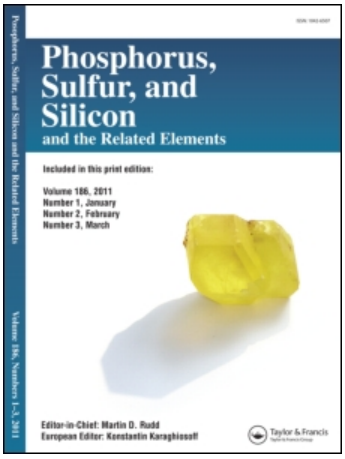

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New Phosphorus-Containing Flame Retardants for Poly-Urethanes and Polyesters

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NEW PHOSPHORUS-CONTAINING FLAME RETARDANTS FOR POLYURETHANES AND POLYESTERS.

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Abstract New phosphorus - containing monomers and oligomers from tetrakis(hydroxymetyl)phosphonium chloride and dialkylphosphites are synthesized. On the basis of new products phosphorus-containing polyesters,polyurethanes and polyuretanesemicazbazides with improved fire resistance are obtained. The dependence of fire resistance of the polymers on the structure of the use flame retardants is investigated.

INTRODUCTION

The phosphorus-containing active and inactive additives, are some of the best-known flame retardants and they are being produced in already considerable quantities.The introduction of new phosphorus-containing retardants is confined by the relatively low availability of the raw materials. With the view of broadening the flame retardants, assortment and improving their quality,our research acticity has been aimed at synthesizing new flame retardants from the industrially produced tetrakis(hydroxymethyl) phosphonium chloride and dialkylphosphites.

RAW MATERIALS-TETRAKIS HYDROXYMETHYL PHOSPHONIUM CHLORIDE

Tetracis(hydroxymethyl)phosphonium cloride and its derivatives are convenient starting compounds for the synthesis of monomers and polymers,containing C-P bonds. Kaba-

chinik and Tsvetkov have shown that under certain conditions tris(chloromethyl)phosphine undergoes the so called "pseudoallyl rearrangment" and is transformed into bis (chlormethyl)methylphosphine oxide:

$$(ClCH_2)_4PCl \xrightarrow{NaOH} P(CH_2Cl)_3 \xrightarrow{HCl} CH_3\overset{O}{\overset{\|}{P}}(CH_2Cl)_2$$

Bifunctional compounds, suitable for polycondensation processes, have been obtained by substituting with different functional groups the cloride atoms in bis(chloromethyl)methylphosphine oxide:

$$ClCH_2-\overset{O}{\overset{\|}{P}}(CH_3)-CH_2Cl + 2NaO-C_6H_4-R \rightarrow R-C_6H_4-OCH_2-\overset{O}{\overset{\|}{P}}(CH_3)-CH_2O-C_6H_4-R$$

where R = COOH, $COOCH_3$, COCl, OH

The possibility for using the synthesizid monomers as reactive flame retardants for increasing the fire resistance of polycondensation polymers has been dcmonstrated and special attention has been paid to modification of the properties of well-known and industrially produced polymers such as polyethyleneterephthalate, nylon 6,6 etc.[1].

Phosphorus - and nitrogen-containing polyols have been synthesized and they have been used for the modification of rigid polyurethane foams and linear polyurethanes[2].

$$(HOCH_2)_3P + HNR_1R_2 \rightarrow (HOCH_2)_2PCH_2NR_1R_2 + H_2O$$

$$(HOCH_2)_2PCH_2NR_1R_2 \xrightarrow{O_2} (HOCH_2)_2\overset{O}{\overset{\|}{P}}CH_2NR_1R_2$$

where $-NR_1R_2 = -N(CH_2CH_2OH)_2$, $-N\langle CH_2-CH_2 \rangle C(=O) NCH_2P(CH_2OH)_2$

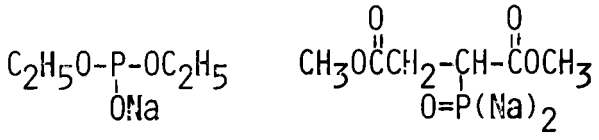
Some of the typical properties of the modified polyurethanes have been investigated. A special attention

has been paid towards examining the dependence of the fire resistance of the polymers on structure of the polyols. It has been shown that the synthesized polyols are suitable flame retardants for rigid polyurethane foams.

RAW MATERIALS - DIALKYLPHOSPHITES

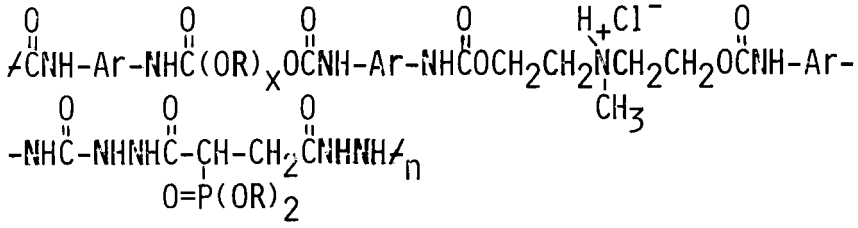
The investigation on the reactivity of dialkylphosphites, carried on by us, showed that the reactions typical for these diesters - trans esterification and addition, allowed for the synthesis of different in structure and composition products.

For example, polyethylene terephthalate has been modified with the sodium salt of diethylphosphite and the disodium salt of 1,2-dicarbomethoxyethanephosphonic acid:



Organophosphorus compounds, obtained from dialkylphosphites, have been used for improving the fire resistence of polyurethanesemicarbazide ionomers.

The dihydrazide of the 2-diethylphosphonylbutanedicarboxilic acid has been used as a modificator for polyurethanesemicarbazides and polyurethanesemicarbazide ionomers[3,4].

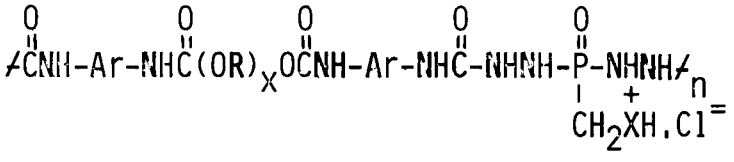


It has been established that the inclusion of phosphorus in the polymer chain of the ionomer does not influence substrantially its physicomechanical properties but does

improve considerably its fire resistance.

The high effectivenes of the flame retardants is probably due also to the structure of the ionomer and mainly to the existing electrostatic interactions.

As flame retardants for polyurethanesemicarbazide ionomers have also been used the dihydrazides of N,N-diethylaminomethylphosphonic and N-morpholinylmethylphosphonic acid. The phosphorus atom in this case is included in the main polymer chain[4]:



$$X = -N(C_2H_5)_2, \quad -N\begin{matrix}CH_2CH_2\\ \\ CH_2CH_2\end{matrix}O.$$

The modified ionomers possess good physicomechanical propertiers and high fire resistance. The limiting oxygen index has been determined to be 34% O_2.

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