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Synthesis of New Phosphorus-, and Chlorine-Containing Inhibitors of Polymer Burning

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New phosphorous and chlorine containing oligomeric and polymeric products are synthesized and their potential as inhibitors of burning for polymeric materials demonstrated.

KEY WORDS Polymers, burning inhibitors, phosphorous, chlorine.

RESULTS AND DISCUSSION

In comparison with low molecular weight substances, polymer and oligomer halogen-containing inhibitors of burning are more preferable, since they show a lower tendency to migrate and can improve some properties of polymer materials. We can relate poly(vinyl chloride), chlorinated polyethylene and chlorinated paraffins that are antipyrine of additive type to such inhibitors.

We have studied a new method of modification of the above-mentioned products by complex compounds of phosphines with Lewis acids, with the purpose of introducing into the structure halogen-containing polymer and oligomer inhibitors of burning reactive phosphorus-containing groups.

According to the data in References 1 and 2, phosphorus hydride, together with aluminium, tin and titanium halogenides, forms complex compounds of various compositions. Phosphine reacts with aluminium trichloride and tribromide at temperatures of 70°–80°C and with aluminium triiodide at 120°–130°C. Under these conditions aluminium trichloride absorbs 0.95–0.99 moles of phosphorus hydride per 1 mole of halogenide to form a complex compound with a melting temperature of 83°C. Aluminium tribromide reacts more actively with phosphorus hydride absorbing 0.98–1.0 moles of PH₃ per one mole of halogenide to form the complex with $T_m = 114–118^\circ\text{C}$. Aluminium triiodide attaches 0.95–0.99 moles of PH₃ above 100°C. All complex compounds of phosphorus hydride with aluminum halogenides are white crystal substances easily sublimated in a vacuum without decomposition.

Titanium tetrachloride absorbs phosphorus hydride at room temperature to form a yellow crystal complex of 1:1 composition that easily decomposes upon heating to 50°C. A similar complex is formed by the interaction of phosphine with titanium tetrabromide. Titanium tetraiodide, in contrast to bromide and chloride, does not interact with phosphine.

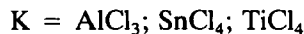
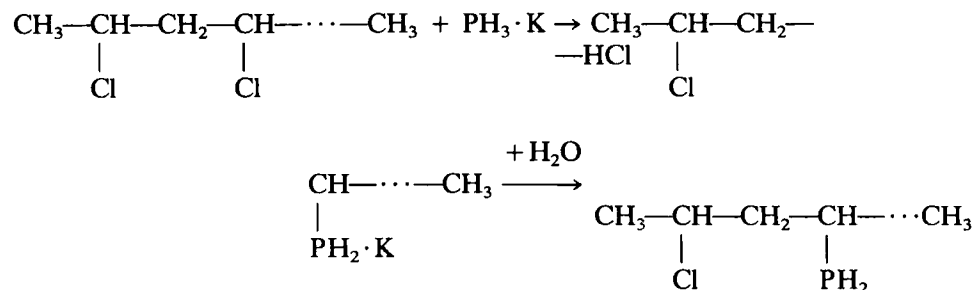
Tin halogenides add phosphorus hydride at 0°C, but like titanium halogenides they are unstable when heated.

For preliminary evaluation of complex reactivity we carried out quatochemical calculations of phosphine complexes with metal halogenides by the Maliken–Wolfsberg–Helmholz method. The results obtained for phosphine complexes with aluminium trichloride are shown in Table I.

From the data obtained it follows that in the phosphorus hydride complex with aluminium trichloride a covalent bond is formed which is not inferior in strength to the P—H and Al—Cl bonds. However, an ionic component of this bond has a “repulsive” character due to the greater positive charges in those atoms.

While the complex is forming, intramolecular redistribution of electronic density occurs of about $\Delta q(\text{H}_3\text{P} \rightarrow \text{AlCl}_3) = 0.556\bar{e}$. Due to this phosphorus and hydrogen atoms get a positive charge (lose electronic density) and an ionic constituent destabilizes the bond, while almost no changes occur in the covalent component. As a result, hydrogen atoms in the complex are partially protonized and become more mobile.

Estimation of phosphorus hydride complexes with metal halogenides was carried out at their interaction with chlorinated paraffins by the following scheme:



In this reaction some commercial paraffins with various chlorine content were used: 28%(CP-28), 41%(CP-418), 49%(CP-470).

Preliminary experiments have shown that the interaction of complex compounds $\text{PH}_3 \cdot \text{AlCl}_3$, $\text{PH}_3 \cdot \text{SnCl}_4$ and $\text{PH}_3 \cdot \text{TiCl}_4$ with chlorinated paraffins proceeds both in the presence and absence of organic solvents. As for the latter, they were used

TABLE I
Quatochemical calculations of complexes*

Bond	$q(\text{P})$	$q(\text{H})$	$\frac{q(\text{H})}{q(\text{P})} \times$	$\rho(\text{P}-\text{H})$	$\rho(\text{P}-\text{Me})$	$\Delta q(\text{PH}_3-\text{acid})$
PH_3	0.0500	-0.0165	-0.000825	0.780	-	-
$\text{PH}_3 \rightarrow \text{AlCl}_3$	0.3820	0.0580	0.0220	0.783	0.7360	0.5560
CH_3PH_3	0.0760	-0.0160	0.0012	0.805	-	-
$\text{CH}_3\text{PH}_2 \rightarrow \text{AlCl}_3$	0.3775	0.0490	0.0180	0.793	0.7460	0.5680

*Quatochemical calculations have been carried out jointly with A. S. Litinskiy.

as chlorinated solvents (chlorobenzene, tetrachloroethane, dichloroethane) as well as aliphatic hydrocarbons (hexane, heptane). The use of proton solvents (tetrahydrofuran, dimethylformamide, nitrobenzene) resulted in decomposition of complex compounds to form a free phosphorous hydride. It has been stated that the phosphorylation degree of chlorinated paraffins is greatly influenced by the following: temperature, nature of solvent used and the phosphorylating agent, and chlorine content in the mother chlorinated paraffins.

With the purpose of discovering optimal conditions, the interaction was carried out at the following temperatures: 0°C, 20°C, 40°C, 60°C, 80°C, 100°C and at the mole reagent relationship from 1:1 to 1:10. As is seen from the data obtained (Table II) under the conditions investigated the most effective phosphorylating agent of chlorinated paraffins is the phosphorous hydride complex with aluminium trichloride. While using it the phosphorylating degree of chlorinated paraffins reaches 48.3%. Increasing the phosphorylation temperature from 0°C to 100°C increases the phosphorus content in the final products from 0.3% to 12.0%, and decreasing the halogen content in the mother chlorinated paraffins increases the phosphorylation degree in the following sequence: CP-28, CP-418, CP-470. In the case of chlorinated paraffins having the least chlorinity (CP-28) the amount of fixed phosphorus attained is 12.0%. When treating chlorinated paraffins by the complexes of phosphorous hydride with titanium tetrachloride and tin tetrachloride we failed to introduce a perceptible amount of phosphorus into the chlorinated paraffins, which is likely to account for their worse solubility in tetrachlorethane and their instability. Although the protonation degree of hydrogen atoms in the $\text{PH}_3 \cdot \text{AlCl}_3$ complex is lower than in the $\text{PH}_3 \cdot \text{SnCl}_4$ complex, due to the greater stability of the former in the reaction under investigation, it turns out to be more effective. The temperature increase of interaction gives rise to decomposition of the phosphorous hydride complexes with SnCl_4 and TiCl_4 into the mother components and as a result of it to the decrease of the phosphorylation degree of chlorinated paraffins. For instance, acting with $\text{PH}_3 \cdot \text{SnCl}_4$ on CP-28 at 20°C we succeed in introducing 0.6% phosphorus into chlorinated paraffin, while at 60°C only 0.3% can be introduced.

The degree of phosphorylation of chlorinated paraffins is appreciably affected by nature of the solvent (Figure 1). Investigation of the phosphorylation of chlorinated paraffins CP-418 by the $\text{PH}_3 \cdot \text{AlCl}_3$ complex at 50°C in tetrachlorethane (curve 1) and chlorobenzene (curve 2) has shown that the reaction in tetrachlorethane proceeds with much greater speed than in chlorobenzene and the obtained phosphorus content in the final product is considerably higher in that case. A similar relationship has also been observed during phosphorylating of other chlorinated paraffins. The difference in the reaction rate of chlorinated paraffins with $\text{PH}_3 \cdot \text{AlCl}_3$ in chlorobenzene and in tetrachlorethane is likely to account for the difference in dipole moments of the solvents mentioned. Chlorobenzene as a polar molecule ($\mu = 1.69$) is likely to solvate the complex of phosphine with aluminium trichloride (makes the chlorine atoms difficult to access) and as a result of this the phosphorylating agent becomes less active. Tetrachlorethane as a symmetric molecule having no dipole moment does not take part in the process of solvation and does not lower the reactivity of the complex.

TABLE II
Influence of reaction temperature and nature of the phosphorylating agent on elemental composition and phosphorylation degree of chlorinated paraffins.
Reactions time, 5 hours; reagent ratio (in moles), 1:1; solvent, tetrachlorethane.

Phosphorylating agent	Reaction temperature, °C	Mother chlorinated paraffins									
		CP-28			CP-418			CP-470			
		Chlorinity, % -28			Chlorinity, % -41			Chlorinity, % -49			
		Degree of phosphorylation of chlorinated paraffins and elemental composition of oligomer phosphines, %									
		Degree of phosphorylation		Degree of phosphorylation		Degree of phosphorylation		Degree of phosphorylation		Degree of phosphorylation	
		P	Cl	P	Cl	P	Cl	P	Cl	P	Cl
$\text{PH}_3 \cdot \text{AlCl}_3$	0	2.2	26.3	8.4	2.1	38.2	5.5	1.9	46.1	4.2	4.2
	20	5.1	21.5	19.5	4.2	34.1	11.0	3.8	43.1	8.3	8.3
	40	6.4	20.1	24.5	5.4	33.5	14.1	4.3	42.5	9.4	9.4
	60	8.1	18.2	31.0	7.6	30.8	19.7	5.2	40.4	11.4	11.4
	80	10.8	9.7	41.4	8.7	25.4	22.8	6.7	35.7	14.8	14.8
$\text{PH}_3 \cdot \text{SnCl}_4$	100	12.6	3.3	48.3	9.8	11.6	25.7	8.1	18.2	17.8	17.8
	0	-	28.1	-	-	40.6	-	-	48.6	-	-
	20	0.6	27.5	2.3	0.5	40.3	1.3	0.3	48.2	0.6	0.6
$\text{PH}_3 \cdot \text{TiCl}_4$	40	0.51	27.7	1.9	0.47	40.7	1.2	0.23	48.7	0.5	0.5
	60	0.3	27.9	1.2	0.2	40.4	0.5	0.1	48.8	0.2	0.2
	0	-	28.2	-	-	40.8	-	-	48.8	-	-
$\text{PH}_3 \cdot \text{TiCl}_4$	20	-	28.1	-	-	40.7	-	-	48.5	-	-
	40	-	28.3	-	-	40.7	-	-	48.6	-	-
	60	-	28.1	-	-	40.6	-	-	48.4	-	-

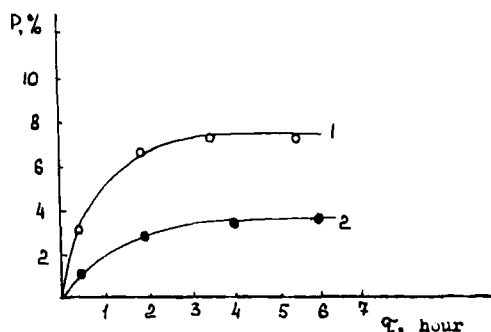


FIGURE 1 Action of solvent nature on phosphorus content in CP-418. Phosphorylating agent, $\text{PH}_3 \cdot \text{AlCl}_3$; reagent relationship, 1:1; temperature, 50°C . (1) Tetrachlorethane; (2) chlorobenzene.

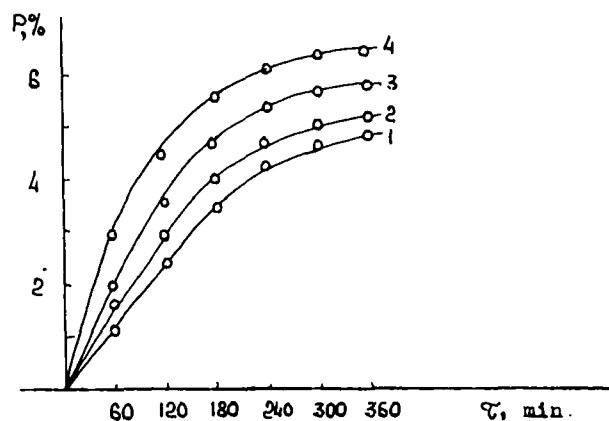


FIGURE 2 Phosphorus content dependence on reaction time in CP-28. Reaction temperature: (1) 10°C ; (2) 20°C ; (3) 30°C ; (4) 40°C .

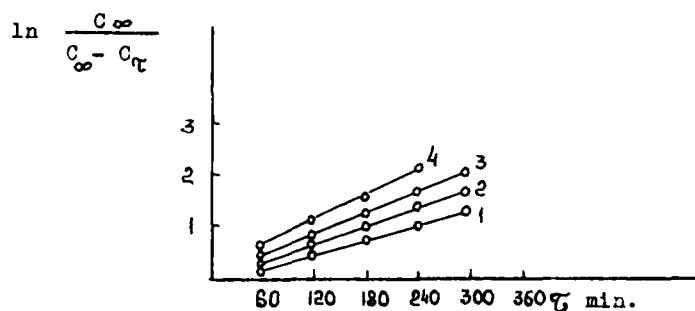


FIGURE 3 Dependence of the value $\ln[C_\infty/(C_\infty - C_\tau)]$ of phosphorus upon reaction time in CP-28. Reaction temperature: (1) 10°C ; (2) 20°C ; (3) 30°C ; (4) 40°C .

In order to determine the activation reaction parameters of chlorinated paraffins with the phosphorus hydride complex and aluminium trichloride we have investigated kinetic regularities of phosphorylation. Figures 2 and 4 show experimental data of the results of changing the phosphorus content in chlorinated paraffins in relation to time at 10°C , 20°C , 30°C , 40°C , making use of tetrachlorethane as a

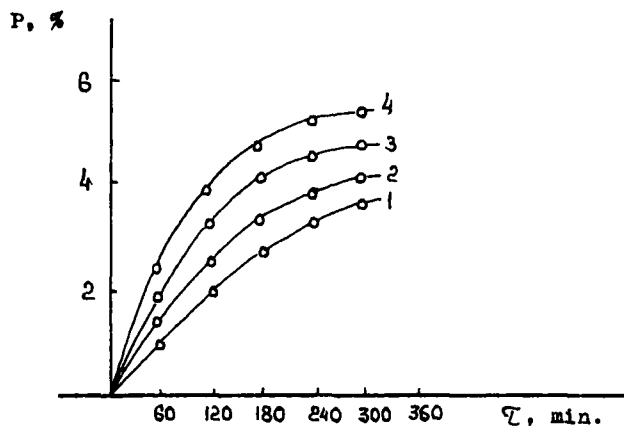


FIGURE 4 Dependence of phosphorus content upon reaction time in CP-418. Reaction temperature: (1) 10°C; (2) 20°C; (3) 30°C; (4) 40°C.

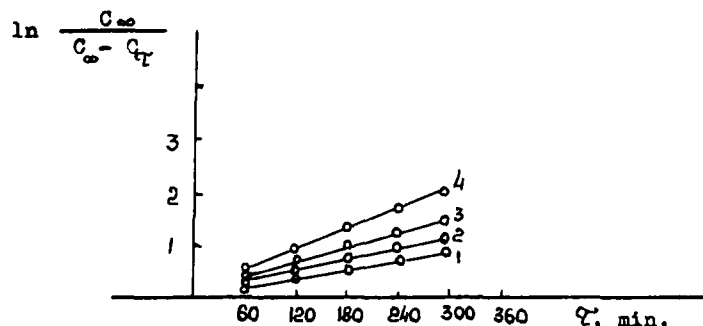


FIGURE 5 Dependence of the value $\ln[C_{\infty}/(C_{\infty} - C_{\tau})]$ phosphorus on reaction time in CP-418. Reaction temperature: (1) 10°C; (2) 20°C; (3) 30°C; (4) 40°C.

solvent. The relationship obtained shows that the phosphorus content increases exponentially as the reaction proceeds. Figures 3 and 5 reflect the dependence of the natural logarithm concentration $\{\ln[C_{\infty}/(C_{\infty} - C_{\tau})]\}$ upon time, where C is the phosphorus content in chlorinated paraffins at a given moment in time. From those figures it can be seen that the dependence of concentration logarithm is a linear function of time $\ln[C_{\infty}/(C_{\infty} - C_{\tau})] = f(\tau)$ indicating to the first order of reaction (points are laid in a straight line). Due to the limited solubility of the phosphine complex with aluminium trichloride the reaction proceeds in the chlorinated paraffin system under constant excess and the reaction rate depends on the concentration of one reagent. The process occurs under variable chlorine concentration and invariable concentration of the complex.

Resulting from the data obtained according to the kinetic equation of the first order the constants of the reaction rate have been calculated in the temperature range being investigated (Table III). The logarithmic values of rate constants as functions of the reverse temperature lie on a straight line (Figure 6). This confirms the performance of the Arrhenius equation in the process under investigation. From the dependence $1/T$, the activation energy of phosphorylation and the value

TABLE III
Phosphorylation kinetics of chlorinated paraffins by the complex $\text{PH}_3 \cdot \text{AlCl}_3$

N	Reagents	Rate reaction constant, 10^{-4} , second $^{-1}$						Mean constant of reaction rate, 10^{-4} , second $^{-1}$						Activation energy E act. kJ/mole	ΔH^\ddagger kJ/ mole	$-\Delta\text{S}^\ddagger$ J/mole gr	ΔG^\ddagger kJ/ mole	Preexponential multiplier
		Temperature, °C			Temperature, °C			Temperature, °C			Temperature, °C							
		10	20	30	40	10	20	30	40	10	20	30	40					
1.	CP-28 $\text{PH}_3 \cdot \text{AlCl}_3$	0.51	0.77	1.03	1.72	1.72	1.63	1.63	1.43	1.43	1.15	1.51	24.8	22.3	10.8	96.2	2.0	
		0.64	0.86	1.07	1.63	1.63	1.43	1.43	1.16	1.16	0.84	1.51	24.8	22.3	10.8	96.2	2.0	
		0.72	0.88	1.24	1.43	1.43	1.16	1.16	1.09	1.09	0.66	1.51	24.8	22.3	10.8	96.2	2.0	
		0.72	0.93	1.29	1.93	1.93	2.40	2.40	1.09	1.09	0.66	1.51	24.8	22.3	10.8	96.2	2.0	
		0.74	0.86	1.16	2.40	2.40	360	360	1.03	1.03	0.66	1.51	24.8	22.3	10.8	96.2	2.0	
		0.65	0.75	1.09	2.40	2.40	360	360	1.03	1.03	0.66	1.51	24.8	22.3	10.8	96.2	2.0	
2.	CP-418 $\text{PH}_3 \cdot \text{AlCl}_3$	0.46	0.67	1.03	1.35	1.35	1.32	1.32	0.99	0.99	0.87	1.17	24.8	22.4	9.7	93.3	2.3	
		0.52	0.68	0.99	1.32	1.32	1.24	1.24	0.97	0.97	0.61	1.17	24.8	22.4	9.7	93.3	2.3	
		0.52	0.69	0.97	1.24	1.24	1.17	1.17	0.85	0.85	0.48	1.17	24.8	22.4	9.7	93.3	2.3	
		0.52	0.64	0.85	1.17	1.17	1.03	1.03	0.74	0.74	0.48	1.17	24.8	22.4	9.7	93.3	2.3	
		0.47	0.58	0.74	1.03	1.03	0.92	0.92	0.65	0.65	0.48	1.17	24.8	22.4	9.7	93.3	2.3	
		0.41	0.43	0.65	0.92	0.92	0.92	0.92	0.65	0.65	0.48	1.17	24.8	22.4	9.7	93.3	2.3	

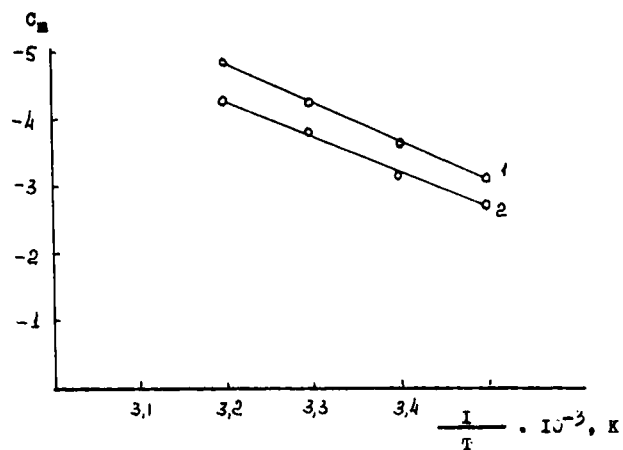


FIGURE 6 Logarithm dependence of mean constant of reaction rate C_m on reverse temperature $1/T$.

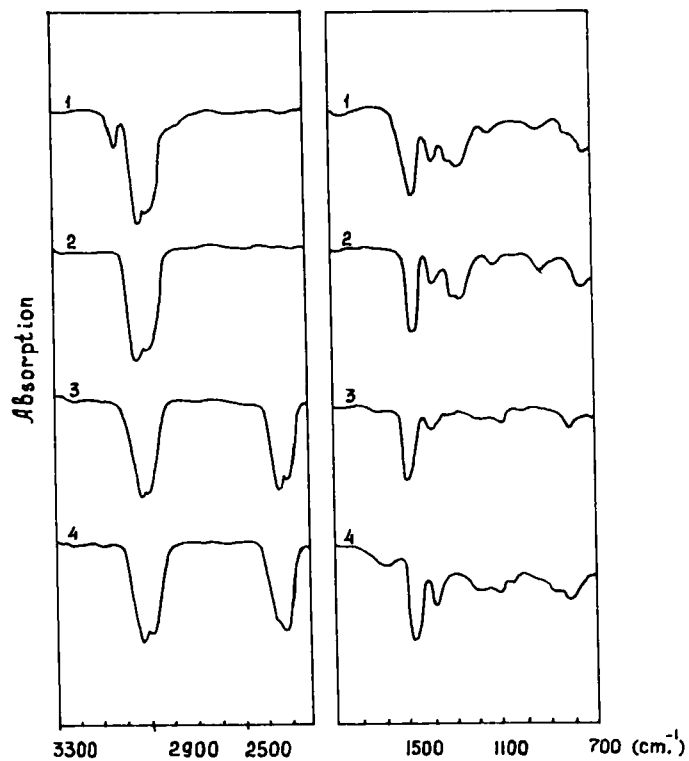


FIGURE 7 Infrared spectra. (1) CP-28; (2) CP-418; (3) CP-28 (phosphorus content, 10.6%); (4) CP-418 (phosphorus content, 9.7%).

TABLE IV
Physicochemical properties of oligomer phosphines

Mother chlorinated paraffin	Physicochemical properties of oligomer phosphines							
	η_D^{20}	d_{20}^4	Molecular mass	η , 50° mpz	P	C	H	Cl
	Elemental composition, %							
CP-28	1.5198	1.020	370	271.8	10.6	74.8	11.7	5.0
CP-28	1.5191	1.015	358	252.4	5.3	75.5	11.3	7.8
CP-28	1.5187	1.011	360	231.8	2.4	74.6	10.9	12.2
CP-418	1.5568	1.151	460	1099.8	9.7	79.6	9.2	6.3
CP-418	1.5425	1.132	456	1032.7	3.4	78.3	9.3	8.2
CP-470	1.5672	1.151	493	1121.7	6.3	79.2	10.1	5.1

TABLE V

The effect of the complex excess $\text{PH}_3 \cdot \text{AlCl}_3$ on the elemental composition and phosphorylation degree of chlorinated paraffins.
Reaction conditions: temperature, 20°C; treatment duration, 5 hours; solvent, chlorine benzene.

Reagent ratio	Mother chlorinated paraffins									
	CP-28 Chlorinity, % - 28			CP-418 Chlorinity, % - 41			CP-470 Chlorinity, % - 49			Degree of phosphorylation
	P	Cl	Degree of phosphorylation	P	Cl	Degree of phosphorylation	P	Cl	Degree of phosphorylation	
1:2	5.3	21.8	20.4	4.2	34.1	11.0	3.9	42.9	8.6	
1:3	5.8	21.6	22.3	4.3	34.1	11.3	3.9	42.8	8.6	
1:4	6.1	20.9	23.4	4.3	34.2	11.3	4.0	42.6	8.8	
1:5	6.5	20.8	24.9	4.5	34.2	11.8	4.1	42.6	8.9	
1:6	6.8	20.7	26.1	4.8	33.9	12.6	4.1	42.5	8.9	
1:7	6.9	20.7	26.5	5.0	33.8	13.1	4.4	42.3	9.5	
1:8	7.0	20.5	26.9	5.2	33.6	13.7	4.7	42.2	10.3	
1:9	7.1	20.1	27.2	5.2	33.6	13.7	4.9	41.9	10.7	
1:10	7.1	20.1	27.2	5.3	33.5	13.9	4.9	41.9	10.7	

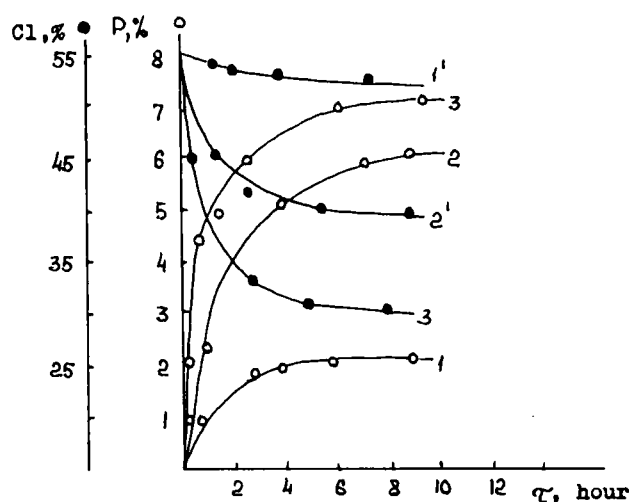


FIGURE 8 The influence of phosphorylation temperature with the complex on the phosphorus and chlorine content in poly(vinyl chloride) (PVC). (1,1') 0°C; (2,2') 20°C; (3,3') 30°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

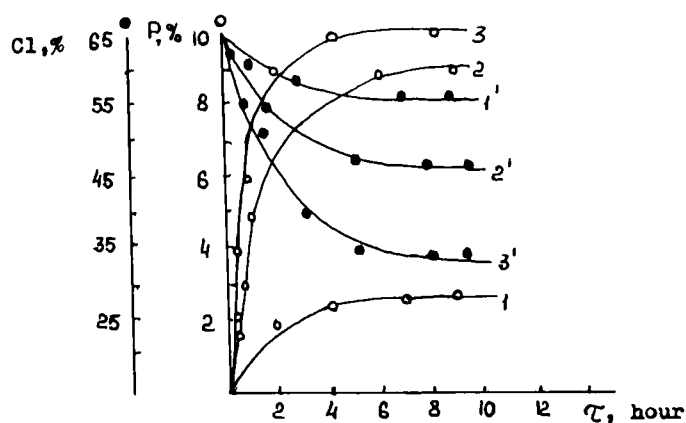


FIGURE 9 The influence of phosphorylation temperature with the complex on the phosphorus and chlorine content in the copolymer of vinyl chloride with vinylidene chloride (1,1') 0°C; (2,2') 20°C; (3,3') 30°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

of the preexponential multiplier have been calculated by the least squares method, while free activation energy, enthalpy and entropy of activation have been calculated by the Airing equation (Table III). With increasing chlorinity in chlorinated paraffins the above-mentioned activation parameters do not practically change. Resulting from the value of the pre-exponential multiplier and low activation energy (24.8 kJ/mole) it can be assumed that the phosphorylation process proceeds according to the ionic mechanism through the formation of an intermediate activated complex.

Infrared spectrum analysis (Figure 7) of the mother and the phosphorylated chlorinated paraffins has shown that in the region of 2300 cm^{-1} of the spectra of

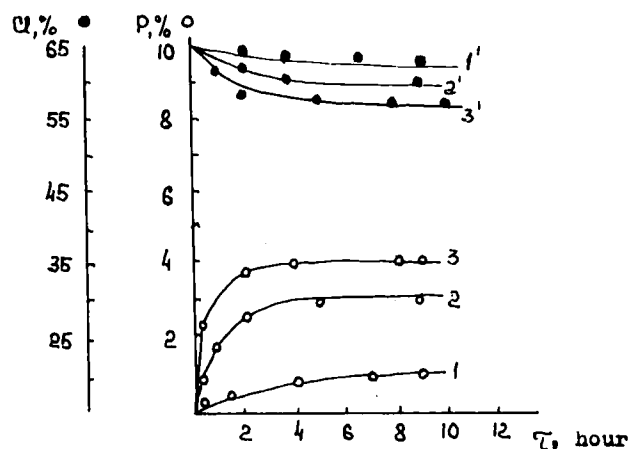


FIGURE 10 The influence of phosphorylation temperature with the complex on the phosphorus and chlorine content in the copolymer of vinylidene chloride with Povidene. (1,1') 0°C; (2,2') 20°C; (3,3') 30°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

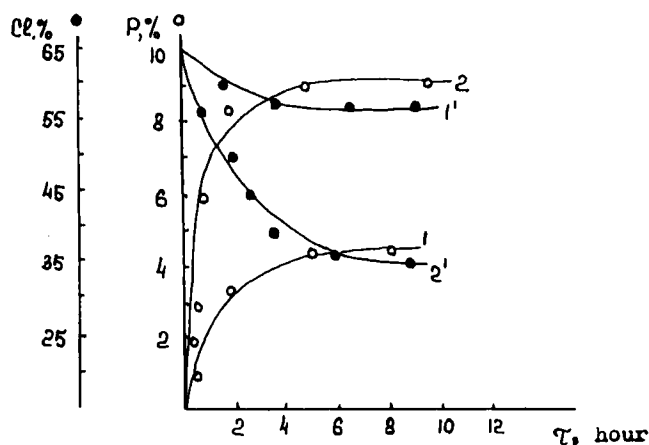
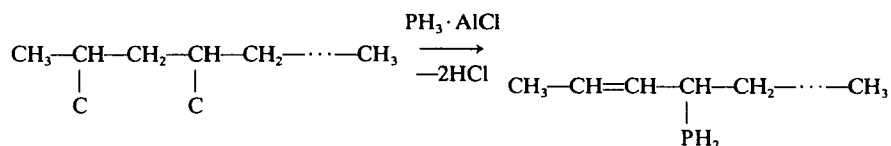


FIGURE 11 The influence of phosphorylation temperature with the complex on the phosphorus and chlorine content in the chlorinated poly(vinyl chloride) (PSC-PS). (1,1') 0°C; (2,2') 30°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

phosphorylating chlorinated paraffins there appear intensive absorption bands related to valence oscillations of PH groups according to data in the literature. The absorption in the region of 810 cm^{-1} is related to deformation oscillations of those groups. For the phosphorylated chlorinated paraffins CP-418 and CP-470 in the region of 1600 cm^{-1} there were discovered absorption bands relating to the valence oscillations of $\text{C}=\text{C}$ bonds. In the case of phosphorylated CP-28 the appearance of this band has not been observed. It is likely to account for the fact that with increasing chlorinity in the mother chlorinated paraffins along with phosphorylation the process of dehydrochlorination proceeds to form double bonds in the following structure:



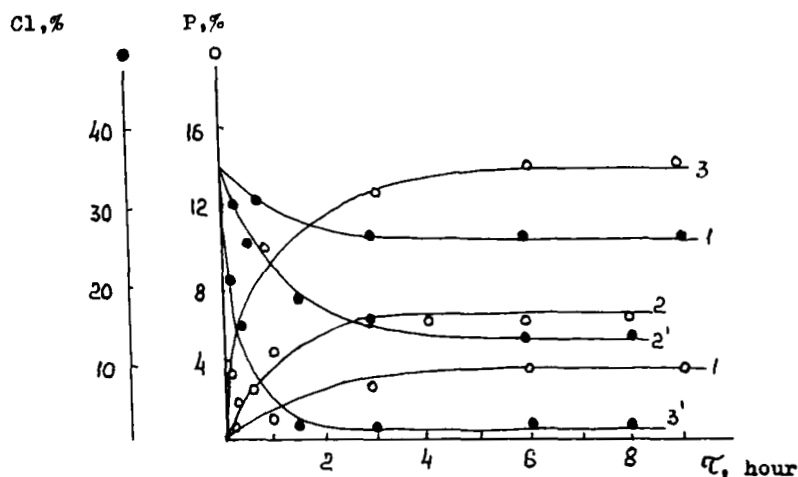


FIGURE 12 The influence of phosphorylation temperature with the complex on the phosphorus and chlorine content in hydrochlorinated natural rubber (HCNR). (1,1') 0°C; (2,2') 20°C; (3,3') 30°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

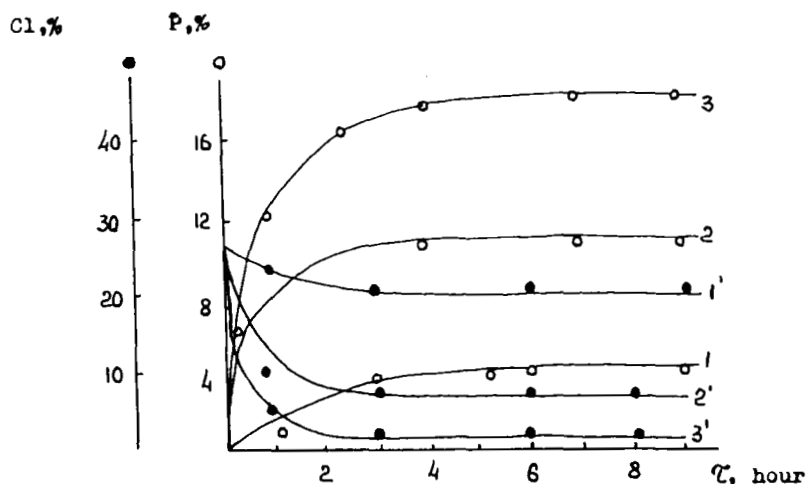


FIGURE 13 The influence of phosphorylation temperature with the complex on the phosphorus and chlorine content in hydrochlorinated isoprene rubber (HCSIR-3). (1,1') 0°C; (2,2') 20°C; (3,3') 30°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

The properties of oligomer phosphines are given in Table IV. The influence of the relationship of the reagent to the degree of phosphorylation of chlorinated paraffins by the complex compound $\text{PH}_3 \cdot \text{AlCl}_3$ is presented in Table V. An increase in phosphorylating agent excess affects an increase in the phosphorylation degree of chlorinated paraffins, but not as greatly as does an increase in temperature. Therefore in the case of the chlorinated paraffin CP-28, increasing the excess of the phosphorylating agent from twofold to tenfold allows the phosphorylation degree to increase by 6.8% and the phosphorus content in the final product to increase by 1.8%.

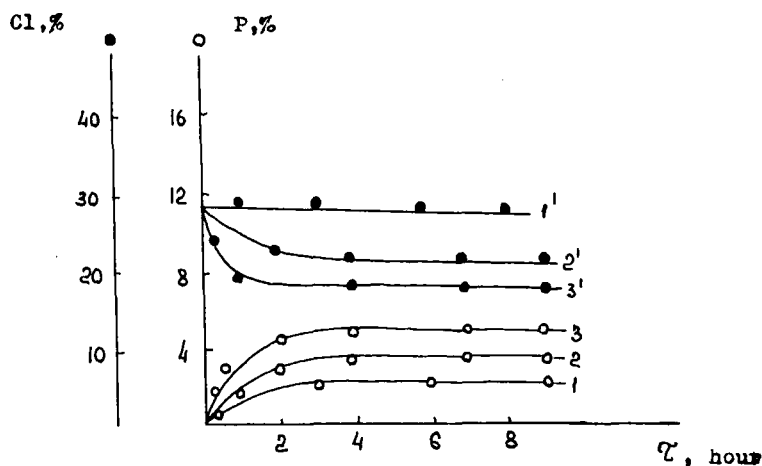


FIGURE 14 The influence of phosphorylation temperature with the complex on the phosphorus and chlorine content in chlorosulphurated polyethylene (CSPE). (1,1') 0°C; (2,2') 20°C; (3,3') 30°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

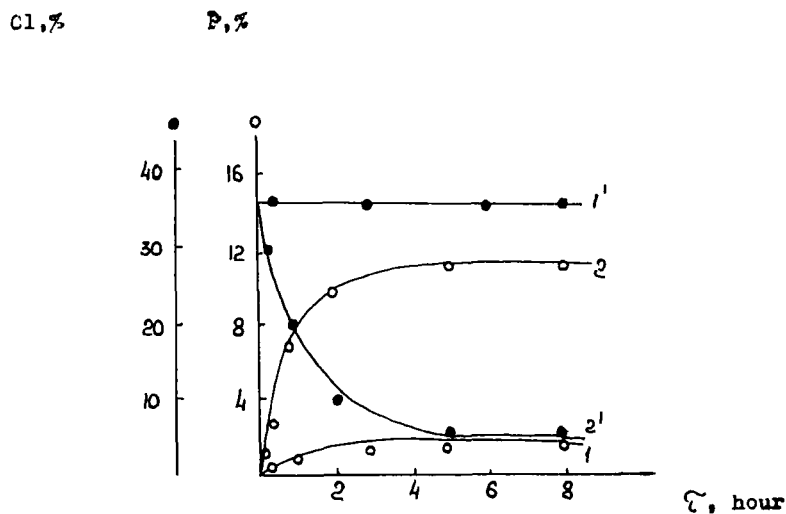


FIGURE 15 The influence of phosphorylation temperature with the complex on phosphorus and chlorine content in chloroprene rubber (CR). (1,1') 20°C; (2,2') 80°C. Reagent relationship, 1:1; solvent, tetrachloroethane.

Thus, the phosphorus hydride complex with aluminium trichloride appears to be the most preferable. This compound has been used as a phosphorylating agent of halogen-containing carbon-chained polymers.

To investigate the action of the complex compound of phosphorous hydride with aluminium trichloride action on chlorine-containing polymers we used poly(vinyl chloride) and copolymers of vinyl chloride with vinylidene chloride, chlorinated poly(vinyl chloride), chlorosulphuric polyethylene, hydrochlorinated isoprene natural rubbers and chloroprene rubber. The polymers mentioned above differ from

TABLE VI

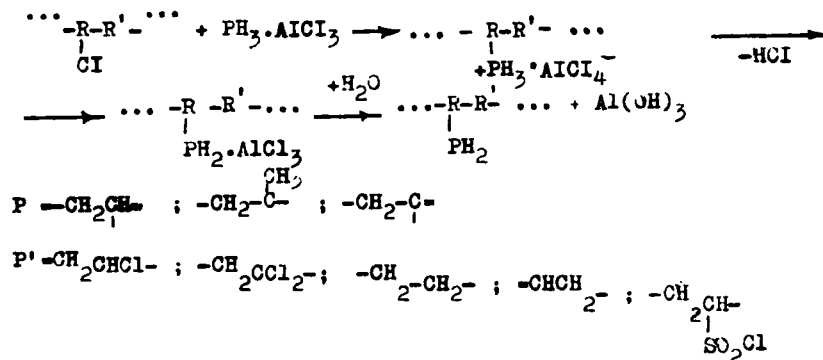
Influence of reaction temperature and the nature of the phosphorylating agent on the elemental composition and the degree of phosphorylation of chlorine-containing polymers.

Reaction conditions: reagent ratio, 1:1; solvent, chlorobenzene; treatment duration, 4 hours.

Phosphorylating agent	Reaction temperature, °C	Mother polymers												
		PVC					PSC-PC							
		Chlorinity, % - 56		Degree of phosphorylation		P	VCVD-40		Degree of phosphorylation		P	Chlorinity, % - 65		
		P	Cl	Degree of phosphorylation	P		Cl	Chlorinity, % - 61	Degree of phosphorylation	P		Cl	Degree of phosphorylation	P
$C_4H_9PH_2 \cdot AlCl_3$	0	4.1	48.5	7.9	4.2	52.6	6.7	6.7	4.8	54.2	7.1	4.8	54.2	7.1
	20	4.6	42.1	8.9	4.7	47.4	7.7	7.7	5.2	51.3	7.7	5.2	51.3	7.7
$C_3H_{11}PH_2 \cdot AlCl_3$	30	5.4	40.3	10.5	5.8	45.1	9.5	9.5	6.1	49.8	9.1	6.1	49.8	9.1
	0	4.8	47.5	9.3	4.6	51.7	7.5	7.5	4.9	53.5	7.3	4.9	53.5	7.3
$C_6H_{13}PH_2 \cdot AlCl_3$	20	5.3	40.6	10.3	5.1	50.5	8.3	8.3	5.3	52.6	7.9	5.3	52.6	7.9
	30	5.8	38.2	11.2	6.3	45.4	10.3	10.3	6.5	47.2	9.6	6.5	47.2	9.6
	0	3.8	46.1	7.4	4.7	50.5	7.7	7.7	5.3	50.6	7.9	5.3	50.6	7.9
	20	4.3	43.7	8.3	5.1	46.9	8.3	8.3	5.7	48.1	8.5	5.7	48.1	8.5
	30	5.2	41.1	10.1	6.3	44.9	10.3	10.3	6.7	42.8	9.9	6.7	42.8	9.9

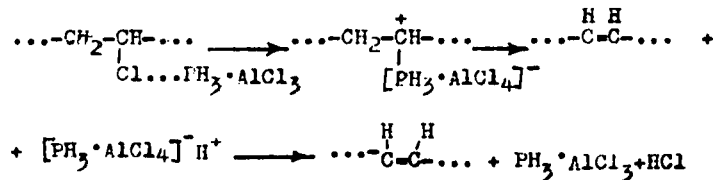
each other in degree of chlorination and position of chlorine in macromolecules. That enables us to compare the reactivity of the $\text{PH}_3 \cdot \text{AlCl}_3$ complex with respect to chlorine atoms attached to secondary and tertiary carbon atoms and to carbon at the double bonds as well. In addition, the polymers mentioned above are produced commercially on a large scale.

The essence of conversions proceeding during the phosphorylating process can be illustrated by the following scheme:³



With the purpose of studying the phosphorylation effect on phosphorus and chlorine content in the polymer phosphines obtained, as well as for the choice of optimal phosphorylation conditions, interaction was carried out at 0°C, 20°C, 30°C, 80°C and using various reagents. Tetrachloroethane and chlorobenzene were used as solvents, as well as at phosphorylating chlorinated paraffins.

Phosphorylation conditions and elemental composition of the obtained carbo-chained polymer phosphines are illustrated in Figures 8–15. The interaction temperature significantly affects the phosphorus content in phosphorylated polymers and the proceeding of side reactions. With its increase the phosphorylation degree also increases, but a significant decrease of chlorinity in products is observed, probably due to the competitive elimination reaction. Dehydrochlorination of chlorine-containing polymers is known to speed up in the presence of Lewis acids. While phosphorylating at a temperature increase, the complex is likely to participate in a side reaction, which may be presented by the following scheme:



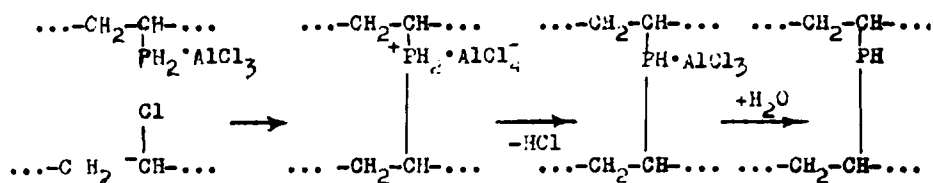
At the initial stage the electrophilic reagent attaches a chlorine atom of the polymer macromolecule, which leads to the formation of a carbo-cation stabilized by proton elimination to form a double bond in a macromolecule. At the final stage there occurs isolation of a free complex and chlorine hydride. Since this reaction proceeds in the macromolecules of phosphorylated polymers, some regions

of polyene structure form accompanied by coloring of the final products of the reaction.

Thus, poly(vinyl chloride) changes its color from light yellow to brown. The investigated polymers, while interacting with the $\text{PH}_3 \cdot \text{AlCl}_3$ complex lose their ability to dissolve in organic solvents, which can probably be explained by either proceeding intermolecular elimination of chlorine hydride:



or by further substitution of chlorine on the reactive $-\text{PH}_2 \cdot \text{AlCl}_3$ groups:



The latter suggestion is consistent with data in Reference 4 according to which on the interaction of $\text{PH}_3 \cdot \text{AlCl}_3$ with haloid alkyls the yield of primary phosphines decreases with a decrease in the length of a carbon hydride radical along with an increase in the simultaneous yield of the secondary phosphines. The authors succeeded in obtaining primary phosphines with rather high yields by using haloid alkyls $\text{C}_6\text{H}_{13}\text{X}$ and higher. As the macromolecules of poly(vinyl chloride) and other chlorine-containing polymers are composed of structural links including not more than four hydrogen atoms, the phosphorylation is likely to be accompanied by the formation of intermolecular phosphorus-containing PH bridges.

The phosphorylation study of chlorine-containing polymers by the $\text{PH}_3 \cdot \text{AlCl}_3$ complex in the temperature range of 0°C – 30°C , mole reagent relationship 1:1 and with the use of tetrachloroethane as a solvent (Figures 8–15) has shown that phosphorylation and elimination rates of chlorine hydride for each separate polymer do not increase correspondingly with an increase in the temperature of phosphorylation. In the case of poly(vinyl chloride) (Figure 8) the phosphorus content in polymer of 0°C increases monotonously with the treatment duration and attains maximum value (2.5%) in 8 hrs. At the same time the course of a side reaction of chlorine hydride elimination is minimal and chlorinity in phosphorylating samples decreases accordingly as the phosphorus content increases. The same regularity is observed upon copolymer vinyl chloride phosphorylating with vinylidene chloride (VCVC-40) (Figure 9) and chlorinated poly(vinyl chloride) (PSC-PS) (Figure 11) into which under these conditions 3.0% and 4.6% of phosphorus are introduced, respectively, chlorinity being 55.0% and 58.0%. Vinylidene copolymer with vinyl chloride (Povidene) are phosphorylated with greater difficulty and after 7 hrs of treatment by the complex contains 1.5% phosphorus and 63% chlorine (Figure 10), which can probably be attributed to a much closer packing of the copolymer chains, a strong intermolecular interaction and as a result less accessibility of chlorine atoms. The amounts of fixed phosphorus for hydrochlorinated isoprene (Figure

13) and natural rubbers (Figure 12) as well as chlorosulphurinated polyethylene (Figure 14) at 0°C do not exceed the values obtained for poly(vinyl chloride) VCVD-40 and PSC-PS. Under these conditions the chloroprene rubber is not phosphorylated, which is likely to account for the following. In chloroprene rubber the main part of the molecular chain is arranged as a result of monomer addition in the 1.4 position to chlorine atom at the double bond. An electro-negative chlorine atom with unpaired electrons draws off an electron cloud π -bond, reducing the electronic density of the C=C bond and forming a general electron cloud. Because of this, chlorine loses its mobility and undergoes substitution reactions with difficulty.

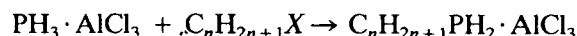
With the temperature rise of phosphorylating PVC, VCVD-40, Providene, chlorinated poly(vinyl chloride), chlorosulphurinated polyethylene, hydrochlorinated isoprene and natural rubbers up to 30°C, we succeeded in introducing significantly greater amounts of phosphorus into polymers for the same interval of time. Under these conditions 5.0% of phosphorus is introduced into poly(vinyl chloride) (Figure 8) for an hour and the maximum amount (8.0%) for 8 hours. The phosphorylating results of VCVD-40 and PSC-PS are represented in Figures 9 and 11. For the same intervals of time 7.0 and 9.8%; 6.0% and 9.5% of phosphorus are being introduced into VCVD-40 and PSC-PS, respectively. For the chlorosulphurinated polyethylene (Figure 14) and Povidene (Figure 10) the amounts of fixed phosphorus are somewhat lower: 3.0% and 4.8%; 3.5% and 5.1%. In the case of chlorosulphurinated polyethylene, an insignificant increase of phosphorus content with temperature rise is likely to account for the presence of SO₂Cl groups in the polymer under whose action partial decomposition of phosphorylating agent into the mother constituents may occur.

The temperature rise in phosphorylation significantly affects the phosphorus content in the products on the basis of hydrochlorinated isoprene (Figure 13) and natural (Figure 12) rubbers. At a temperature of 30°C, for one hour of interaction with the complex PH₃ · AlCl₃, 14.0% and 10.0% of phosphorus are being introduced into the above-mentioned polymers, respectively, and 18.0% and 14.0% for 8 hours.

Chloroprene rubber reacts with the complex at the phosphorylation temperature rise up to 80°C and the polymer phosphines obtained contain up to 11% phosphorus (Figure 15).

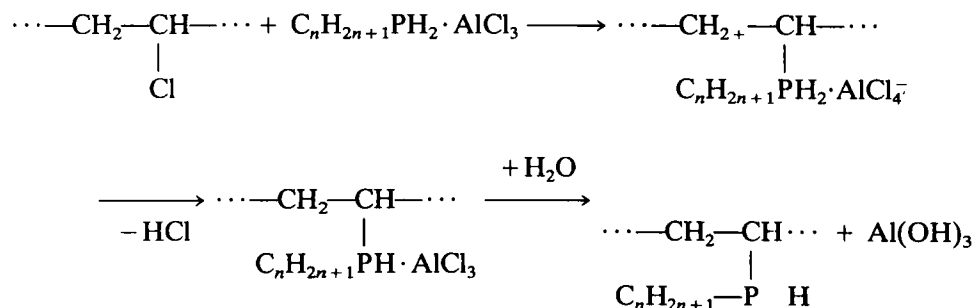
With the phosphorylation temperature rise for all investigated polymers disagreement between the eliminated chlorine and the amount of introduced phosphorus has been observed which confirms the fact that the side reaction of dehydrochlorination occurs.

Since phosphorylation of chlorine-containing polymers by the complex PH₃ · AlCl₃ proceeds to form polymer phosphines insoluble in organic solvents, an attempt has been undertaken to reduce the reactivity of the complex by its preliminary treatment with halogen-containing alkyls according to the following scheme:⁵



where $n = 4-6$, $X = \text{B}_2, \text{Cl}$ and by subsequent phosphorylation of chlorine-

containing polymers being formed by the $C_nH_{2n+1}PH_2 \cdot AlCl_3$ complexes. In this case, for instance, phosphorylation of poly(vinyl chloride) can be represented by the following scheme:



Preliminary treatment of the complex compound of phosphorus hydride with aluminium trichloride by the equimolecular amounts of halogen-containing alkyls was conducted at 80°C. Butyl chloride and butyl bromide, pentyl chloride, hexyl chloride were used as halogen-containing alkyls. Subsequent polymer phosphorylation was conducted in chlorobenzene. The results of phosphorylation are given in Table VI. In all cases, the polymer phosphines obtained were light yellow powders dissolved in organic solvents. These data confirm the fact that chlorine-containing polymers, when treated with complex $PH_3 \cdot AlCl_3$, lose their solubility not because of intermolecular elimination of chlorine hydride, but because of further substitution on reactive $PH_2 \cdot AlCl_3$ groups. The availability of chemically fixed phosphorus and the structure of polymer phosphines are confirmed by elemental analysis and infrared spectroscopy.

Thus, complex compounds of phosphines with Lewis acids can be used as effective modifying agents while creating new phosphorus and chlorine-containing inhibitors of polymer burning. In comparison with the known phosphorylating agent, phosphorus trichloride, when using the complex of hydrogen phosphide with aluminium trichloride we were successful in introducing two- and threefold additional amounts of phosphorous into the polymers under investigation and attaining higher degrees of phosphorylation under more favorable conditions and for a shorter period of time.

Synthesized oligomer and polymer phosphorus- and chlorine-containing products can be recommended as reactive inhibitors of composite material burning.

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