except for the use of a slightly lower (1.5)  
formaldehyde-phenol ratio and the use of 50 mole percent di-  
20 ethylene glycol and 50 mole percent glycerine (both based on  
phenol). The first product had a viscosity of 560 cps at  
25°C while the second product had a viscosity of 170 cps at  
25°C.

          Preparation of polyurethane foams from these two  
25 resins proved difficult. Using the formulations given in  
the reference, the first resin gave a foam which shrank  
while attempts to foam the second resin were unsuccessful.

An attempt was made to analyze the first resin by  
proton NMR. However, the resin contained such a high level  
of unreacted diethylene glycol that the diethylene glycol  
resonance obscured the spectrum in a critical region and  
5 little information on the resin structure could be obtained.

The preparation of the diethylene glycol modified  
resin was repeated except that the amount of glycol used was  
reduced from 44 percent of the charge (in the first prepara-  
tion) to 9 percent (typical of the level used in the present  
10 invention). This resulted in a reduction in the amount of  
free glycol and gave a product having a viscosity of 3400  
cps at 25°C.

Proton and  $C^{13}$  NMR examination of the latter  
product showed the presence of unreacted diethylene glycol  
15 and no evidence for any reacted glycol as well as the  
absence of any dibenzyl ether, methylene bridging in both  
ortho and para positions of the phenol ring, high level of  
methylol phenol, and a very low multiple ring (>2) con-  
tent. Thus, the product of Great Britain 2,033,413 not only  
20 contains a considerable amount of unreacted glycol but the  
basic structure and composition of the resin is different  
from the products of the present invention.

Claims

1. A modified benzyl ether-containing resole polyol obtained by a process comprising reacting at 100°C to 130°C

- 5 (a) a phenol which is free of ortho substituents,
- (b) a molar excess relative to the phenol of a nonaqueous aldehyde having the formula RCHO where R is hydrogen, an alkyl group of 1 to 6 carbon atoms, or a halogenated alkyl group of 1 to 3 carbon atoms, and
- 10 (c) less than fifty mole percent relative to the phenol of an aliphatic hydroxyl compound having a functionality of 1 to 4, 1 to 12 carbon atoms, and 0 to 5 ether oxygen atoms,
- 15 in the presence of a catalytic amount of a metal derivative selected from the group consisting of (i) carboxylate salts of divalent ions of Mn, Zn, Cd, Mg, Co, Ni, Fe, Pb, Ca, Ba,
- 20 and  $\text{di}(\text{C}_1\text{-C}_5 \text{ alkyl})\text{tin}$  where the carboxylate ions each contains 1 to 20 carbon atoms, and (ii)  $(\text{C}_n\text{H}_{2n+1})_4\text{TiO}_4$  where n is an integer of 3 to 8.
- 25

2. The modified benzyl ether-containing resole  
polyol of claim 1 wherein the polyol is produced using an  
aldehyde-phenol mole ratio of 1.1 to 2.25, an amount of  
modifying polyol equal to 5 to 35 mole percent of the  
5 phenol.

3. The product of claim 2 wherein the catalyst is  
selected from the group consisting of lead naphthenate, zinc  
neodecanoate, and dibutyltin dilaurate.

10 4. The product of claim 3 wherein the phenol is a  
mixture of phenol and 0 to 20 weight percent of a p-alkyl-  
phenol where the alkyl group contains 1 to 12 carbon atoms,  
the nonaqueous aldehyde is paraformaldehyde used in a ratio  
of 1.5 to 1.75 moles formaldehyde per mole of total phenol  
15 and the modifying polyol is 1,4-butanediol used in an amount  
equal to 10 to 20 mole percent of the total phenol.

5. The product of claim 4 wherein the formal-  
dehyde/phenol mole ratio is 1.6:1 and the amount of 1,4-  
20 butanediol is 16 mole percent of the phenol.

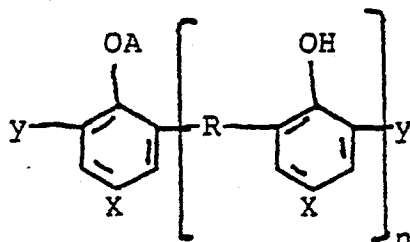
6. The rigid cellular composition obtained by the  
process comprising reacting the product of claim 1 with an  
organic polyisocyanate, a polymerization catalyst, and a  
blowing agent.

25 7. The rigid polyurethane foam obtained by the  
process comprising reacting the product of claim 3 with

polymethylene polyphenylene polyisocyanate, a polyurethane catalyst, and a blowing agent.

8. The rigid polyurethane foam obtained by the process comprising reacting the product of claim 5 with polymethylene polyphenylene polyisocyanate, a polyurethane catalyst, and a blowing agent selected from the group consisting of water, low boiling halocarbons such as fluorotrichloromethane or methylene chloride, or mixtures thereof.

9. A modified benzyl ether-containing resole polyol having a viscosity of 5000 to 650,000 cps at 25°C and a hydroxyl number of 375 to 675 and comprising compounds having the following formula:



where n is 1, 2, 3, or a higher integer;

X is H, halogen,  $C_1-C_{12}$  alkyl, or a mixture thereof;

y is a mixture of hydrogen and  $-CH_2OA$ ;

A is a mixture of hydrogen and a radical or mixture of radicals resulting from removal of a hydroxyl group from an aliphatic hydroxyl compound having 1 to 12 carbon atoms and 0 to 5 ether oxygen atoms and a hydroxyl functionality of 1 to 4;

R is  $-\text{CH}_2\text{OCH}_2-$  or a mixture of  $-\text{CH}_2\text{OCH}_2-$  and  $-\text{CH}_2-$  with the ratio of  $-\text{CH}_2\text{OCH}_2-$  groups to  $-\text{CH}_2-$  groups being greater than 1; and wherein the amount of substituent radical A is at least 5 mole percent but less than 35 mole percent of the phenol rings present.

10. The product of claim 9 wherein the substituent radical, A, is derived from a diol having 2 to 12 carbon atoms and 0 to 5 ether oxygen atoms.

10 11. The product of claim 10 wherein the diol is 1,4-butanediol or diethylene glycol.

12. The product of claim 11 wherein the diol is used in an amount of 10 to 20 mole percent of the phenol.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0116308

Application number

EP 84 10 0380

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D, Y	GB-A-2 033 413 (THE BAXENDEN CHEMICAL) * Claims *	1-12	C 08 G 18/54 C 08 G 8/36
Y	US-A-4 120 847 (H.M. CULBERTSON) * Claims *	1-12	
P, X	US-A-4 404 334 (L.F. BORNSTEIN) * Claims; column 4, lines 1-12 *	1-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-05-1984	Examiner DERAEDT G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	