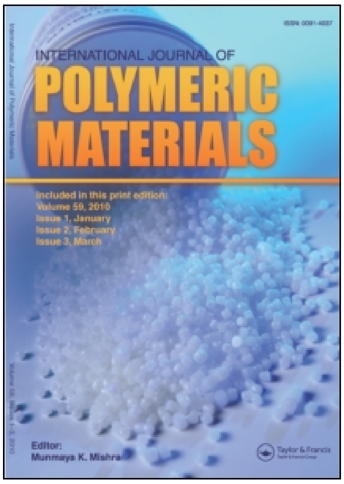

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P. A. Kirpichnikov[a]; N. A. Mukmenyova[a]; O. A. Cherkasova[a]
[a] S. M. Kirov Institute of Chemical Technology, Jatar ASSR, USSR

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Efficiency and Mechanism of Stabilizing Effect of Organic Phosphorous Acids in Polymers

P. A. KIRPICHNIKOV, N. A. MUKMENYOVA, O. A. CHERKASOVA

S. M. Kirov Institute of Chemical Technology, Kazan, Jatar ASSR, USSR

The relationship between phosphorus acids structure and their stabilizing effects on polymers has been investigated by IR, NMR-spectroscopy and other physico-chemical methods. It was shown that acids decompose hydroperoxide and influence on the process of hydrocarbons, polyolefines and other polymers autooxidation. Many chemical reactions lead to polymer stabilization due to some reaction centers in molecules of the acids.

KEYWORDS: Stabilization, hydroperoxides, phosphorous dithioacids, inhibition of oxidation, autooxidation, synergism

The compounds of 3-coordinated phosphorus atom, mainly neutral phosphite esters draw the greatest attention as polymer stabilizing agents. A series of studies has been carried out for this class of compounds, the cardinal properties of phosphites established and the basic mechanisms of their inhibiting and color stabilizing effect defined and proved.[1]

Utilization of phosphite esters as stabilizing agents is supported theoretically by the unique ability of phosphorus atom for undergoing electron interactions of various types chiefly due to the possibility to vary the phosphorus atom coordination number. As a rule, stabilization processes result in going from phosphite esters to 4-coordinated derivates, particularly to dialkyl (aryl) phosphorus acids. From this point of view phosphorous acids are of considerable interest, being highly reactive materials, they can serve as versatile agents of homolytical and heterolytical reactions in polymer stabilization.

This report deals with the basic reactions of certain phosphorous acids (arylenephosphorous acids, phosphorous dithioacids) responsible for polymer stabilization processes (i.e. reactions with $RO_2^{\cdot}$; $RO^{\cdot}$, ROOH, C═O-group, $(CH{=}CH)_n$ etc.) and with the relationship between their reactivity, structure and stabilizing effect.

KINETICS AND MECHANISM OF REACTIONS WITH HYDROPEROXIDES

Arylenephosphorous acids (APA)

The investigation of kinetics of cumene hydroperoxide (CHP) reactions with phosphorous acids of this class show that the initial rate of CHP decomposition under the influence of APA follow the kinetic equation:

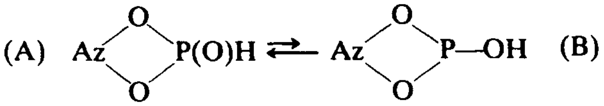
$$W_0 = k[\mathrm{CHP}]^2[\mathrm{InH}]$$

Rate constants calculated from the equation of tri-molecular reactions are given in Table I.

The reactivity of phosphorous acids to CHP is closely related to their acidic properties, the latter being estimated by method of potentiometric titration.

Correlation between kinetic parameters of APA–CHP reaction and ionization constant values makes it evident that acids defined by high pKa values (>9) are inert against CPH. CPH decomposition takes place only under the influence of strong acids ($pKa < 9$) (see Table I).

It is shown that the change in ring size from five- to eight-membered one results in significant decrease in protonodonating properties of cyclic phosphorous acids, making them comparable to their acyclic analogs in terms of their acidic properties. The part of (A) structure increases similarly in the tautomeric equilibrium



with being completely dominated in the eightmembered cyclic derivative, that follows from ^{31}P NMR spectra and pKa values.[2]

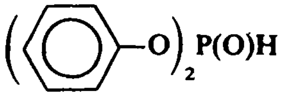
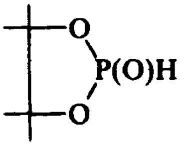
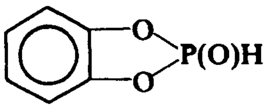
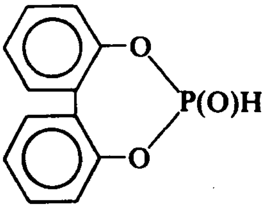
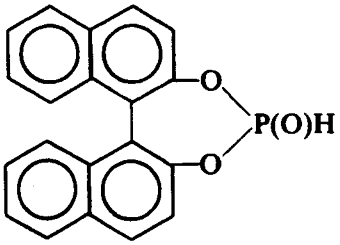
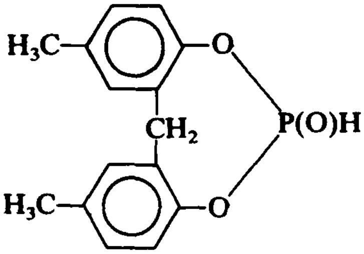
Strong phosphorous acids decompose CHP catalytically that being confirmed by the consumption of CHP while adding it portionwise to the reaction system (Figure 1) and also by high values of stoichiometric coefficients of reaction (ν) (Table I).

It is found that the catalytic decomposition of CHP under the influence of acids is attenuated due to parallel reactions resulting in the formation of products low active towards CHP. For example, in the case of pyrocatecholphosphorous acid there are identified basing on the ^{31}P NMR and the counter-synthesis, the following phosphorous containing products: dibenzospirohydrophosphorane δ_p 22(J_{pH} 900 Hz), O,O-phenylene-*O*-cumylhydroxyphosphorane δ_p 4(J_{pH} 740 Hz), pyrocatecholcumylphosphonate δ_p36 ppm, pyrocatecholcumylphosphate δ_p13 ppm, pyrocatecholphosphoric acid δ_p 5 ppm, phosphorous acid δ_p 4 (J_{pH} 670 hz).

The contribution of radical and non-radical routes of reaction with CHP has been estimated. Negative polarization of ^{31}P nuclei was recorded by the NMR-method (Figure 2).[3] Evidently, a quick sequence of reactions involving radicals occurs, resulting in formation of phosphate and phosphonate structures. However in the absence of chemical polarization no signals were detected in the regions of lines assigned to these products and hence, the contribution of radical mechanism is negligible. The CHP decomposition rate independent of ionol—a typical radical acceptor, and only 0.2 mass % of radical CHP decomposition products detected (gas-liquid chromatography method) confirm the dominance of non-radical catalytical CHP decomposition.[4]

TABLE I

Kinetic parameters of CHP decomposition reaction under the influence of arylenephosphorous acids

Formula (or compound)	CHP, 100°C		pK_a^{25}		
	v	$\frac{K_1, L^2}{mol^2 \cdot s}$	Propanol	Water–ethanol (1:1)	δ_p, ppm τ_{PH}, Hz
	11	0.6	11.46	7.49	0(750)
	30	1.2	8.54	2.37	−20(705)
	100	210.0	4.19 10.57	2.44	129 126
	15	0.4	10.68	2.52 7.26	6(720)
	0.5	—	10.76	2.52 7.58	6(730)
	0.5	—	12.54	—	2(735) 5(700)

+ : —$C(CH_3)_3$.

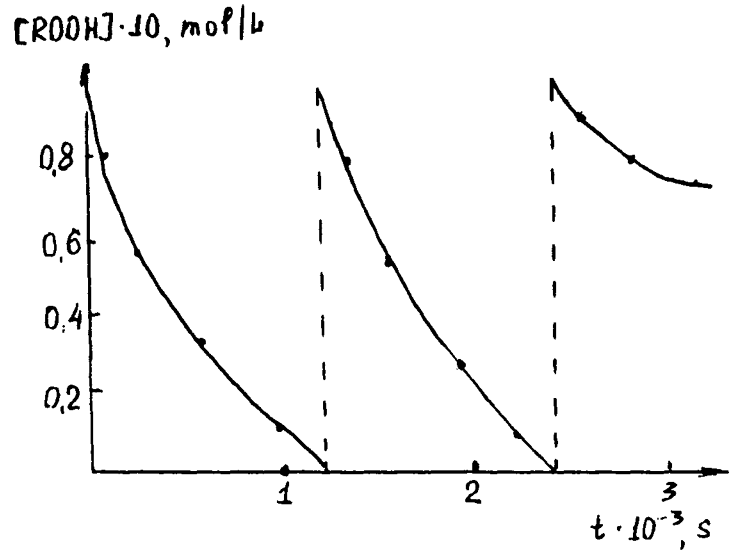


FIGURE 1 Kinetic curves of CHP decomposition under the influence of pyrocatecholphosphorous acid, 100°C, chlorbenzene, $[CHP] = 1 \cdot 10^{-1}$ mol/L $[PPh] = 1.33 \cdot 10^{-3}$ mol/L.

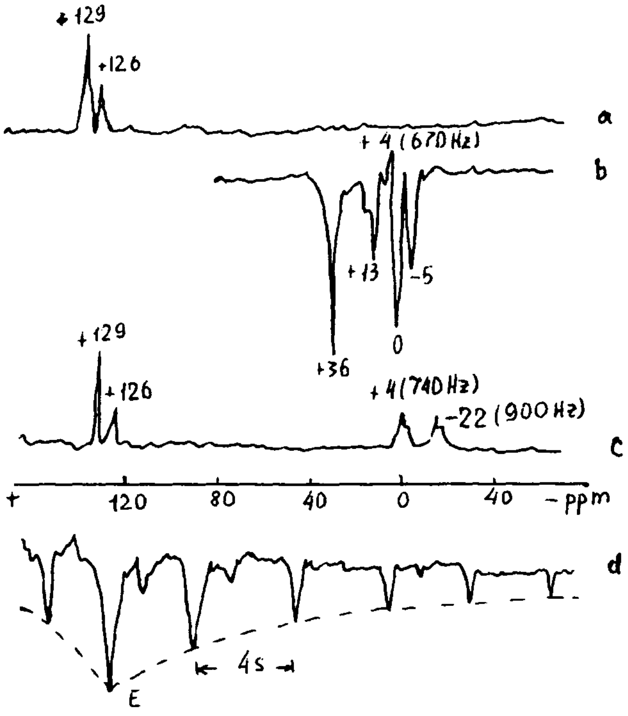


FIGURE 2 ^{31}P NMR spectra of: a—pyrocatecholphosphorous acid, b,c—products of reaction in benzene, d—phosphonate region (+30 +40 ppm) of reaction products. $[PPhA] = 1.8$ mol/L

Phosphorous dithioacids (DTA)

Dithiophosphoric acids with clearly pronounced acidic properties show a high activity in reactions with CHP. Gross decomposition of CHP in the presence of DTA is distinguished by abnormally high stoichiometric ratios (7000 to 25 000), pointing out the catalytical character of CHP decomposition. This has been confirmed, just as in the case of dialkyl(aryl) phosphites, by investigations of the CHP flow rate while adding it portionwise to the reaction system. With that the reaction rate is held the same and the inductive period in kinetic curver of CHP decomposition is absent. Acid catalyzed CHP decomposition is described by equation of the second order reaction for CHP and by that of the first order reaction for the acid.[6]

Reaction mechanism and correlation between DTA reactivity were studied using the steric model [5].

Steric effects of phosphorus atom substituents in DTA, containing three potential reactive centers (P,S-thiolic, S-thionic), were calculated. Stoichiometric coefficients and rate constants were chosen as measured of DTA reactivity in reactions with CHP.

Correlation analysis carried out by least square method showed that satisfactory correlations of v and k with DTA structures could be observed only for the case of R_S constants describing the steric effects of thiolic sulphur atom substituents (Table II). It proves that precisely the thiolic sulphur atom (or S—H bond) is the reactive centre in this reaction.

As follows from the obtained results, stoichiometric ratios are increased with increase of steric effect of substituents at sulphur atom while rate constants of interaction of DTA and CHP are decreased.

In the course of investigation of the reaction by nuclear chemical polarization method NMR signals were obtained for products with polarized phosphorus nuclei. Emission lines belong to dithiophosphates. A small portion of radical route apparently results in the emergence of bis(thiophosphoryl)disulphide as a product of reaction, which can react with CHP homolytically.

Dithiophosphates, monothiophosphoric acids, bis(phosphoryl)disulphide were identified as products of reaction [6].

INHIBITION OF OXIDATION PROCESSES BY PHOSPHOROUS ACIDS

Initiated oxidation

Initiated oxidation reactions have been studied for the case of low-molecular hydrocarbon—styrene and isotactic polypropylene.

The efficiency of arylene phosphorous acids in the inhibition of radical process of styrene oxidation has been found out. Their antioxidizing properties have been shown to decrease with the increase of the ring size of acid molecule. Acyclic phosphorous acids catalyze styrene oxidation (Table III).

APA can serve as inhibitors of the initiated solid polypropylene oxidation (see Table III).

Stoichiometric ratios of inhibition (f) in comparison with those for the liquid phase, slightly decrease. However k_7 values of compounds investigated are 1 to 2

TABLE II

Kinetic parameters of reaction between CHP and phosphorous acids (100°C, [CHP] = 0.1 m/L) steric R_s constants for sulphur atom substituents

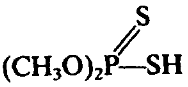
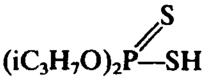
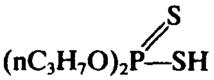
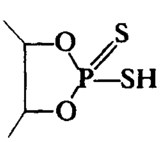
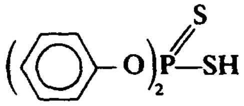
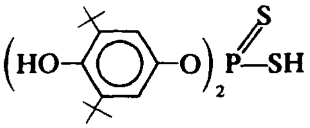
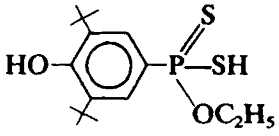
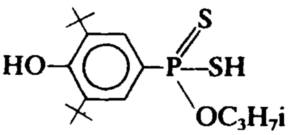
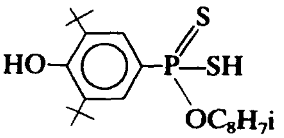
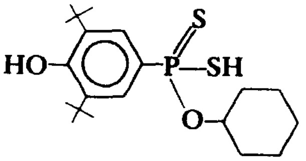
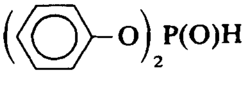
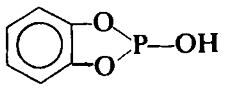
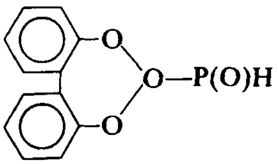
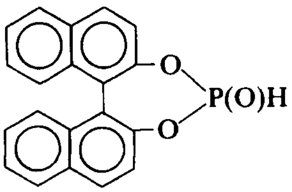
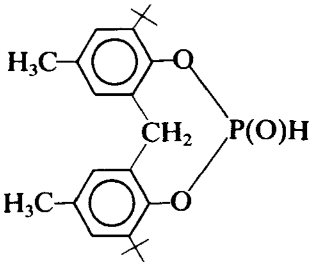
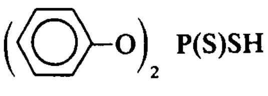
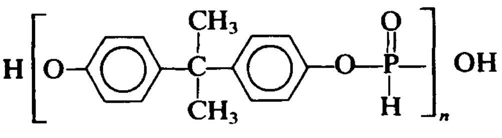
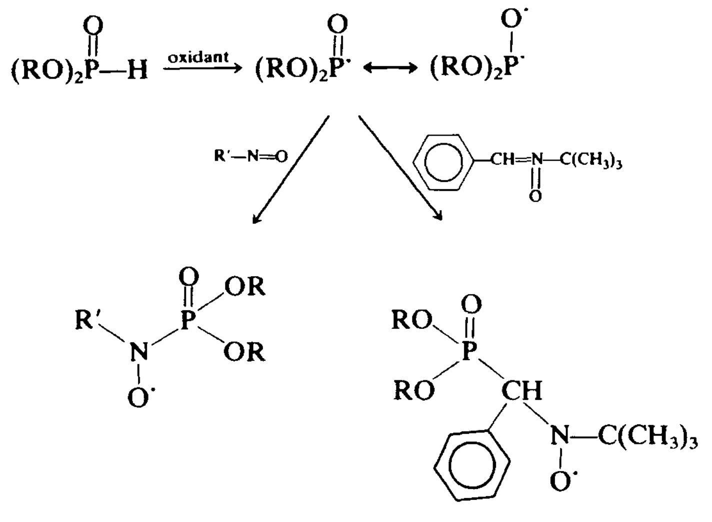
Formula (or compound)	ν_{CHP}	K, 100°C ($L^2 \cdot m^{-2} \cdot s^{-1}$)	$-R_s$	$\Sigma\sigma^*$
 $(CH_3O)_2P(=S)—SH$	15000	—	3.00	3.46
 $(iC_3H_7O)_2P(=S)—SH$	20000	16.7	3.78	3.46
 $(nC_3H_7O)_2P(=S)—SH$	18000	—	3.53	3.46
	22000	13.3	3.84	3.46
	25000	—	4.13	4.72
	10000	1.67	5.99	—
	1800	14.4	4.65	2.28
	2000	—	4.92	2.28
	2000	3.20	5.27	—
	2500	5.5	5.12	2.28

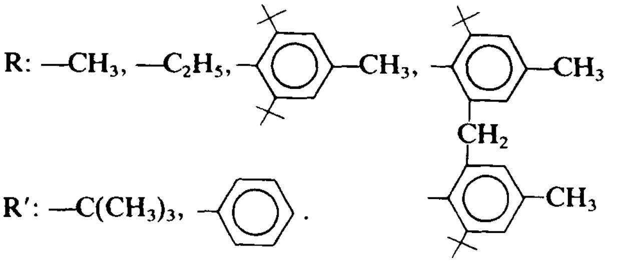
TABLE III

Kinetic parameters of phosphorous acids inhibiting effect in the course of the initiated oxidation of styrene (50°C) and polypropylene (85°C)

	Styrene		Polypropylene	
Compound	*f*	$K_7 \cdot 10^{-4}$ $L \cdot mol^{-1} s^{-1}$	*f*	$K_7 \cdot 10^{-3}$ $kG \cdot mol^{-1} \cdot s^{-1}$
	0.60	0.71	0.61	2.7
	1.35	81.0	—	5.85
	1.33	1.4	1.2	3.38
	1.35	4.6	—	—
	0.8	0.18	—	—
$(iC_3H_7O)_2P(S)SH$	0.35	120.0	0.9	8.69
	0.02	70.0	—	—
	1.25	6.16	0.75	2.93

orders less than those in the course of styrene oxidation, that should be apparently related to the peculiarities of reactions in the solid phase. At the same time the results of the inhibition are also caused by the efficiency of RO_2 binding and depend on stability and routes of transformation of intermediate phosphonyl radicals formed; the latter can be identified by transforming into the nitroxyl radicals[7] detectable by the ESR method.

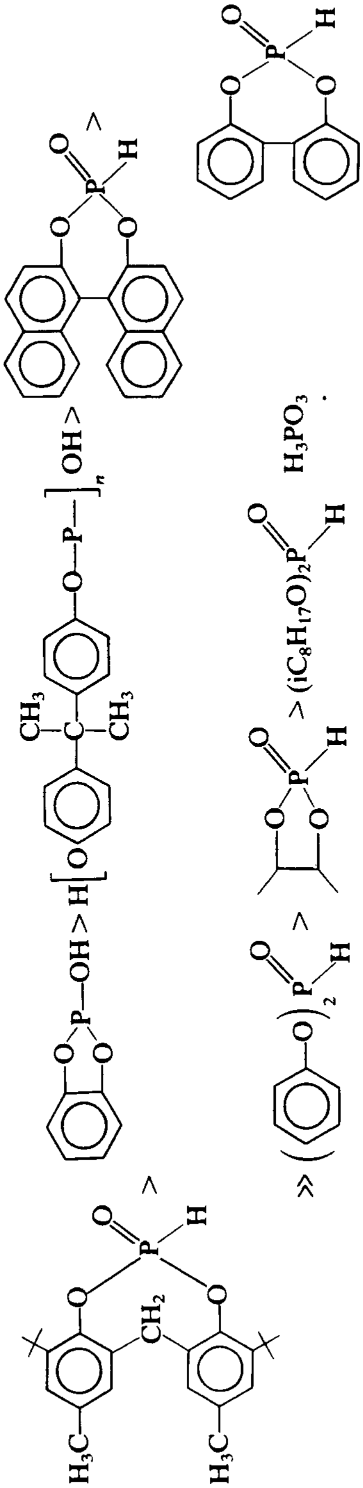




AUTOOXIDATION

The inhibiting effect of APA under the autooxidation conditions (200°C, $P_{O_2} = 250$ Torr) is characterized by low critical concentrations (0.007–0.003 mol/kG) and considerable induction periods (τ) in stationary region of oxidation. According to autooxidizing properties, they can be arranged in the following sequence:

Physico-mechanical parameters of high-density polyethylene (PE HD) films after 75 hours of aging in the presence of phosphorous acids, have the same or better values than those for the effective phenolic antioxidants.


>
>
>
>
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>
>>
(iC8H17O)2P
H3PO3
CH3
CH3
H3C
H3C
CH2
OH
n
2

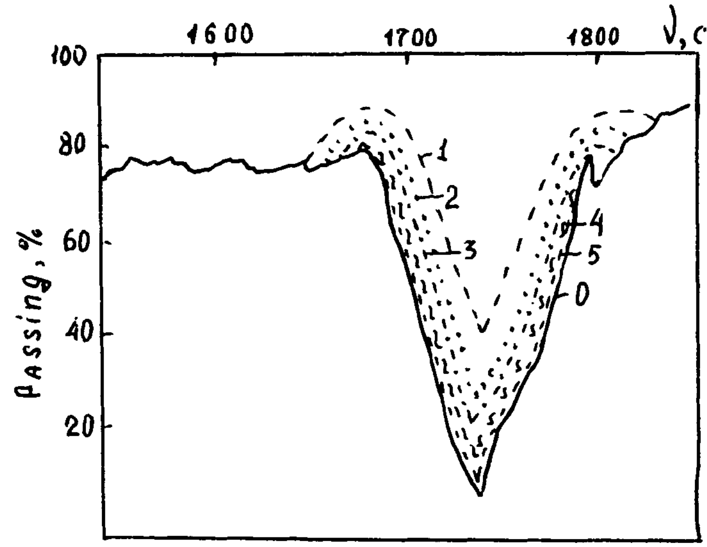


FIGURE 3 Kinetics of the formation of carbonyl groups in PEHD during thermooxidation, 110°C, in the presence of 5% mass: 0—no admixtures, 1—$(iC_8H_{17}O)_2P(O)H$, 2—$(iC_8H_{17}O)_3P$, 3—$(iC_8H_{17}O)_2POC_6H_5$, 4—$(iC_8H_{17}OP(OC_6H_5)_2$, 5—$(C_6H_5O)_3P$.

REACTIONS OF PHOSPHOROUS ACIDS WITH MOLECULAR PRODUCTS OF THERMAL AND THERMOOXIDATIVE POLYMER DESTRUCTION

Under conditions of the developed process of polymers oxidation reactions of phosphorous acids with active functional groups and with molecular products of degradation (carbonyl containing groups, isolated and conjugated double bonds, etc.) become of great significance. The regularities were established for the destruction of carbonyl-containing products by esters of phosphorus acids.[8]

Thus, in the course of PE HD autooxidation in the presence of phosphites, a considerable retardation of growth of intensivity $\nu_{C=O}$ was observed in comparison with non-stabilized sample. The efficiency of phosphites in reactions with carbonyl groups increased with the growth of the acid concentration. When diisooctylphosphorous acid concentration is 5 mass %, no formation of C=O-groups is observed at all within 900 hours (see Figure 3).

Similar results were obtained for the model reaction with previously oxidized PE HD. After 95 hours of PE aging, phosphites were added to it; the decrease of the ν 1720 cm^{-1} band intensity as great as $18 \div 45\%$ in IR spectra was then observed.

The reactivity of phosphites toward the carbonyl groups in polymers considerably depends on structure of the former and increases with transition from neutral to acidic phosphite esters and with substitution of aromatic radicals by alyphatic ones. To identify products of interaction C=O-groups of polymer, IR spectra are recorded for PEHD after removal excess of the phosphorous admixture by means of overprecipitation. The obtained spectra are distinguished by lower intensity of carbonyl absorption band (1720 cm^{-1}), by the intensive peaks at 1020–990 cm^{-1} (P—O—C) and 1280–1250 cm^{-1} (P=O), making phosphorylation of PEHD evident.

The IR spectra data of modified polymer as well as the results of studying model reactions of phosphites with low molecular analog of the oxidized PE allow to conclude that phosphorylation of the polymer proceeds with the formation of α-oxy-phosphonate structures.

The phosphorous acids are also capable to desactivate the reactive centres formed in the course of destruction of polyvinylchloride (PVC), that is proved by decrease in the rate of dehydrochlorination and in the colour intensity of the partially dehydrochlorinated PVC. Thus, thermal treatment causes monotonic increase of the amount of phosphorus in the destructed PVC due to the interaction of phosphites with active groups in polymer as far as those groups are forming.[9]

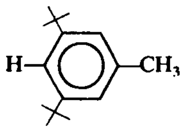
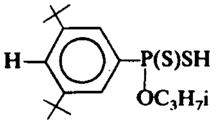
The observed PVC phosphorylation should be related first of all to the interaction of phosphites with the oxygen-containing fragments. In the case of formation of poly-conjugated structures (chromofors) in macromolecules, phosphites are capable to split the conjugated chains with the discoloration of polymer ("sympthomatic" stabilization).[10]

THE SYNERGISM

The increase of the induction period in the course of autooxidation of polyolefines has also been observed when the following synergetic mixtures were used: a) dithiophosphate or pyrocatechol phosphorous acid with the known inhibitor of free-radical oxidation-2,2′-methylene-bis(4-methyl-6-tert.-butylphenyl) (τ 8–9 hours) and b) 2,2′-methylene-bis-(4-methyl-6-tert.-

TABLE IV

Formation of internal synergism

Compound	ν_{CHP}	$K_7 \cdot 10^4$ $L \cdot mol^{-1} \cdot sec^{-1}$	f	τ_{PE}, min 200°C
$(iCH_3H_7O)_2P(S)SH$	20 000	120	0.35	75
	—	0.81	2.0	70
	2000	3.16	3.0	1060

butylphenyl)phosphorous acid or *O,O'*-binaphtylphosphorous acid with dilaurylthiodipropionate—the known destructor of hydroperoxides (τ 14–28 hours). The synergism in such systems proves possibilities of the polyfunctional stabilization by the phosphorous acids (the inhibition of free-radical oxidation and suppression of the degenerated branching) in thermooxidative destruction of polymers.

On the whole the obtained data can serve as a basis for purposeful synthesis of highly effective stabilizers. As a matter of fact, including into the molecule of a potential stabilizer fragments of the sterically hindered phenols responsible for the inhibition and groups capable to interact with hydroperoxides results in the significant increase of stabilizing effect of such a polyfunctional compound (Table IV).

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