

# Synthesis and Studies of Phosphorus-Containing Polyurethane Foams Based on Tetrakis(hydroxymethyl)phosphonium Chloride Derivatives

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## Synopsis

A phosphorus- and nitrogen-containing polyol is prepared by condensing tetrakis(hydroxymethyl)phosphonium chloride with diethanol amine in aqueous medium. The newly synthesized polyol-bis(hydroxymethyl)-*N,N*-bis(2-hydroxyethyl)aminomethylphosphine oxide (AMPO) is used in the preparation of rigid polyurethane foams with a various phosphorus content. With the view to comparing their properties, polyurethane foams are also prepared on the basis of the commercially available flame retardant diethyl-*N,N*-bis(2-hydroxyethyl)aminomethylphosphonate (Fyrol 6). The flammability, thermal stability, and thermomechanical properties of the polyurethane foams obtained are studied. A certain difference in the behavior of the two modified polyurethane foams is observed. The polyurethane foams with AMPO exhibit a slight increase in the resistance to combustion (oxygen index) and a noticeable improvement in the thermal and mechanical properties. These differences probably arise as a result of structural and functional differences between the two types of phosphorus-containing flame retardants.

## INTRODUCTION

The use of phosphorus-containing flame retardants is one of the well-known methods for improving the resistance to combustion of polyurethane foams.<sup>1,2</sup> Tetrakis(hydroxymethyl)phosphonium chloride and its tris(hydroxymethyl)phosphine and tris(hydroxymethyl)phosphine oxide derivatives noted for their high reactivity, as well as for their accessibility, are convenient starting compounds for the synthesis of monomers and polymers with C—P bonds.<sup>3,4</sup> The phosphorus methylol derivatives are also successfully employed as reactive flame retardants in the preparation of polyurethanes with reduced flammability and improved stability to hydrolysis. Tetrakis(hydroxymethyl)phosphonium chloride and its derivatives,<sup>5</sup> as well as their reaction products with alkylene oxides<sup>6,7</sup> and hydroxyl group containing compounds,<sup>8,9</sup> have been separately or in mixtures with commercially available polyols.

Aminomethylphosphine oxides prepared from tetrakis(hydroxymethyl)phosphonium chloride and polyfunctional amines find considerable application in improving the resistance to combustion of textiles.<sup>3,4,10</sup> The products, crosslinked polymeric aminomethylphosphine oxides, have not been isolated, but are formed on impregnation and subsequent treatment of the textile mate-

rials. Methylol derivatives of phosphorus with secondary amines have been reported; they are, however, mainly tris(aminomethyl)phosphine or phosphine oxides.<sup>11-14</sup> They are devoid of reactive substituents, and in this way their usefulness in the field of polymers is limited.

The aim of the present work is the synthesis of a phosphorus- and nitrogen-containing polyol from tetrakis(hydroxymethyl)phosphonium chloride and diethanol amine and its use in the preparation of rigid polyurethane foams with reduced flammability. The structure and composition of the synthesized polyol were also examined with the view to elucidating their influence on certain properties, chiefly the resistance to combustion, of the polyurethane foams. In order to compare the efficiency of the newly synthesized polyol were prepared rigid polyurethane foams from the commercially available phosphorus-containing polyol diethyl-*N,N*-bis(2-hydroxyethyl)aminomethylphosphonate (Fyrol 6).

## EXPERIMENTAL

### Reagents

Tetrakis(hydroxymethyl)phosphonium chloride (80% aqueous solution) and diethanol amine were FLUKA commercial products and were used without further purification.

The polyols Propylan RF 55 and Propylan RF 66 were obtained from Lankro Chemicals Ltd. (Britain); the phosphorus-containing flame retardant Fyrol 6 was from Stauffer Chemical Co. (U.S.A.). The properties of these polyols as well as their chemical structure are listed in Table I.

The remaining substances used in the present case for preparing rigid polyurethane foams, i.e., Caradate 30 (polymeric MDI), the catalyst Dabco R 8020 (20% solution of triethylenediamine in *N,N*-dimethylethanol amine), silicon oil Silicon L 5340, and foaming agent Arcton 11 (CFC<sub>13</sub>) were supplied respectively by the firms Shell (Britain), Air Products and Chemicals Inc. (U.S.A.), Union Carbide Corp. (U.S.A.), and ICI Ltd. (Britain).

### Preparation of the Phosphorus- and Nitrogen-Containing Polyol

Tetrakis(hydroxymethyl)phosphonium chloride (80% solution) (119.0 g, 0.5 mol) and water (200 mL) are placed in a three-necked flask provided with a stirrer, reflux condenser, and an argon inlet; the flask is placed in a cold water bath. A sodium hydroxide solution (20.0 g, 0.5 mol) in 200 mL of water is added dropwise with continuous stirring and bubbling argon through until a red color appears (phenolphthalein). Stirring is continued for another 2 h after which to the resulting solution of tris(hydroxymethyl)phosphine is added diethanol amine (52.5 g, 0.5 mol) dissolved in 50 mL of water. The mixture is heated at 90–100°C for 0.5 h, and the water is then removed under reduced pressure (ca. 15 mm Hg) at 50°C. Dry ethanol (400 mL) is added to the paste, and the solid residue (NaCl) filtered off. Carbon tetrachloride (77 mL) is added to the ethanolic aminomethylphosphine solution and the mixture refluxed for 4 h. The reaction mixture is then filtered, the solvents distilled off to give a viscous yellow residue—bis(hydroxymethyl)-*N,N*-bis(2-hydroxyethyl)aminomethylphosphine oxide (Table I) in quantitative yield (113.5 g);  $n_D^{20} = 1.5272$ ,

TABLE I  
Properties of Polyols

Polyol	Chemical formulas*	OH no. (mg KOH/g)	Function- ality	Phosphorus content (%)
Propylan RF 55	$H(X)_nOCH_2 \left[ \begin{array}{c} \text{CH} \\   \\ \text{OXX} \end{array} \right]_n \left[ \begin{array}{c} \text{CH}_2\text{OX} \\   \\ \text{H} \end{array} \right]_n H$	495	6	—
Propylan RF 66	$\left[ \begin{array}{c} \text{N}[(X)_nH]_2 \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{CH}_2 \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{N}[(X)_nH]_2 \end{array} \right]_n + N[CH_2CH_2OX]_n H_2$	495	3.65	—
Fyrol 6 AMPO	$(C_2H_5O)_2P(O)CH_2N(CH_2CH_2OH)_2$ $(HOCH_2)_2P(O)CH_2N(CH_2CH_2OH)_2$	440 850	2 4	12.16 13.65

\* X =  $-\text{CH}_2-\text{CH}-\text{O}-$   
 $\quad \quad \quad |$   
 $\quad \quad \quad \text{CH}_3$

hydroxyl value 850 mg KOH/g, molecular weight as determined cryoscopically in glacial acetic acid—215 (theoretical 227).

ELEMENTAL ANAL.  $C_7H_{18}NO_5P$ : Calcd for C, 37.00%; H, 7.93%; N, 6.16%; P 13.65%. Found: C, 36.81%; H, 7.73%; N, 6.28%; P, 13.51%.

### Preparation of the Rigid Polyurethane Foams

The rigid polyurethane foams are prepared by the so-called "one-shot" procedure by manually mixing the starting compounds in quantities listed in Table II. The mixture is poured into a container with dimensions  $18 \times 18 \times 22$  cm after intensive mixing. The polyurethanes are kept at  $60^\circ\text{C}$  for 24 h and, after bringing to room temperature, are cut into samples from the various studies.

### Investigation of the Rigid Polyurethane Foams

#### *Compressive Strength*

The determination of the compressive strength of the rigid polyurethane foams is conducted on an FU 1000e (GDR) instrument using samples with dimensions of  $5 \times 5 \times 5$  cm each. The compression parallel to the growth of the polyurethane causing 10% deformation is determined.

#### *Thermomechanical Properties*

The thermal stability of the rigid polyurethane foams is studied by determining the temperature of softening ( $T_s$ ) at 10% deformation of the sample according to DIN 53424-1964. The evaluation is carried out using samples with dimensions of  $4 \times 4 \times 2$  cm each at loads of  $0.25 \text{ kg/cm}^2$  and a rate of heating of  $50^\circ\text{C/h}$  on a Vicat apparatus (GDR).

#### *Thermal Analysis*

The polyurethane foams are also examined thermogravimetrically under dynamic conditions making use of a derivatograph type MOM (Hungary) under the following conditions for each polyurethane foam: weight of sample 100 mg, rate of heating  $9^\circ\text{C/min}$ , atmosphere air.

TABLE II  
General Prescription for Preparing Rigid Polyurethane Foams

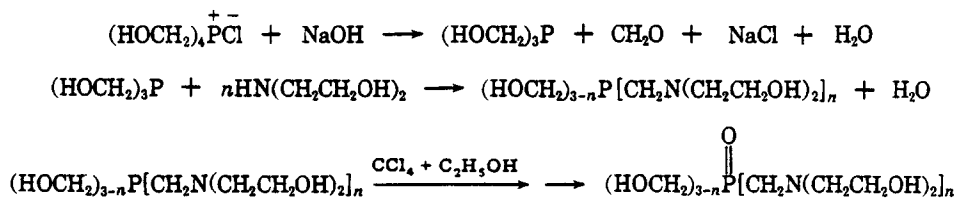
Composition of starting mixture	Wt fraction
Phosphorus-containing polyol	X
Propylan RF 66	30
Propylan RF 55	70-X
Silicone L 5340	1.5
Dabco R 8020	1
$\text{CFCl}_3$	32
Caradate 30	120-150

*Resistance to Combustion*

The ease of ignition of the rigid polyurethane foams is studied by the oxygen index method (according to ASTM D-2863) and flame propagation by ASTM D-1692. The oxygen indexes are determined on a Module FTA instrument [Stanton Redcroft (Britain)] using samples with dimensions of  $15.0 \times 1.3 \times 1.3$  cm. Samples with dimensions of  $15.0 \times 5.0 \times 1.3$  cm, as required by ASTM D-1692, are employed in the flame propagation evaluations.

**RESULTS AND DISCUSSION***Phosphorus- and Nitrogen-Containing Polyol*

The synthesis of the phosphorus- and nitrogen-containing polyol can be schematically depicted as follows:



where  $n = 1$ .

The first stage of the overall reaction consists in neutralizing tetrakis(hydroxymethyl)phosphonium chloride with aqueous sodium hydroxide at a comparatively low temperature. The tris(hydroxymethyl)phosphine formed as a result of this process is highly reactive, especially with respect to amines.<sup>3,15</sup> The aminomethylphosphine formed in the second stage, an obnoxious smelling product, is converted into the corresponding phosphine oxide by a known procedure.<sup>16</sup> The first two stages of the process leading to the phosphorus- and nitrogen-containing polyol take place subsequently without isolating the intermediate tris(hydroxymethyl)phosphine.

The obtained phosphorus- and nitrogen-containing polyol—bis-(hydroxymethyl)-*N,N*-bis(2-hydroxyethyl)aminomethylphosphine oxide (AMPO)—is a yellow viscous liquid, odorless, soluble in ethanol and water. The product is characterized by elemental analysis, refractive index, hydroxyl value, and molecular weight (determined cryoscopically).

The infrared spectra support the structure of the AMPO obtained. The following characteristic absorption bands are observed: C—O in primary alcohols ( $1070\text{--}1040\text{ cm}^{-1}$ ); CH<sub>2</sub> groups ( $2970\text{--}2830$  and  $1430\text{ cm}^{-1}$ ); P = O ( $1150\text{ cm}^{-1}$ ); OH groups (broad band in the  $3400\text{--}3100\text{ cm}^{-1}$  region).

**Rigid Polyurethane Foams**

Rigid polyurethane foams containing various amounts of AMPO in the polyol mixture, with various amounts of phosphorus in the end product, respectively, are synthesized. Polyurethane foams are also prepared with Fyrol 6 with the

view to comparing the properties of the newly synthesized polyurethane foams and for studying the efficiency of AMPO mainly in improving the flame resistance of the polymers. There is a certain structural difference between the two phosphorus-containing flame retardants which should be reflected on the properties of the final polymeric products as well.

AMPO is a tertiary phosphine oxide; the phosphorus is in the main polymeric chain and is directly bonded to the carbon atoms. Fyrol 6 is a phosphonate in which are present P—C and P—O—C bonds; the phosphorus is the side chains to the main polymeric chain. It is to be expected that these structural and functional differences between the two types of phosphorus- and nitrogen-containing polyols should affect in some way some characteristic properties of the newly prepared polyurethane foams.

The results from the investigations carried out on the two types of polyurethane foams are given in Tables III and IV. The density of the obtained products ( $31 \pm 2 \text{ kg/m}^3$ ), as well as their compressive strength measured parallel to the growth of the polyurethane foams, remain insignificantly affected with increasing the amount of phosphorus present in the polyol. An exception is the polymer containing 30 weight parts of AMPO in which case the compressive strength is lower than in the products.

The polyurethane foams prepared with the newly synthesized phosphorus- and nitrogen-containing AMPO show an increased resistance to combustion. The relationship between the flame propagation, given as the length of the burnt part of the sample and the phosphorus content of the polyurethane foams (ASTM D-1692) is depicted in Figure 1. According to the test, the two types of phosphorus-containing polyurethanes are classified as polymers with self-extinguishing properties (SE). From the character of the curves in Figure 1 it can be seen that there is a minimal but real difference in the efficiencies of the two types of phosphorus-containing polyols.

The differences in the efficiencies becomes even clearer on examining the data from the studies on the flammability of the polyurethane foams carried out by the oxygen index method (ASTM D-2863). As can be seen from Figure 2, the oxygen index of the polymers increases with increasing the phosphorus content. The curves show a tendency of leveling off towards a limiting value. A similar behavior is observed often in similar studies and is due to the fact that phosphorus catalyzes the process of coking (the oxygen index of the pure porous carbon being about 36%  $\text{O}_2$ <sup>17</sup>).

The flammability data obtained from the rigid polyurethane foams, and especially the oxygen index data, indicate that there is a more notable effect of delaying the flammability in favor of AMPO.

This observation is also corroborated by the recently established relationship between the oxygen index and the amount of phosphorus in rigid polyurethane foams.<sup>18</sup> The linear character of the dependency can be described by the equation:

$$\Delta\text{OI} = A + B \cdot \ln(1 + C_p)$$

where  $\Delta\text{OI} = \text{OI} - (\text{OI})_0$ , OI is the oxygen index of the phosphorus-containing polyurethane foams (%  $\text{O}_2$ ),  $(\text{OI})_0$  is the oxygen index of the standard polyurethane foam that does not contain phosphorus (%  $\text{O}_2$ ),  $C_p$  is the phosphorus content of the polyurethane foams (wt %), and  $A, B$  are coefficients.

TABLE III  
Properties of Rigid Polyurethane Foams Based on AMPO

No.	AMPO (parts by wt)	Compressive strength (kg/cm <sup>2</sup> )	T <sub>g</sub> (°C)	M <sub>c</sub> <sup>a</sup>	Phospho- rus con- tent (%)	OI <sup>b</sup> (% O <sub>2</sub> )	$\frac{\text{ASTM D-1692}^c}{L \text{ (cm)}} V \text{ (cm/min)}$
1	0	2.08	164.0	290.6	—	20.0	>12.5
2	10	2.45	183.0	289.6	0.58	21.6	6.4
3	15	2.37	190.0	289.0	0.86	22.4	4.4
4	20	2.45	186.0	288.6	1.12	22.8	3.8
5	30	1.64	181.0	287.7	1.63	23.4	3.5

<sup>a</sup> Average molecular weight per crosslink.

<sup>b</sup> Oxygen index.

<sup>c</sup> L = the length of the burnt part of the polymer sample; V = burning rate.

TABLE IV  
Properties of Rigid Polyurethane Foams Based on Fyrol 6

No.	Fyrol 6 (parts by wt)	Compressive strength (kg/cm <sup>2</sup> )	$T_g$ (°C)	$M_c$	Phosphorus content (%)	OI (% O <sub>2</sub> )	ASTM D-1692	
							$L$ (cm)	$V$ (cm/min)
1	0	2.08	164.0	290.6	—	20.0	>12.5	19.19
2	10	2.30	165.5	313.8	0.54	21.6	7.3	8.45
3	15	2.26	162.5	332.8	0.82	22.2	5.5	6.15
4	20	2.31	162.5	341.4	1.10	22.7	4.4	5.15
5	30	2.10	153.0	374.7	1.66	22.8	3.6	5.09
6	35	2.08	153.0	394.0	1.94	22.9	3.4	3.87

According to the authors,<sup>18</sup> this equation can be compared with that suggested by the Kresta and Frish<sup>17</sup> relationship; it proffers, however, a better correlation with the experimental data in regions of lower phosphorus content in polyurethanes.

The values for  $A$  and  $B$  in the equation for the two types of phosphorus-containing polyurethane foams are obtained by the least squares method using a

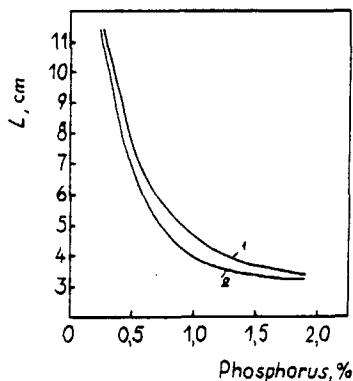


Fig. 1. Phosphorus content of rigid polyurethane foams vs. their flammability [given as the length of the burnt part of the sample (ASTM D-1692)] relationship: (1) polyurethanes containing Fyrol 6; (2) polyurethanes containing AMPO.

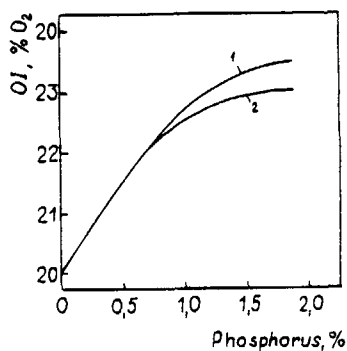


Fig. 2. Phosphorus content of rigid polyurethane foam vs. their oxygen index (ASTM D-2863) relationship: (1) polyurethanes containing AMPO; (2) polyurethanes containing Fyrol 6.



Wang computer. The following equations are obtained, respectively, for the rigid polyurethane foams synthesized with AMPO and Fyrol 6:

$$\text{AMPO: } \Delta\text{OI} = 0.2066 + 4.3026 \cdot \ln(1 + C_p)$$

$$\text{CD} = 0.9835, \quad \text{CC} = 0.9917, \quad \text{SEE} = 0.22$$

$$\text{Fyrol 6: } \Delta\text{OI} = 0.2811 + 3.0368 \cdot \ln(1 + C_p)$$

$$\text{CD} = 0.9465, \quad \text{CC} = 0.9729, \quad \text{SEE} = 0.38$$

where CD is a determination coefficient, CC is a correlation coefficient, and SEE is the standard error of the determination.

The values for the coefficient  $B$  indicate that the phosphorus of the flame retardant AMPO is more efficient in reducing the flammability of the rigid polyurethane foams than the phosphorus of Fyrol 6. This different influence of the flame retardants on the burning properties of the polyurethane foams is probably due to structural differences between the organophosphorus compounds and the different position of the phosphorus in the polymer chain. Recent investigations have shown that different types of phosphorus-organic flame retardants exhibit differing mechanisms in delaying combustion.<sup>19,20</sup> Because of this, as is also our case, the polyurethane foams modified with phosphorus-containing flame retardants do not possess the same resistance to combustion.

The influence of the structural differences between AMPO and Fyrol 6 on the properties of the polymeric products becomes especially clear on comparing the thermomechanical properties of the two types of polyurethane foams (Fig. 3). The introduction of AMPO sharply improves the thermal stability of the polyurethane foams which reaches its maximum in the polymer containing 15% of flame retardant in the initial polyol mixture. The polyurethanes modified with Fyrol 6 do not show any changes with up to 20% of flame retardant; however, increasing the latter's presence above this value brings about a decrease in the heat resistance of the polymer. The different thermomechanical behavior of the two types of polyurethanes, reflected in their temperatures of softening, is probably due to the different functionalities of the phosphorus-containing polyols, which in turn are reflected in the density of crosslinking in the polyurethane foams. The influence of the functionalities of the flame retardants used on the density of crosslinking is given in Tables III and IV in which are listed

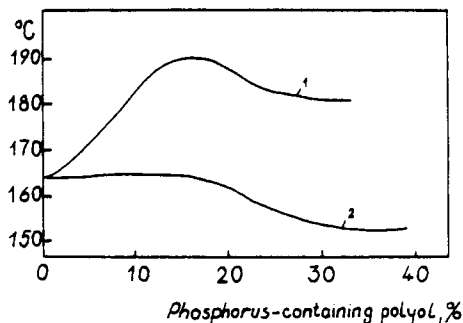


Fig. 3. Relationship between the content of phosphorus-containing polyol (%) in the polyol mixture and the thermomechanical properties of polyurethane foams as expressed by their temperature of softening (DIN 53424-1964): (1) polyurethanes containing AMPO; (2) polyurethanes containing Fyrol 6.

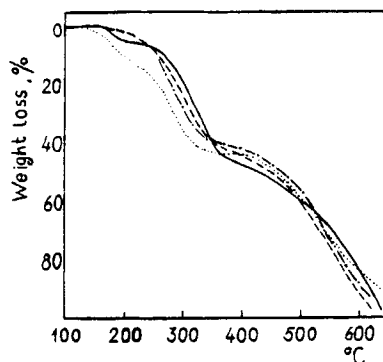


Fig. 4. Thermogravimetric analysis of polyurethane foams containing AMPO. Content of AMPO (%) of the polyol mixture: (—) 0; (---) 10; (-·-·-) 15 and 20; (····) 30.

the calculated average molecular weights per crosslink  $M_c$  according to Ref. 21. The results obtained in the present study are similar to other data,<sup>22</sup> which indicate that phosphorus-containing polyols with more than two hydroxyl groups improve the thermomechanical properties of the rigid polyurethane foams.

In Figure 4 are given the results from the gravimetric analysis of polyurethane foams modified with AMPO. The introduction of phosphorus causes a decrease in the initial temperature of destruction. In the 370–500°C region, however, the residue of the phosphorus-containing polymers is comparatively greater than one of polyurethane foams that do not contain phosphorus. For the sake of comparison, the polyurethane containing 20 weight fractions of Fyrol 6 is subjected to thermal destruction; the destruction curve, however, almost completely coincides with that corresponding to the behavior of the polyurethane containing 20 weight fractions of AMPO.

## CONCLUSION

Some differences in the behavior of the two types of polyurethanes are observed on modifying rigid polyurethane foams with the phosphorus- and nitrogen-containing polyol bis(hydroxymethyl)-*N,N*-bis(2-hydroxyethyl)aminomethylphosphine oxide (AMPO) and the commercial Fyrol 6 synthesized by us. A relative increase in the resistance to combustion (oxygen index) and a marked improvement in the thermomechanical properties of the polyurethane foams containing AMPO is observed. These differences are probably due to differences in structure and functionality of the two types of phosphorus-containing flame retardants.

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