INTERACTION BETWEEN HYPOPHOSPHOROUS ACID SALTS AND ISOCYANATES AND POSSIBILITIES OF USING THEM AS FLAME RETARDANTS FOR RIGID POLYURETHANE FOAMS

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Abstract—The interaction between hypophosphorous acid salts and isocyanates proceeds heterogeneously in a complex manner affording isocyanurates and compounds with carbon–phosphorus bonds. There is a possibility of using the salts as reactive flame retardants for rigid polyurethane foams. They lead to improved mechanical properties, self-extinguishing characteristics and higher limiting oxygen index.

INTRODUCTION

Hypophosphorous acid is unstable and is used in aqueous solution. For these reasons, it is not employed as a flame retardant for polyurethane foams. Its sodium, potassium and ammonium salts are stable up to 200° but their insolubility in polyol mixtures renders them unusable as polyurethane flame retardants. These salts can however be efficiently employed under suitable conditions since they have a high phosphorus content and also because of the possibility of a reaction between the hydrogen atoms attached to the phosphorus with isocyanates, as for phosphines and dialkyl phosphites [1, 2].

EXPERIMENTAL

The following reagents were used: phenyl isocyanate (Koch–Light), analytical grade; toluylene diisocyanate (Fluka), a mixture of 2,4- and 2,6-isomers in 4:1 ratio; 1,1-diphenylmethane-4,4-diisocyanate (Merk–Schuchardt), analytical grade; hexamethylene diisocyanate (Merk–Schuchardt), analytical grade; sodium hypophosphite, m.p. 236° (decomposition at 310°); potassium hypophosphite, m.p. 200° (with decomposition); ammonium hypophosphite, m.p. 200° (decomposes at 240°); polyols—Propylane RF 66 (propoxylated mixture of an aniline formaldehyde resin) and Propylane RF 55 (propoxylated sorbitol).

Interaction between hypophosphorous acid salts and diisocyanates

Powdered sodium hypophosphite (0.88 g, 0.01 mol) and 2,4-toluylene diisocyanate (6.96 g, 0.04 mol) are placed in a flask containing conc. KOH solution and provided with a thermometer and gas in- and outlets. At 130° there is considerable evolution of gas from the KOH solution; the reaction mixture becomes homogeneous and a solid porous substance is formed. The temperature of the reaction mixture sharply rises above 155° and the reaction is over in about 1 min. The flask shows a weight loss of 0.1966 g (Table 1). Titration of the KOH solution with HCl using phenolphthalein and methyl orange as indicators (Werder's method) revealed the loss of 0.1945 g of carbon dioxide. The porous solid material is powdered and extracted with butyl acetate. The latter is distilled off and the residue (3.27 g) analysed for phosphorus, the i.r. spectrum recorded and a

derivatographic analysis conducted. The residue is extracted with hot water to remove 0.37 g of unchanged sodium hypophosphite and give a solid material (4 g) not melting until 260°.

Table 1 shows the reaction conditions and the reaction products from the interaction between sodium hypophosphite and 2,4-toluylene diisocyanate, 1,1-diphenylmethane-4,4-diisocyanate and hexamethylene diisocyanate in the mole ratio 1:4. Table 2 refers to the interaction between ammonium hypophosphite and these reagents; Table 3 refers to the interaction with potassium hypophosphite.

Preparation of rigid polyurethane foam with participation of sodium hypophosphite

In a metal vessel are placed the polyol Propylane RF 66 (30 parts by weight) and the polyol Propylane RF 55 (65 parts), sodium hypophosphite (5 parts), the catalyst Dabco R 8020 (1 part), silicon oil Silicon 5340 (1.5 parts), freon (32 parts). The mixture is homogenized with a mechanical stirrer; the sodium hypophosphite remains however insoluble in the mixture. To it is added 1,1-diphenylmethane-4,4-diisocyanate (134.7 parts), a Desmodur 44V20 commerical product, and the mixture energetically stirred for about 12 sec and poured into a container with dimensions of 18 × 18 × 22 cm. After standing for 1 to 2 hr, the polyurethane block is removed, cut up into standard samples and analysed. Polyurethane foams are thus prepared with 10 and 15 parts by weight of sodium hypophosphite. To compare their properties, two series of polyurethane foams are prepared under the same conditions, one involving the flame retardant Fyrol 6[(diethyl-*N*,*N*-bis)2-hydroxyethylphosphonate] and the other the unreactive flame retardant ammonium hydrogen phosphate.

RESULTS AND DISCUSSION

Reactions between salts and isocyanates were conducted at the mole ratios 1:2, 1:4 and 1:20. The interactions with phenyl isocyanate (PIC), 2,4-toluylene diisocyanate (TDC) and 1,1-diphenylmethane-4,4-diisocyanate (DPC) proceed with the liberation of CO_2, which was determined gas-chromatographically, giving porous products. The reaction with hexamethylene diisocyanate (HMC) proceeds without the evolution of gases and leads to solid resinous products. It was found that the addition of amine catalyst does not affect the reaction temperatures and final

Table 1. Interaction between 0.04 mol of 2,4-toluylene diisocyanate and 0.01 mol of hypophosphorous acid salts MOP(O)H$_2$

M	CO_2 (g)	Product (%)	Melting point (°C)	%P found	%P calc.	Unreacted salt (%)
Na	0.1966	41.3	122	4.09	4.19	41.3
NH$_4$	0.2120	42.8	110	4.12	4.22	46.0
K	0.1712	39.0	133	3.98	4.10	45.1

products. Extraction with warm water of the reaction products showed that, with phenyl isocyanate, the amount of chemically bonded salt is very small (about 5%); for this reason, no further experiments were conducted with PIC.

The products extracted with butyl acetate were examined by i.r. spectroscopy in KBr pellets. The spectra showed absorption bands characteristic of P=O at 1190 cm^{-1}, P—H at 2360 cm^{-1}, P—C at 1320 cm^{-1}, isocyanate groups at 2275 cm^{-1}, isocyanuric groups at 1720, 1425 and 765 cm^{-1} [3]. Absorption bands at 2160 cm^{-1} characteristic of carbodiimide functions (N=C=N) are exhibited by the products from aromatic diisocyanates, but not by those from hexamethylene diisocyanate. Bands at 1780 cm^{-1}, characteristic of C=O in dimeric urethane moieties [4], are absent.

The derivatograms of the products indicate that, under thermo-oxidative destruction, loss in weight

dioxide is also liberated in the reaction with aromatic isocyanates as a result of carbodiimide formation. Doubtless, the hypophosphorous acid salts catalyse this reaction as do hypophosphites [8]. It is very likely that the yields of the main products, i.e. those extracted with butyl acetate, are limited and prevent the direction of the desired reaction by the heterogeneity and high conversion rate leading to solid products.

The residue after extracting with butyl acetate was treated with warm water to remove the unreacted salt. The residue is a polymer that does not melt below 260° and contains a negligible amount of phosphorus.

The following probable formulae can be assumed on the basis of the phosphorus contents of the products isolated via extraction with butyl acetate (Tables 1-3) as well as from the i.r. spectra and derivatograms:

Where M = Na, K or NH$_4$
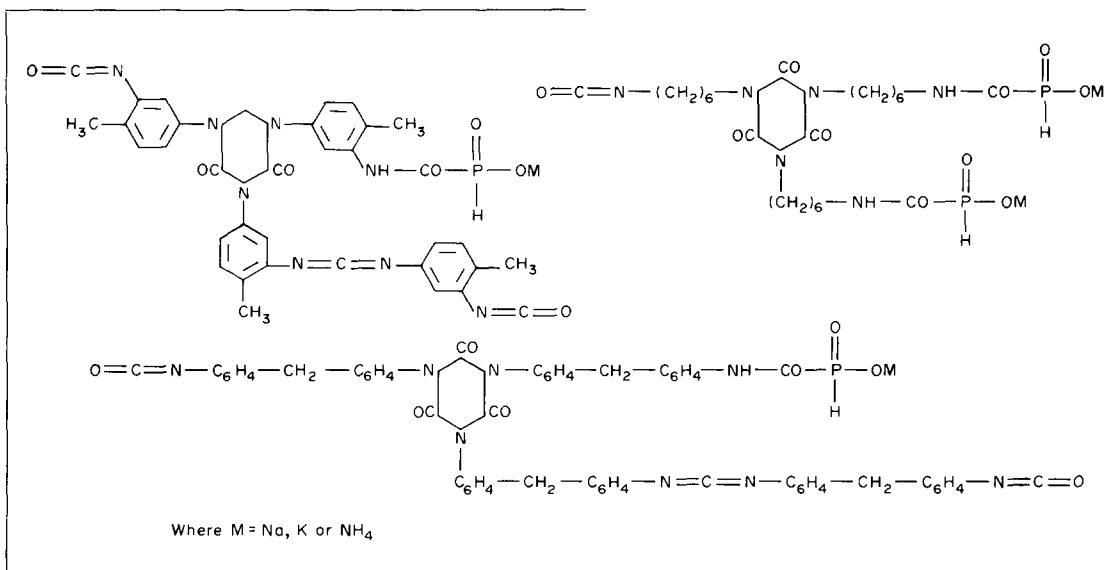
begins above 270°. At 450° there are endothermic peaks characteristic of isocyanuric ring systems [5].

These results show that a complex heterogeneous interaction occurs in the isocyanates—hypophosphorous acid salts system. The same products are formed, containing in their molecule a phosphorus atom, which results from the addition of a hydrogen atom, attached to phosphorus, to the isocyanate group (Tables 1-3); this is observed irrespective of the reactant mole ratios. Another interaction leads to the formation of isocyanurates. It follows that the hypophosphorous acid salts act catalytically, as do other salts and substituted phosphites [6, 7]. A third notable point is that carbon

It follows that the hypophosphorous acid salts enter into complex interaction with diisocyanates. Our attemps to employ them as flame retardants for rigid polyurethane foams was based on this observation.

Complete studies were conducted for foams obtained with sodium hypophosphite. The marked increase of the temperature of softening of the polyurethane foams (according to standard no. 53424 of 1964 of the German Democratic Republic, as determined on a Vikat apparatus) which changes from 154° for foams without flame retardant to 198° for foams with 15 parts by weight of sodium hypophosphite, is worth noting. In general, all additives to

Table 2. Interaction between 0.04 mol of 1,1-diphenylmethane-4,4-diisocyanate and 0.01 mol of $MOP(O)H_2$

M	CO_2 (g)	Product (%)	Melting point (°C)	%P found	%P calc.	Unreacted salt (%)
Na	0.1629	36.2	142	2.81	2.97	50
NH_4	0.1644	37.4	136	2.79	2.99	53
K	0.1426	32.7	147	2.75	2.92	58

Table 3. Interaction between 0.04 mol of hexamethylene diisocyanate and 0.01 mol of $MOP(O)H_2$

M	CO_2 (g)	Product (%)	Melting point (°C)	%P found	%P calc.	Unreacted salt (%)
Na	—	28.4	93	9.21	9.12	37
NH_4	—	29.1	86	9.13	9.28	37
K	—	26.5	95	8.56	8.70	40

the polyol mixture lead to deterioration of this index, an effect which is most marked for unreactive additives (the temperature of softening of a polyurethane foam with 20 parts by weight of ammonium hydrogen phosphate is 161°). This effect is due to the formation of isocyanuric structures in the polyurethane foams under the catalytic effect of sodium hypophosphite during the reaction. Sodium hypophosphite is a better flame retardant as shown by the better limiting oxygen index, shorter burnt part of the sample and lower combustion rate in comparison with the polyurethane foams containing the flame retardants Fyrol 6 or ammonium hydrogen phosphate.

When sodium hypophosphite is present as an unreactive additive, i.e. the amount of diisocyanate corresponds only to the polyol in the mixture, there is a sharp decrease in the softening temperature and of the limiting oxygen index, similar to the corresponding indexes of polyurethane foams containing ammonium hydrogen phosphate as flame retardant. It can be deduced that the isocyanate reacts more quickly with the polyol hydroxyl groups and, after they are consumed completely, the remaining isocyanate reacts with the hydrogen atoms attached to the phosphorus in the sodium hypophosphite; this happens when the temperature has been sufficiently increased. Catalytic formation of isocyanuric and carbodiimide structures also occurs in this stage. This

reaction course could explain the formation of polyurethane foams with high softening temperature and improved limiting oxygen index.

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