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Organophosphorus Stabilisers of Polymers: Efficiency and the Mechanisms of Action

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The review is devoted to studies constituting the scientific basis of the search for and selection of highly effective organophosphorus stabilisers of polymeric materials. The physical chemistry of the potential organophosphorus stabilisers and the stabilisers used in practice are examined from this standpoint. The mechanisms of the inhibiting effect of organic phosphites in various compositions are discussed and the relative contributions of the mechanisms considered to the overall inhibiting activity are estimated. The dependence of the reactivity of phosphites on their structure is examined and the quantitative characteristics of the main reactions of phosphites are discussed. The results obtained make it possible to predict the effectiveness of phosphites with different structures as inhibitors of the chain autoxidation and degradation reactions of polymers. The bibliography includes 100 references.

CONTENTS

I. Introduction 1051
II. Stabilisation of polymers at the degradative process initiation stage 1052
III. Stabilisation of polymers at the oxidation chains propagation and degenerate branching stages 1054
IV. The improvement of the effectiveness of organophosphorus stabilisers (synergism) 1058

I. INTRODUCTION

The effective protection of polymeric materials against ageing is an important scientific-technological problem. Numerous studies devoted to the urgent problem of the elucidation of the scientific basis of the ageing and stabilisation of polymers have been published in recent years. They were initiated by the work of Academician N.M.Emanuel'[1,2], who formulated the principles of the ageing and stabilisation of polymers.

Among the wide variety of organic compounds used as stabilisers, organic phosphites (OP) occupy a special place. They are used as stabilisers of polyolefins, raw and cured rubbers, heterochain polymers, and poly(vinyl chloride), and also as inhibitors of the polymerisation of diene hydrocarbons[3]. Numerous investigations in this field have been carried out in Kazan[4-7]. It has been estabilished that the most powerful stabilising antioxidant activity is shown by the aromatic and aromatic alkyl-substituted esters of phosphorous acid which do not colour polymeric materials during their processing and use, exhibit a considerable synergistic effect in mixtures with phenols, are readily blended, are involatile, and their susceptibility to oxidation by molecular oxygen is low.

Qualitative model estimates involving the interaction of phosphites with 1,1-diphenylethyl hydroperoxide[8] and the stable diphenylpicrylhydrazyl radical[9] made it possible to classify phosphites as inhibitors with a combined type of activity: they decompose hydroperoxides, supressing degenerate branching, and can terminate chains by reaction with peroxy-radicals; on the other hand, they are capable of enhancing the activity of catalytic admixtures of variable-valence metals and of blocking weak (as regards degradation) sites in the polymer chain. We shall note the most important phenomenological consequences of such polyfunctionality of organic phosphites.

Firstly, the reactions of organic phosphites with hydroperoxides lead to the intensification (synergism) of the action of typical inhibitors (phenols) in their mixtures with phosphites in the autoxidation of polymers, i.e. under conditions where the main source of radicals is the accumulating hydroperoxides.

Secondly, organic phosphites induce the destruction of peroxy-radicals, which leads to the appearance of induction periods in polymer oxidation processes. As will be shown below, the inhibiting effect of phosphites is associated with the kinetics of their radical-chain oxidation. This is indicated by the broad distribution of the stoichiometric inhibition coefficients for the oxidation reactions carried out in different phases (liquid and solid).

Table 1. Changes in the content of the inner $\diagdown C{=}C \diagup$ bonds $\bar{\gamma}$ in PVC macromolecules on heat treatment in the presence of organic phosphites (353–373 K).[17]

Composition	[OP], mol/mol PVC	τ, h	T, K	$[\eta]_0$, dl g^{-1}	$[\eta]$, dl g^{-1}	$10^4 \cdot \bar{\gamma}$, mol/mol PVC
PVC($\bar{M}_w^0$ = 127 500)	—	—	—	1.23	1.19	1.0
PVC + (I)	0.02	2	100	1.23	1.23	0
PVC + (I)	0.02	8	100	1.23	1.22	0
PVC + (II)	0.02	5	80	1.23	1.23	0
PVC ($\bar{M}_w^0$ = 99 000)	—	—	—	1.02	0.92	1.4
PVC + (I)	0.01	11	80	1.02	1.02	0

Notation: τ is the heat treatment time, $\bar{M}_w^0$ the viscosity-average molecular weight of the initial PVC, and $[\eta]_0$ and $[\eta]$ are the intrinsic viscosities of the PVC solutions before and after ozonisation respectively.

Thirdly, since reactions of organic phosphites with both peroxy-radicals and with hydroperoxides develop simultaneously in the polymer during its oxidation, the observed inhibiting effects under the conditions of the degenerate-branched chain oxidation can be accounted for by the combination of these two mechanisms or their competition.

Finally, the effects of the non-chain inhibition and colour-stabilisation of polymers of phosphites are closely related with the supression of the initiation and development of degradative processes.

The wide variety of the possible mechanisms of the stabilising effect of organic phosphites complicate the theoretical analysis of the process involving the stabilisation of polymers by phosphites. A series of studies have been carried out recently in which the principal properties of organophosphorus compounds as stabilisers of polymeric materials have been established and the principal mechanisms of their inhibiting and colour-stabilising action have been formulated and proved.

The aim of the present review is to analyse the present state of the experimental and theoretical studies (during the period 1973–1983) of the stabilisation of polymers by organophosphorus compounds. The review deals with the principal results of these studies and also with new systems whereby it is possible to represent more fully the kinetic model of the stabilising action of organophosphorus stabilisers.

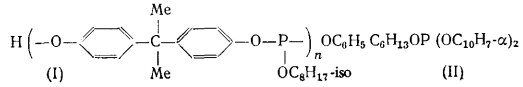
II. STABILISATION OF POLYMERS AT THE DEGRADATIVE PROCESS INITIATION STAGE

1. Poly(vinyl chloride)

The ability of organic phosphites to interact with "weak" sites in macromolecules[10], at which the decomposition of the polymer is initiated in the first place, was observed and demonstrated for the first time in relation to poly(vinyl chloride). As a consequence of the reaction of organic phosphites with the "weak" sections, the degradative processes are inhibited at the initiation stage, which increases the thermal stability of the polymer and leads to the preservation of its initial colour during ageing.

Until recently, in considering the mechanism of the stabilising action of organic phosphites, the complex poly(vinyl chloride) (PVC) dehydrochlorination process was regarded as a single-stage reaction[11–16]. The available literature data therefore make it possible to estimate only the overall effect of phosphites as regards PVC. Minsker et al.[17] published the results of a more detailed study of the influence of phosphite esters on the rate of dehydrochlorination of PVC.[18] The overall result is determined by the superposition of statistical dehydrochlorination processes at a rate w_c, leading to the random formation of isolated double bonds at any site within the macromolecules, and the HCl elimination process leading to the formation of a system of conjugated double bonds at a rate w_n.

It has been established[17] that the action of the phosphites



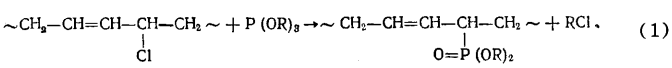
(I) (II)

is manifested by an appreciable decrease (by more than an order of magnitude) of the rate of statistical dehydrochlorination w_c (Fig.1) (with retention or even some increase of the rate of formation of polyene sequences).

This suggests new pathways in the mechanism of the stabilisation of PVC biphosphites: organic phosphites interact with isolated unsaturated bonds >C=C< in the PVC macromolecules. As a consequence, the product of this reaction is not ozonised with subsequent oxidative cleavage; the molecular weight of PVC (a quantitative measure of the statistical dehydrochlorination of the polymer[19]) does not change.

Apart from the data presented in Fig.1, the quantitative "closure" of the inner >C=C< bonds in the polymer chains on heat treatment of PVC in the presence of phosphites constitutes an argument in support of this reaction (Table 1). Among the mechanisms of the stabilising action of organic phosphites in relation to PVC proposed previously, the possibility of the interaction with isolated >C=C< bonds was not taken into account.

The effects associated with the increase of the stability of PVC were usually attributed to the interaction of phosphites with a chlorine atom in the β-position relative to the >C=C< bond in the chloroallyl group[14,20]:



(1)

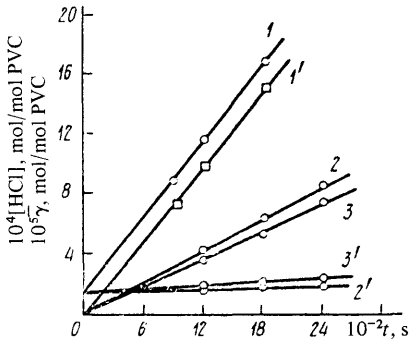
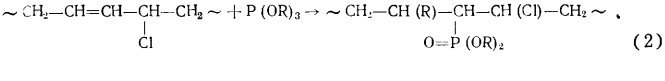


Figure 1. The overall (lines *1*–*3*) and statistical (lines *1′*–*3′*) dehydrochlorination of PVC in the prsence of 0.02 of a mole of phosphites per mole of PVC (448 K, $p = 10^{-2}$ mmHg, $M_w^0 = 127500$, 0.02 of an equivalent of $(C_{17}H_{35}COO)_2Ba$ per equivalent of PVC: 1) and 1′) without phosphite; 2) and 2′) in the presence of compound (I); 3) and 3′) in the presence of compound (II).[17]

The presence and formation of chloroallyl groups in the macrochains was believed to be the main cause of the activation of the HCl elimination process[21–24]. Taking into account the experimentally observed addition of organic phosphites to anomalous groups involving the saturation of the >C=C< bonds, an alternative mechanism was proposed[8]:



(2)

However, using a low-molecular-weight analogue of these groups (4-chloropent-2-ene), it has been shown in relation to model reactions that phosphites (353 K, 100 h; 443 K, 30 h) do not react with the β-chloroallyl groups (neither via the >C=C< bond nor via the C–Cl bond[25]). On the other hand, PVC treated with organic phosphites (with subsequent elimination of the latter) is characterised by a low initial rate of the HCl elimination reaction, the relation being analogous[17] to that described by curves *2* and *3* in Fig.1.

Thus reactions (1) and (2) cannot be adopted as the basis of the mechanism of the stabilising action of organic phosphites in relation to PVC, because this does not reflect the true nature of the phenomenon. This conclusion is particularly valid since it has been shown[18,26,27] that the β-chloroallyl groups are not responsible for the high rate of dehydrochlorination of PVC and that the low stability of

the polymer is caused by the presence in the macromolecules of the carbonylallyl groups ~C(=O)–CH=CH–CH(Cl)~, formed on oxidation of the chloroallyl groups[27]. The interaction of organic phosphites with the carbonylallyl groups in PVC, which leads to a decrease of their content† in the polymer macromolecules (Fig. 2) [28] and hence to a considerable decrease of the initial rate of dehydrochlorination of PVC (Fig. 3), proceeds also at room temperature[28]. Since the organic phosphite is introduced in a large excess relative to the carbonylallyl groups (this corresponds to the real PVC stabilisation conditions), the reaction proceeds in a pseudounimolecular regime and its rate is determined solely by $\bar{\gamma}_0$ (the kinetic plots for the consumption of the carbonylallyl groups can be made linear in terms of semi-logarithmic coordinates). The effective rate constants k for the interaction of organic phosphite with the carbonylallyl in PVC have been calculated for tri-isobutyl phosphite ($k = 0.11 \times 10^{-3}$ s^{-1} at 298 K) together with the parameters of the Arrhenius equation: $E_a = 71.4$ kJ mol^{-1} and $\lg A = 10 \pm 1$.

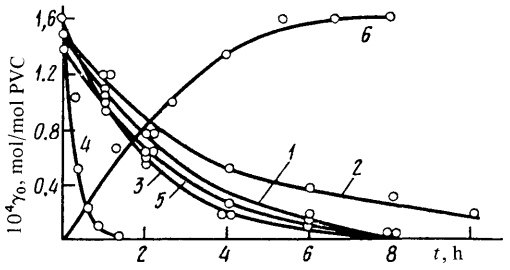


Figure 2. Dependence of the content of ketochlorallyl groups $\bar{\gamma}$ on the time of contact of PVC specimens with $(iso\text{-}C_8H_{17}O)_3P$ at different temperatures (lines *1*–*5*) and on the degradation time (448 K, 10^{-2} Pa) of modified PVC (line *6*); initial content ($10^4\bar{\gamma}_0$, mol/mol PVC): 1) and 6) 1.52; 2)–4) 1.62; 5) 1.42; temperature (K): 2) 289; 3)–5) 298; 4) 313.[28]

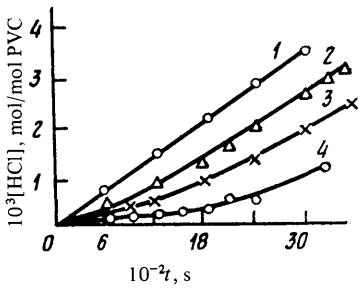
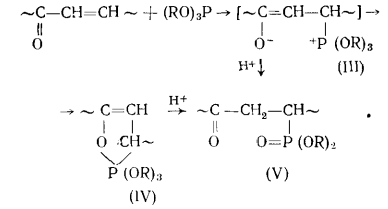


Figure 3. The elimination of HCl from PVC ($\bar{\gamma}_0 = 1.52 \times 10^{-4}$ mol/mol PVC) not containing $(iso\text{-}C_3H_7O)_3P$ (line *1*) and PVC subjected to a preliminary treatment with phosphite at 298 K; treatment time (h): 2) 1; 3) 2; 4) 6.[28]

†The quantitative content of the carbonylallyl groups $\bar{\gamma}$ is calculated from the viscosity-average molecular weight after the alkaline hydrolysis of the $(RO)_3P$-modified polymer[19].

It has been established that the interaction of phosphites with PVC proceeds via the ketovinyl fragment of the carbonylallyl group[29]:



(3)

This is demonstrated by the results obtained in the study of the competitive reactions of the phosphite (tributyl phosphite) with a mixture of methyl vinyl ketone (a model of the ketovinyl fragment) and 4-chloropent-2-ene, which models the β-chloroallyl group (353 K, equimolar reactant ratio). The phosphite reacts selectively with methyl vinyl ketone, while 4-chloropent-2-ene is isolated from the reaction mixture in an unchanged form apart from a certain amount of its dehydrochlorination products—piperylene and HCl.

The final reaction product—butyl 3-oxobutylphosphonate (V), identified by infrared spectroscopy ($\nu_{P=O} = 1250$ cm^{-1}, $\nu_{C=O} = 1730$ cm^{-1}), NMR($\delta_{^{31}P} = +31$ p.p.m.), and elemental analysis, is formed in the presence of a proton donor (HCl in the given reaction) as a consequence either of the protonation of the dipolar ion (III) or the conversion of the intermediate oxophospholen (IV) ($\delta_{^{31}P} = -31$ p.p.m.) into compound (V).[30] Under the real PVC stabilisation conditions, the proton donors can also be either HCl, always present in the polymer during its heat treatment even at relatively low temperatures, or other acid admixtures, H_2O, and phosphite hydrolysis products (alcohols, phenols, etc.).

At the same time during the degradation of the stabilised PVC the rate of evolution of HCl increases[28] to the value characteristic of the initial polymer. The content of the carbonylallyl groups increases in the same way (Fig. 2, curve *6*), which indicates the thermal decomposition of the saturated ketophosphonate groups under the PVC degradation conditions. Treatment of the curve for the accumulation of the carbonylallyl groups during the thermal degradation of the modified PVC in terms of the first-order reaction equation yields $k_{decomp} = (0.93 \pm 0.06) \times 10^{-3}$ s^{-1} at 448 K. At the polymer degradation temperature the ratio $k/k_{decomp} > 10^3$ ($k = 1.8$ s^{-1} at 448 K, calculated from E_a). Thus the high stabilising effectiveness of organic phosphites in relation to the thermal decomposition of PVC is caused, apart from other factors, by the high ratio of the rate constant for the formation of saturated ketophosphonate groups on interaction of organic phosphites with the carbonylallyl groups in PVC and the rate constant for the decomposition of the ketophosphonate groups under the conditions of the thermal degradation of the polymer.

It is significant that the correlation between the activity of phosphites in reactions with α,β-unsaturated ketones and their stabilising effect in PVC made it possible to demonstrate independently that the relatively high overall rate of dehydrochlorination of PVC is in fact determined mainly by the content of the ketochloroallyl structures in the polymer macromolecules.

Thus a new selective phosphorylation reaction, involving the ketovinyl groups of the "anomalous" ketochloroallyl fragments, was discovered for PVC at the degradative process initiation stage. The consumption of the inner double bonds in the carbonylallyl groups, as a result of such interaction of organic phosphite with PVC, results in the breakdown of conjugation in these groups and leads to a sharp decrease of the rate of dehydrochlorination of PVC.

This reaction is in fact the main cause of the inhibition of the formation of polyene sequences inducing the decomposition and colouring of the polymer.

Turning now to the reactions of phosphites with PVC considered in the literature, one should note that, in the inhibition of the decomposition of PVC, the reactions with HCl [31,32] hardly occur under the conditions of the real stabilisation of PVC in the presence of thermostabilisers; the reactions with polyenes $(\sim CH{=}CH\sim)_n$ can develop only under specific conditions[33]; as shown above, the reactions with the β-chloroallyl fragments also fail to make an appreciable contribution to the stabilisation of PVC. All these reactions can be interpreted as concomitant, playing a secondary role in the inhibition of the degradation and colouring of PVC.

2. Polyolefins

The active centres of the degradation process in polyolefins are double bonds, branches in the polymer chains with mobile hydrogen atoms, and carbonyl-containing groups[34].

In the study of polyethylene polymers containing various functional groups, it was found that phosphites are inert[35,36] in relation to hydroxy-groups and double bonds. However, phosphites effectively bind carbonyl groups, reducing their concentration in the initial polymer by a factor of 2–3. Analogous results were obtained in polyethylene (PE) and hexadecane subjected to preliminary oxidation. The introduction of phosphite esters lowers appreciably the intensity of the absorption band of the $>C{=}O$ group in the region of 1720 cm^{-1} in the infrared spectra of the polymer specimens.

The reactivity of phosphite esters in relation to carbonyl groups increases on passing from the full to the acid esters and on replacement of aromatic substituents in the phosphite molecules by aliphatic substituents. Thus, under identical conditions, the concentration of the $>C{=}O$ groups is reduced to the extent of 45, 28, 20.5, and 18% by di-iso-octylphosphorous acid, 2,2′-methylenenbis(6-t-butyl-4-methylphenyl)phosphorous acid, tri-iso-octyl phosphite, and di-iso-octyl phosphite respectively. The observed decrease of the concentration of the $>C{=}O$ groups present in polyethylene, observed after the introduction of phosphites, must be attributed to the chemical interaction of the latter with the carbonyl groups, resulting in the formation of hydroxyphosphonate structures[37].

Thus a general trend in the stabilisation of the colour of polymers by phosphites, namely the deactivation of the reactive centres of macromolecules ("weak" bonds) initiating degradative processes, has been discovered in relation to polymers with fundamentally different decomposition mechanisms (PVC and polyolefins). Reactions of these types involve the chemical modification of macromolecules by polymer-analogue reactions, leading to an increase of the intrinsic stability of the polymer.

It is logical to assume that the observed reactions of phosphites with active anomalous fragments in macromolecules can occur also in the inhibition of the degradation of other polymers containing "weak" bonds of a similar type.

III. STABILISATION OF POLYMERS AT THE OXIDATION CHAIN PROPAGATION AND DEGENERATE BRANCHING STAGES

A problem concerning the stabilisation of polymers, which is important from the standpoint of practical applications, is that of the inhibition of the propagation and degenerate branching of chains in thermo-oxidative degradative processes, responsible for the natural ageing of carbochain polymers.

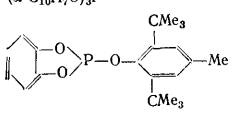
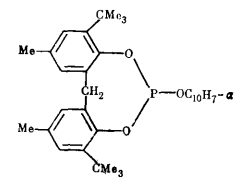
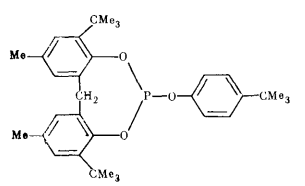
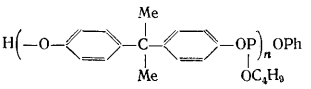
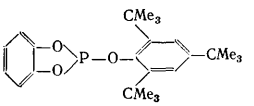
1. Inhibition of Chain Oxidation Processes

The liquid-phase oxidation of phosphorous acid esters by hydroperoxides and peroxy-radicals constitutes a good model for the understanding of their inhibiting effect in the oxidation of polyolefins[38].

(a) *Kinetics and mechanism of the reactions with hydroperoxides.* Quantitative tests of phosphites as hydroperoxide decomposing agents have been carried out by kinetic polarographic and radical trapping methods[39–42].

The kinetics and mechanism of the interaction of phosphorous acid esters depends significantly on their structure. The consumption of hydroperoxides in reactions with the full esters of phosphorous acids obeys first order kinetics with respect to each component. The rate constants for the reactions of phosphites do not vary over a wide range of reaction rates (10^2–10^3) and their stoichiometry is simple (1:1); certain typical values of k are listed in Table 2.

Table 2. The rate constants k, the activation energies E, and the pre-exponential factors A for the reactions of phosphites with cumenyl hydroperoxide (293 K).[38]

No.	Structure of phosphite	10^3k, litre mol^{-1} s^{-1}	E, kJ mol^{-1}	A, litre mol^{-1} s^{-1}
1	$(C_4H_9O)_3P$	83.3	24.7	$3.2\cdot10^3$
2	$(C_8H_{13}O)_3P$	77.9	25.5	$3.8\cdot10^3$
3	$(\alpha\text{-}C_{10}H_7O)_3P$	5.0	37.6	$4.9\cdot10^4$
4		1.3	45.6	$3.2\cdot10^5$
4*	ditto*	3.0 (calc.)	60.3	$6.0\cdot10^7$
5		0.8	58.5	$5.8\cdot10^7$
6		0.8	57.5	$3.8\cdot10^7$
7		12.6	54.8	$1.6\cdot10^8$
8		3.8	58.5	$2.4\cdot10^8$
9	$(PhO)_3P$ **	10.7 (calc.)	34.7	$1.2\cdot10^4$

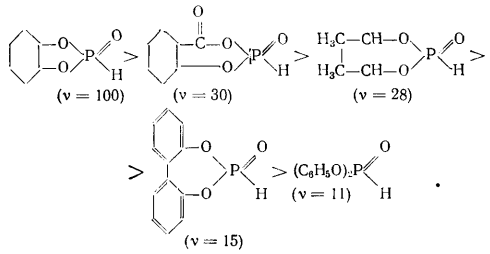
*Data obtained by Humpris and Scott[43].

**E and A obtained[44] for t-butyl hydroperoxide.

The reactions of hydroperoxides with the acid esters of phosphorous acids having the general formula

$$(RO)_2P(=O)H,$$

which are in tautomeric equilibrium with another reactive form, namely $(RO)_2POH$, have been investigated[45]. The rate constants have been calculated from the kinetic equation for termolecular reactions having kinetic orders $n = 2$ and 1 with respect to the hydroperoxide and the acid respectively[46]. The acids can be arranged in the following sequence in terms of the stoichiometric coefficients ν for the consumption of cumenyl hydroperoxide (CHP):



The Arrhenius relation governing the rate constant (20–100 °C) has been derived for *o*-phenylenephosphorous acid (PPA), which decomposes CHP catalytically:

$$k\ (\text{litre}^2\text{mol}^{-2}\ \text{s}^{-1}) = 2.5 \cdot 10^{11} \exp(-15.6/RT).$$

Comparison with the ionisation constants determined by potentiometric titration[47] permits the conclusion that the acids having high pK values (>8) do not react; CHP is decomposed only by the strongest acids of the above series (pK < 8). This indicates qualitatively the involvement of the tautomeric forms of the test acids containing phosphorus (III) in the decomposition reaction of CHP as reactive species catalysing its decomposition. The same conclusion has been confirmed by the ^{31}P NMR spectra for PPA ($\delta_{^{31}P}$ = +129, +126 p.p.m.). The presence of two lines at the centre is apparently due to the presence of two conformers with a tervalent phosphorus atom.

Phosphorodithioic acids, having pronounced acid properties, show a high reactivity in reactions with CHP.[48] The study of the consumption of CHP in reactions with phosphorodithioic acids has shown that the latter participate in the reaction with anomalously high stoichiometric coefficients (in the range 7000–25000), which indicates the catalytic character of the decomposition of the CHP. As in the case of dialkyl(aryl) phosphites[47–49], this has been confirmed by the study of the consumption of CHP in the course of its stepwise addition to the reaction system. The rate of decomposition of CHP then remains the same as before, i.e. phosphorodithioic acid is the catalyst. This is also indicated by the absence of an induction period from the kinetic CHP decomposition curve.

The acid-catalysed decomposition of CHP apparently takes place via the mechanism of proton catalysis and is described by a second-order equation with respect to CHP and a first-order equation with respect to the acid[48].

From the standpoint of the effectiveness of the stabilising action of phosphites and acids, the determination of the contributions of the radical and non-radical pathways in the reactions with hydroperoxides is important. The yield of the radicals in the hydroperoxide + phosphite system has been estimated from the consumption of the stable nitroxy-radicals as "counters" of active radicals[40]; it proved to be from 0.02% for aliphatic phosphites to 5% for aromatic phosphites. For phosphorodithioic acids, the contribution of the radical pathway, estimated from the consumption of ionol, increases significantly (to 40%) as a function of structure.

The study of the chemically induced ^{31}P nuclear polarisation (^{31}P CINP) [50,52] in the reactions of phosphites with hydroperoxides has demonstrated unambiguously that the reactions proceed via two parallel (competitive) pathways—non-radical and radical, and that the radical mechanism, which leads to nuclear polarisation, plays a secondary role. Such competition is apparently due to the fact that, for the formation of the primary radical pair $[R'\dot{O}\ HO\dot{P}(OR)_3]$, the reaction of the phosphite with the hydroperoxide should be as a whole either strongly exothermic or it should proceed with a high activation energy, as shown in Fig. 4. The presence of the competitive non-radical pathway therefore enables the reaction to proceed to the formation of molecular products, bypassing the high-energy (endothermic) state of the radical pair[38].

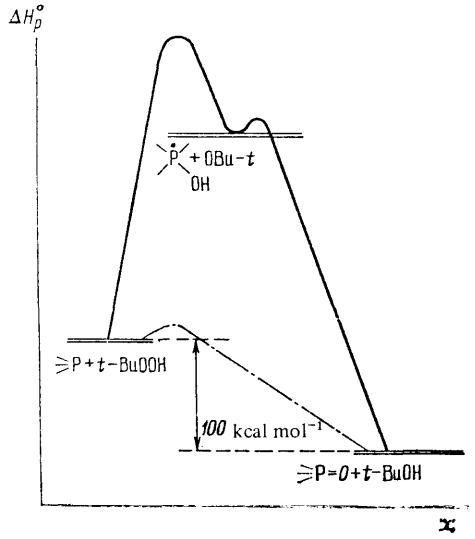


Figure 4. Schematic thermochemical diagram of the possible pathways in the reactions of phosphites with hydroperoxides[38].

The NMR spectra of the products of the reactions of phosphorus dithioacids with hydroperoxides also reflect the effects of nuclear polarisation during periods comparable to the reaction times[53].

Thus, one may conclude that reactions with hydroperoxides via several parallel mechanisms are characteristic of a wide range of esters of phosphorus acids.

(b) *Kinetics and mechanism of the initiated oxidation of organic phosphites.* The reactions of the radicals RO$^\cdot$ and $RO_2^\cdot$ with phosphites are classical objects of studies in the homolytic chemistry of phosphorus[54,55]; the results available in this field have been subjected to a critical analysis in a review[56]. Trialkyl phosphites are vigorously oxidised by alkylperoxy-radicals $RO_2^\cdot$ at 403 K; the oxidation has a chain mechanism and continues until the phosphite is completely exhausted. We shall adopt the conventional term "spontaneous oxidation" of phosphites.

The study of the kinetics of the comparatively weak ^{31}P CINP, observed in the oxidation of trialkyl phosphites under the conditions of an unbranched reaction (azobisisobutyronitrile, O_2, 338 K), demonstrated for the first time[57,58] that this reaction involves phosphorus-containing radicals and their radical pairs. Chemically induced nuclear polarisation occurs only in triethyl phosphite molecules formed in the kinetic chain cross-termination steps:

$$\left[\text{—}\dot{P}\text{—OR}\,\dot{O}_2\,(RO)\,P\text{—}\right] \rightarrow \text{—}P^*\text{=O} \quad .$$

Since the same product is formed in the chain propagation steps

$$RO_2^{\cdot} + \text{—}P \rightarrow \text{—}\dot{P}\text{—}O_2R \rightarrow \text{—}P\text{=O} + \dot{O}R \ ;$$

$$RO^{\cdot} + \text{—}P \rightarrow \text{—}\dot{P}\text{—OR} \rightarrow \text{—}P\text{=O} + \dot{R} \xrightarrow{O_2} RO_2^{\cdot} \text{ etc.},$$

the molecules of phosphate with polarised nuclei are actually greatly "diluted" by the molecules of phosphate arising in the chain propagation reactions. Kinetic proof of this mechanism of the CINP has been presented[59] and the causes of the low polarisation coefficient (chain reaction with long chains) have been stated.

In order to discover the principal trends in the "spontaneous oxidation" of phosphites, the rates w_p of their chain oxidation have been analysed as a function of the rate of initiation w_i and the concentration of phosphites. The chain length ν is appreciably reduced (from $\sim 10^4$ units for trialkyl phosphites to 5–130 units for aromatic phosphites, particularly when shielded phenoxy-fragments are introduced into the phosphite molecule). Furthermore, on passing from aliphatic to aromatic phosphites, the $w_p \cong w_i^{1/2}$, relation observed for the former, changes to a relation of the type $w_p \cong w_i$, i.e. there is a change in the mechanism of the oxidation chain termination: the bimolecular chain termination is replaced by linear termination by secondary phenoxy-radicals. The latter can be formed via substitution reactions from kinetically unstable phosphoranyl radicals:

$$(ArO)_3\dot{P}OR \rightarrow (ArO)_2POR + ArO^{\cdot} \xrightarrow{RO_2^{\cdot}} \text{chain termination.}$$

This is precisely why the chemically induced ^{31}P nuclear polarisation is not observed in the chain oxidation of aromatic phosphites.

The appearance of phenoxy-radicals in the initiated phosphite oxidation reaction generates an additional chain transfer mechanism [taking into account the main $RO_2^{\cdot}(RO^{\cdot})$ + phosphite chain transfer pathway]; thus the addition of unsubstituted phenol stimulates the overall phosphite oxidation reaction.

(c) *Kinetics of the inhibition of oxidation processes by organic phosphites.* We shall examine the kinetic parameters, obtained recently characterising the effect of organic phosphites on the initiated oxidation of polyolefins in the solid phase and in the melt[57,60–63], as well as model oxidation reactions of low-molecular-weight substrates.

Fig. 5 presents the kinetic curve for the absorption of oxygen, typical for the phosphite-inhibited oxidation of both model hydrocarbons (styrene, tetralin, benzaldehyde, and low-molecular-weight polyethylene) and solid polyolefins (low-pressure polyethylenes, isotactic polypropylene). The inhibition parameters (determined from the O_2 absorption kinetics) in various substrate + oxygen + initiator + organic phosphite systems are presented in Table 3. The full organic phosphite esters terminate kinetic styrene and tetralin oxidation chains faster by more than an order of magnitude than a typical inhibitor (ionol). The rate constants for the reactions of the polymeric radicals $RO_2^{\cdot}$ with phosphites are comparable to (in solid polypropylene) or even smaller than (in fused polyethylene) the constants k_7 for the known amine and phenolic antioxidants as well as nickel and zinc carbamates. After the introduction of shielded phenoxy-groups into the phosphite molecule, the chain termination rate constant (k_7 or k_7/k_2) almost always increases; however, at the same time there is an increase in the stoichiometric inhibition coefficient f.

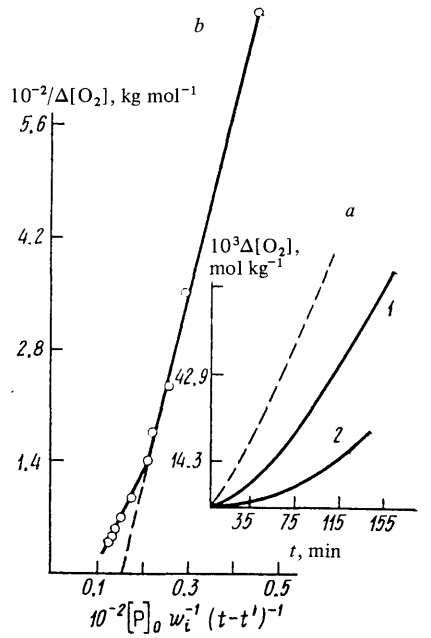


Figure 5. *a*) Kinetics of the initiated oxidation of polypropylene ($w_i = 3.8 \times 10^{-7}$ mol kg^{-1} s^{-1}, 358 K, p_{O_2} = 650 mmHg) in the presence of 1×10^{-2} [of a mole?] (line *1*) and 3×10^{-2} [of a mole?] (line *2*) of triphenyl phosphite (the dashed line represents the kinetics in its absence); *b*) linear kinetic plot in terms of the variables of the equation quoted by Denisov[64].

Table 3. Kinetic characteristics of the reactions of peroxy-radicals with organic phosphites[42].

Composition of medium***	$(C_6H_5O)_3P$		$(Me\text{-}C_6H_3(CMe_3)\text{-}O)_3P$		$(H_{19}C_9\text{-}C_6H_4\text{-}O)_3P$	
	f	$\lg k_7$	f	$\lg k_7$	f	$\lg k_7$
Solid PE at 390 K (MW 6×10^4; $\alpha = 0.82$)	0.63	3.63*	0.97	3.83*	—	—
Fused PE at 1170 K (MW 2350)	—	—	0.63	3.43*	—	—
Solid isotactic polypropylene at 358 K (MW 4.9×10^5; $\alpha = 0.80$)	$6.6 \cdot 10^{-2}$	3.85*	0.12	4.49*	—	—
Styrene + chlorobenzene (50 vol.%) at 323 K	$1 \cdot 10^{-2}$	4.86	$6.3 \cdot 10^{-2}$ ($8 \cdot 10^{-2}$)	4.76 (4.62)**	0.27	4.76
Tetralin + chlorobenzene (50 vol.%) at 323 K	$1.5 \cdot 10^{-2}$	5.00	$4.9 \cdot 10^{-2}$	5.49	—	—
Benzaldehyde (0.2 M) + chlorobenzene at 323 K	0.5	6.20	2.0	6.49	3.4	6.74

*The rate constant is effective; the measured ratio k_7/k_2 is quoted.

**The parameters were evaluated by the computer modelling of the kinetics of the absorption of O_2.

***α = degree of crystallinity.

Direct quantitative estimates of the effectiveness of phosphites have convincingly demonstrated the validity of the early idea[4-7] that aromatic phosphites with shielded (or electron-donating) substituents should be more effective polyolefin stabilisers.

The interaction of aliphatic phosphites with peroxy-radicals proceeds with formation of alkyl radicals, which are actively involved in the oxidation chain propagation (i.e. powerful chain terminating agents—secondary radicals, for example aryloxy-radicals—are not formed). This is why the polymer is oxidised at a high rate even when the constant k_7 for trialkyl phosphite (for example, tri-iso-octyl phosphite) is greater than the constant k_2 for the chain transfer to the substrate[42].

In order to identify the reaction products of aromatic phosphites in the oxidation of a polyolefin, for example, polyethylene, the experiments were interrupted[61] at the end of the inhibited oxidation period (when the oxidation passed to the regime with the usual initiated reaction), while the low-molecular-weight products were extracted by carbon tetrachloride. Absorption frequencies characteristic of the C–O–P linkage and the aromatic ring were detected in the infrared spectra of the oxidised polymer; the inhibitor conversion products extracted from polyethylene contain the P=O and C–O–P fragments. This result can be explained qualitatively within the framework of the mechanism proposed:

$$R'OOR' \xrightarrow{w_i} R'O^{\cdot} \xrightarrow{RH} R^{\cdot},$$

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \xrightarrow[k_2]{RH} R^{\cdot},$$

$$R^{\cdot} + RO_2^{\cdot} \rightarrow \text{products},$$

$$RO_2^{\cdot} + \text{—}P^{III}\text{—} \xrightarrow{k_7} \text{—}P^{V}(=O)\text{—} + RO^{\cdot}; \qquad (4)$$

$$RO^{\cdot} + \text{—}P^{III}\text{—} \rightarrow \left[RO\text{—}\dot{P}\text{—}\right] \rightarrow RO\text{—}P^{III}\text{—} + ArO^{\cdot}, \qquad (5)$$

(OAr)

$$ArO^{\cdot} + RO_2^{\cdot}\ (ArO^{\cdot}) \rightarrow \text{products}.$$

The mechanism postulates that the phosphite is oxidised by the $RO_2^{\cdot}$ radical to the phosphate [reaction (4)]; in addition, a reaction takes place in which a phosphite molecule is "inserted" in a seocndary alkoxy-macroradical $RO^{\cdot}$ with elimination of a phenoxy-radical (aryloxy-radical) [reaction (5)]. In conformity with the evidence presented by Denisov[64], the mechanism also includes the oxidation chain termination via the reaction between the alkyl macroradical ($\dot{P}$) and the peroxymacroradical ($PO_2^{\cdot}$).

The marked weakening of the inhibiting activity of tri-(6-t-butyl-4-methylphenyl) phosphite (VI) in fused polyethylene (Table 3) is apparently associated with the fact that diffusion- and structure-dependent hindrance, caused by the specific features of the solid phase, diminishes and the contribution of new chains, arising via the reaction of secondary phenoxy-radicals (from the phosphite) not only with the inhibitor but also with the polymer macromolecules, increases. In the liquid phase the coefficient f decreases still more markedly; in this case the chain "spontaneous oxidation" reaction of the phosphite plays an active role, creating powerful additional channels for the consumption of the inhibitor. In fact, in the inhibition of the oxidation of both styrene and tetralin, the coefficient f increases from $(1-1.5) \times 10^{-2}$ for $(PhO)_3P$ to $(5-6) \times 10^{-2}$ for the "shielded" phosphite (VI), i.e. in proportion to the reciprocal of the "spontaneous oxidation" chain length for these phosphites (the corresponding values of ν are 0.6×10^2 and 0.2×10^2 respectively) in *o*-dichlorobenzene[59]. Computer calculation of the rate of consumption w_p of the inhibitor (VI) in styrene showed[63,65] that it exceeds by an order of magnitude the "specified" rate of initiation w_i. Thus the phosphite is consumed via a chain mechanism with a chain length $\nu = 0.1 \times 10^2$. (The value obtained is close to the value of ν determined independently in experiments on the initiated oxidation of the same phosphite.)

If the effectiveness of the inhibition of oxidation by phosphites is determined by comparatively large rate constants k_T for their reactions with peroxy-radicals, then the duration of the stabilising action of the phosphites depends on the intensity of their competitive (coupled) chain "spontaneous oxidation", which determines the stoichiometric coefficient f of the inhibition. The set of such closely related processes is a specific feature of the inhibiting activity of organophosphorus oxidation inhibitors. Knowing these characteristics of the behaviour of organic phosphites, it is possible to predict the most effective regimes for the stabilisation of polyolefins (under storage and operating conditions) when the "spontaneous oxidation" of phosphite is suppressed and the duration of their stabilising action increases significantly.

Thus, in the oxidation reactions of both low-molecular-weight hydrocarbons and polyolefins, the most effective inhibition mechanism involves the interactionof the phosphites with peroxy-radicals.

The results presented above show that, in the presence of aromatic phosphites, the oxidation of polyolefins (in the solid phase and in the melt) and model hydrocarbons is a chain reaction with linear chain termination by phosphite molecules, i.e. typical mechanisms of the action of oxidation inhibitors operate.

2. Molecular Reactions of Organic Phosphites with the Products of the Thermal and Thermo-oxidative Degradation of Polymers

Under the conditions of an advanced polymer oxidation process, the non-chain inhibition reactions—via the interaction of phosphites with active functional groups and molecular decomposition products (peroxides, carbonyl-containing groups, isolated and conjugated double bonds, etc.)—also acquire a considerable importance.

The development of reactions of organic phosphites with the C=O groups formed in the thermo-oxidative degradation of polymers has been established for polyolefins[66,67], polychloroprene[68], etc.

Thus, under the conditions of the autoxidation of polyethylene in the presence of phosphite esters, a considerable retardation of the formation of carbonyl groups is observed compared with the polyethylene specimen not containing the organophosphorus additive[36]. It is noteworthy[66,67] that the polymer is then phosphorylated: the infrared spectra of the polyethylene reprecipitated after oxidation contains the absorption frequencies of the phosphoryl groups corresponding to the products of the reactions of phosphites with carbonyl compounds. The effectiveness in the reactions with carbonyl groups increases with increase of the concentration of the organophosphorus compound. When polyethylene contains ≥5 wt.% of the organophosphorus additive, the spectrum altogether fails to show the absorption lines of C=O groups in the course of 900 h.[66]

The ability of organophosphorus compounds to interact with C=O groups is correlated with the improvement of the operating characteristics of the polymer.

Experimental evidence for deactivation, under the influence of phosphites, of the reaction centres formed at the stage of extensive degradation of poly(vinyl chloride) and responsible for its colour is provided by the decrease of the rate

of dehydrochlorination and the weakening of the colour of the partly dehydrochlorinated PVC.[33] At the beginning of its heat treatment in the presence of phosphites, the latter reacts vigorously with the reaction centres present in the polymer; subsequent heat treatment leads to a monotonic increase of the amount of phosphorus in the degraded PVC as a consequence of the interaction of the phosphite with the active groups in the polymer as they are formed.

The observed phosphorylation of PVC must be attributed primarily to the interaction of the phosphites with the oxygen-containing fragments [reaction (3)]. When polyconjugated structures (chromophoric groups) arise in the macromolecules, organic phosphites weaken the colour of the polymer by breaking the conjugation chain ("symptomatic" stabilisation).

When the binding of the HCl evolved in the degradation of PVC and the formation of complexes of HCl with the double bonds intensifying the colour of the polymer are not effective, phosphites are capable of binding the HCl, which also leads to a weakening of the dehydrochlorination process and the stabilisation of the colour of the polymer[33]. The efficiency of the stabilising action of phosphites, due to their combination with HCl, depends on the degree of their dealkylation under the influence of HCl and the composition of their dealkylation products; the complete dealkylation, characteristic of $(RO_3)P$, leads to the formation of acid products of the type of $ROP(OH)_2$ and H_3PO_3, which accelerate the dehydrochlorination of PVC; aromatic phosphites $(ArO)_3P$ do not react with HCl. Mixed phosphites of the type of $ROP(OAr)_2$ are the most effective stabilisers of PVC; their interaction with HCl results in the formation of only $(ArO)_2P(=O)H$, which are inert on further exposure to HCl.[33]

It is significant that, under the conditions of the inhibition of advanced degradative processes, phosphites are capable of functioning as a "depot" of stabilisers[2], forming under the influence of dealkylating agents (the polymer decomposition products, particularly H_2O, HCl, RCOOH, etc.) the corresponding diaryl(alkyl) phosphites. The latter are active *in statu nascendi*, i.e. their main bulk exists in a bound state and the active form of the stabiliser is evolved from the latter gradually. This is particularly likely since dialkyl(aryl)phosphorous acids are extremely reactive in relation to free radicals[69,70], conjugated polyene systems[71], carbonyl compounds[72,73], etc.

Overall, the general trends in the structural selectivity of phosphites in reactions with the active centres for the decomposition and colouring of polymers have been discovered[74]; in relation to electrophiles (hydroperoxides, carbonyl-containing compounds, activated unsaturated structures, H_2O, HCl, etc.), the reactivity of phosphites decreases in the sequence

$$(RO)_3P > (RO)_2POAr > ROP(OAr)_2 > P(OAr)_3 .$$

Phosphites containing electronegative substituents R in the ester group are effective in reactions with polyene systems $(\sim CH{=}CH\sim)_n$ with $n \geq 4$, which are powerful nucleophiles.

Thus the study of the mechanism of the stabilisation of polymers by phosphites at advanced stages of the degradation makes it possible to predict effective procedures for the secondary stabilisation of polymeric products, i.e. the suppression of the processes which alter significantly the operating properties of the polymer. This means that phosphites are not merely the usual auxiliary additives; they acquire an independent and sometimes a decisive importance.

IV. THE IMPROVEMENT OF THE EFFECTIVENESS OF ORGANOPHOSPHORUS STABILISERS (SYNERGISM)

A distinctive property of organophosphorus stabilisers is their ability to exhibit synergistic effects in a mixture with other additives[3]. The synergism can be achieved either as a result of the enhancement of the functions of organophosphorus stabilisers as inhibitors of free-radical oxidation or by increasing their contribution to the non-chain inhibition processes. We shall consider certain examples of such synergism.

1. Kinetics and Mechanism of the Synergism in the Action of (M + P) Pairs in the Inhibition of an Initiated Oxidation Reaction

The phenomenon of a sharp intensification of the effectiveness of aromatic phosphites as inhibitors of the initiated oxidation of low-molecular-weight hydrocarbons (styrene, tetralin) and polyolefins under the influence of quadrivalent titanium compounds[75] and transition metal acetylacetonates $Macac_n$, where M = Co^{2+}, VO^{2+}, Cr^{3+}, Ni^{2+}, etc., has been observed[76]. The most important general properties of this phenomenon have been established.

In the presence of metal acetylacetonates the dependence of the induction period on the phosphite concentration has a "critical" character (Fig.6). This agrees well with the hypothesis[1] of the formation of a new, more effective inhibitor—a complex of the metal ion with the phosphite, which reacts vigorously with the peroxy-radical.

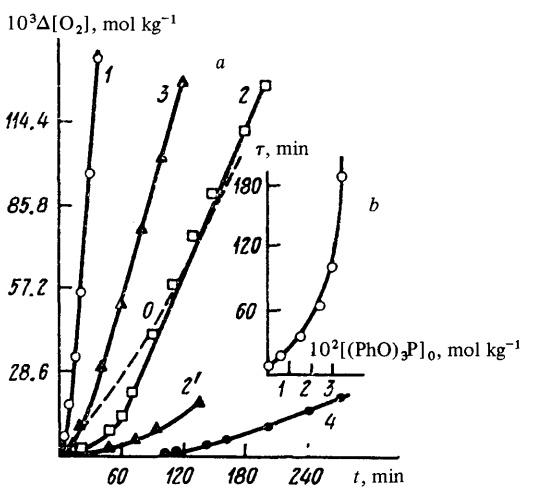


Figure 6. *a*) Kinetic curve for the absorption of oxygen by solid polypropylene (358 K, p_{O_2} = 650 mmHg, $w_i = 3.8 \times 10^{-7}$ mol kg^{-1} s^{-1}) in the presence of 3×10^{-3} mol kg^{-1} (line *1*) or 6×10^{-4} mol kg^{-1} (line *3*) of $Coacac_2$, of a mixture of 3×10^{-3} mol kg^{-1} of $Coacac_2$ + 3×10^{-2} mol kg^{-1} of $(PhO)_3P$ (line *2*), of a mixture of 6×10^{-4} mol kg^{-1} of $Coacac_2$ + 3×10^{-2} mol kg^{-1} of $(PhO)_3P$ (line *4*), and of 3×10^{-2} mol kg^{-1} of $(PhO)_3P$ (line *2'*); 0) curve for initiated oxidation in the absence of the metal complex and phosphite; *b*) dependence of the observed induction period τ on the initial $(PhO)_3P$ concentration in the oxidation of polypropylene in the presence of an initiator and 6×10^{-4} mol kg^{-1} of $Coacac_2$.[76]

Using the "critical" concentration of the phosphite, the rate constant k'_7 for the inhibition of the oxidation of styrene by the coordinated phosphite was obtained and was found to be much greater than not only the constant k_7 for the free phosphite but also the constant k_7 for the metal acetylacetonate and for the familiar reference inhibitor (ionol). The "activation" of the phosphite as an inhibitor when it is coordinated to the metal ion is satisfactorily confirmed by the computer calculation of the kinetics of the oxidation of styrene and its inhibition by the metal ion–phosphite composition[65,77].

The chain oxidation reaction passes from the region of the rapid distinctly catalytic process (in the presence of metal ions) to the region of a slow process with linear chain termination by the molecules of the coordinated phosphite. The study of the kinetics of this process made it possible to determine the quantitative parameters of the observed synergism[76]. Analysis of these parameters shows that the catalytic oxidation of polypropylene by metal ions is suppressed most effectively by the phosphite for the ratio $[M]/[P] \leq 6 \times 10^{-2}$, i.e. when the metal concentration in the polymer does not exceed 0.02 wt.% and the phosphite concentration is close to values usually employed (0.5–1.0 wt.%). The manifestation of "critical" concentrations is in fact characteristic of this range of [M]/[P] ratios.

The series of the relative "synergistic" activities of metal ions in compositions with phosphites in styrene, tetralin, and solid polypropylene have been established on the basis of the analysis of the quantitative parameters of the oxidation inhibition process[38]; overall they have the same direction in terms of the "strength" of the synergism, which implies that the nature of the observed synergism is the same in all cases regardless of the type of substrate oxidised. It has been discovered that the "strongest" compositions are those (based on $Niacac_2$) in which the organometallic component exhibits only a weak catalytic activity; this tendency can be used as a rule in selecting other compositions.

The general characteristics of the behaviour of the kinetically labile metal–phosphite complexes established in oxidation systems with participation of peroxy-radicals make it possible to predict the activity of a new class of oxidation inhibitors—individual stable metal complexes containing molecules of organic phosphites as the main ligands. A remarkable feature of these complexes, for example, the copper(I) complexes is, according to the literature[78–83], a significant increase of the stoichiometric inhibition coefficient, which implies that the reactions involving the additional consumption of the phosphite bound in the complex by a chain process are virtually suppressed. The study of the initiated oxidation of styrene and solid isotactic polypropylene has shown[78] that the copper(I) phosphite complexes (CuP) are more effective than the free non-coordinated phosphite; the quantitative characteristics of the inhibiting action of these complexes have been calculated and it has been shown that the termination of the kinetic oxidation chains by the inhibitor molecules involves the oxidation of the coordinated phosphite without change in the degree of oxidation of the central metal ion.

It is noteworthy that the reactions of the metal complex inhibitor or the products of its reaction with the polymeric hydroperoxide are important for polypropylene undergoing oxidation in the presence of an initiator. It has been found[78] that these reactions have a radical mechanism and proceed at high rates. They are in fact responsible for the "inhibitor $\rightleftharpoons$ catalyst" transition in the kinetic behaviour of the copper(I) phosphite complex observed in the course of the oxidation. In other words, when CuP is used favourable possibilities are created for controlling the regime of the polymer stabilisation under natural conditions, when there is no initiator (controlled stabilisation under uncontrolled conditions). An increase of the duration of the stabilising action of the CuP complexes can be achieved primarily by suppressing the hydroperoxide initiation channel. Below we shall consider a number of experimental facts confirming this idea.

2. The Synergism of Mixtures of Phosphite Complexes with Aromatic Amines

The aromatic amines *p*-toluidine, *o*-toluidine, and diphenylamine have been investigated[81] as "deactivators" of the ROOH groups, but the expected effect was observed only for *p*-toluidine (T) (we may note that *p*-toluidine inhibits weakly the oxidation of polypropylene).

Fig.7 presents as an example typical time variations of the absorption of O_2 in the system comprising polypropylene undergoing oxidation to which T + $Cu[(PhO)_3P]Cl$ or CuP mixtures have been added, the molar concentration ratios of the latter amounting to 0.5–2.0. The character of these relations indicates the occurrence of synergism and at the same time the actual suppression of the secondary processes involving the initiation of the oxidation of polypropylene. The synergistic effect depends in a definite manner on the inhibitor/deactivator ratio and on the concentration of the metal complex additive.

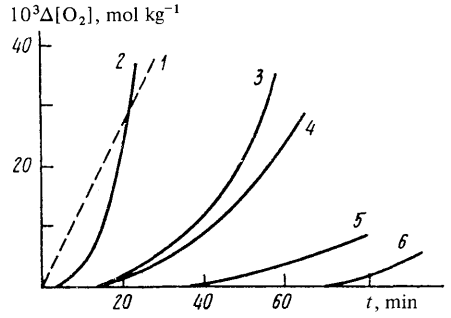


Figure 7. Kinetic curves for the absorption of oxygen by polypropylene undergoing oxidation (358 K, $w_i = 2.5 \times 10^{-6}$ mol kg^{-1} s^{-1}, $p_{O_2} = 650$ mmHg) in the absence of an inhibitor (line *1*) and in the presence of inhibitors: 2) [CuP] = 5×10^{-3} mol kg^{-1} and [T] = 2.5×10^{-3} mol kg^{-1}; 3) [CuP] = 5×10^{-3} mol kg^{-1} and [T] = 1×10^{-2} mol kg^{-1}; 5) [CuP] = 1×10^{-2} mol kg^{-1} and [T] = 1×10^{-2} mol kg^{-1}; 6) [CuP] = 1×10^{-2} mol kg^{-1} and [T] = 5×10^{-3} kg^{-1}.[78]

Thus, when [CuP] = 1×10^{-2} mol kg^{-1} and for the ratio [CuP]/[T] ≥ 1, there is a sharp increase of the induction period τ (see curves *5* and *6* in Fig.14); when [CuP] = 5×10^{-3} mol kg^{-1} for the ratio [CuP]/[T] = 0.5–2.0, the synergism is either much weaker (curves *3* and *4* in Fig.14) or is not observed at all (curve *2* in Fig.14). If the concentration of the amine exceeds that of the phosphite complex, the induction period, defined here as the time during

which $\Delta[O_2]$ reaches 5×10^{-3} mol kg^{-1}, at a constant overall mixture concentration [CuP] + [T] = 1.5×10^{-2} mol kg^{-1} diminishes as a consequence of the probable displacement of the phosphite as a ligand from the coordination sphere of the copper ion by the amine. This means that, in the presence of synergistic amine additives, the phosphite complex retains its key function—it terminates the kinetic chains in the oxidation of polypropylene.

The maximum value of f for the conditions [CuP] = 1×10^{-2} mol kg^{-1} and [CuP]/[T] = 2 amounts to 0.7, which exceeds by a factor greater than two the corresponding value of f obtained for CuP without an amine additive.

An inhibition mechanism has been proposed, in which the amine occupies a free site in the coordination sphere of the ion after the phosphite has been "converted" in the kinetic oxidation chain termination steps into phosphate incapable of coordination; the secondary complexes formed actively decompose the polymeric hydroperoxide to products which do not participate in the polymer oxidation chain propagation reactions. The mechanism has been confirmed kinetically and by analysing the reaction products[77].

3. The Functions of Organophosphorus Compounds in Polymer Systems Containing Phenolic Antioxidants

The effective stabilisation of polymers under the conditions of the development and branching of degradative processes is observed when phosphites are used also in combination with other additives, in the first place[84-86] polymer oxidation inhibitors (phenolic antioxidants). By binding the $RO_2^{\cdot}$ radicals, the latter suppress the spontaneous oxidation reactions of phosphites and thereby enhance the functions of phosphites as inhibitors of non-chain oxidation processes and colour stabilisers.

Not only phosphites[85,86] but also diarylphosphorous and diarylphosphorodithious acids[53] exhibit a high effectiveness with mixtures of phenolic antioxidants. The stabilising effect of the organophosphorus compounds then obtains primarily as a result of the decomposition by the latter of the hydroperoxides ROOH as well as other reactive molecular polymer decomposition products which have accumulated in the polymer undergoing oxidation. The synergistic effect (determined from the colour stability index) in the presence of binary mixtures of phosphites and phenolic antioxidants is characterised by a prolonged retention of the initial colour by such polymer systems and is due to the ability of the phosphites to decompose the chromophores formed as a result of the reactions of phenols and the associated admixtures, in particular of coordination-unsaturated metal ions[86-89].

It has been shown that a characteristic feature of the phosphites[90-92] and phenolic antioxidants[93-96] is the formation of coloured complexes with vanadium, titanium, etc. chlorides (modelling the components of the catalytic polymerisation systems), which are the cause of the appearance of colour in high-density polyethylene immediately after the introduction of phosphite and phenolic stabilisers (inert medium).

In the presence of phosphites, the colour stabilisation effect under the conditions of atmospheric ageing is due to the high rate of the subsequent inner-sphere hydrolysis of the phosphite coordinated to the metal (K_{hydr} = 10 s^{-1}), which leads to the formation of colourless products.

The effectiveness of the colour stabilisation is determined mainly by the competition between the phosphites and phenolic antioxidants in the formation of complexes with variable valence metals[91]. Thus chemical equilibrium is established in the ternary phosphite–bisphenol–metal chloride system (subject to the condition of similar stability constants of the phenolic and phosphite metal complexes) at comparable concentrations of the phosphite and bisphenol; the equilibrium shifts towards the formation of the phosphite complex in the presence of an excess of the phosphite:

$$VOCl_3 + L' \rightleftarrows VOCl_3 \cdot L' \rightleftarrows VOCl_3 \cdot L'' + L'$$

where L′ is the bisphenol and L″ the phosphite. A similar complex is formed after the introduction of an excess of the phosphite (2-ethylhexyl phosphite) into a hydrocarbon solution of the phenol [2,2′-methylenebis(6-t-butyl-4-methyl phenol)] complex of $VOCl_3$; the infrared spectra of the reaction mixture show an intense band in the region of the absorption of the hydroxy-group.

Analogous features of the behaviour of phosphites are observed also in a polymer system. Thus the effectiveness of the colour-stabilising action of phosphites in relation to high-density polyethylene depends on the stability of the phenolic metal complexes; when the stability constant of the complex of 2,2′-methylenebis(6-t-butyl-4-methylphenol) and $VOCl_3$ is $K_{St} = 8.7 \times 10^4$ litre mol^{-1}, an excess of the phosphite relative to the phenol concentration is necessary (by a factor of 3–7); for the higher stability constant $K_{St} = 3.5 \times 10^6$ litre mol^{-1} of the complex of 2,2-thiobis-(4-methyl-2-methylbenzylphenol) and $VOCl_3$, the required phosphite concentration increases by a factor of 5–10.

The greatest effectiveness in neutralising the action of coordination-unsaturated metals is to be expected for the sterically unhindered esters of the type of $(ArO)_3P$, $(ArO)_2$.POR, and $(RO)_3P$, etc. in conformity with the formation constants of their complexes with polyvalent metal ions.

A practical rule has been formulated on the basis of the results obtained: for the effective stabilisation of the colour of polymers containing coordination-unsaturated metal ions by vinary organic phosphite—phenolic antioxidant mixtures, it is desirable to introduce the components consecutively: the phosphite is introduced intitially and then the phenolic additive[97].

On the other hand, the chromophoric products of the oxidation of phenolic antioxidants, mainly quinonoid compounds, play a significant role in the appearance of a colour in the stabilisation polymers by phenols[91]. In this case the introduction of organic phosphites also leads to the elimination of colour from the polymer, which is associated with the conversion of the coloured quinonoid compounds into colourless benzene structures.

The reactivity of phosphites in relation to quinones decreases on passing from aliphatic phosphites of the type $(RO)_3P$ (E_a = 22–29 kJ mol^{-1}) to mixed alkyl aryl phosphites $(RO)_2POAr$ and $ROP(OAr)_2$ (E_a = 34–42 kJ mol^{-1}) and further to aromatic phosphites $(ArO)_3P$ (particularly those with an alkyl substituent in the ring)[98].

It is noteworthy that organic phosphites which hardly interact with quinones in model liquid-phase reactions are incapable of weakening appreciably the intensity of the colour of polyolefins even when present in a fourfold excess relative to the concentration of the product of the oxidation of the phenolic antioxidant in the polymer.

Thus new reactions of phosphites, involved in the stabilisation of the colour of complex polymer systems, have been discovered; they involve the chemical binding of the admixtures and the reaction products of the additives introduced. The observed features make it possible to recommend phosphites as synergistic additives for the enhancement of a specific functional activity in devising effective compositions, containing phenolic antioxidants, which do not become coloured.

4. The Stabilising Effects of Phosphite–Phosphite Systems

On the basis of the classification of phosphites in terms of their functional activity under the conditions of the development and branching of degradative processes in polymers, new types of synergistic mixtures have been proposed which make it possible to achieve the effective stabilisation of polymers[99,100]. These mixtures contain phosphites with different types of activity: an inhibitor of radical processes (a sterically hindered aromatic phosphite) and an acceptor of molecular polymer reaction products (aliphatic and mixed alkyl aryl phosphites).

In particular, mixtures of polyphosphite (I), 2,6-di-t-butyl-4-methylphenyl *o*-phenylene phosphite (VII) and 2,2-methylenebis(6-t-butyl-4-methylphenyl) naphthyl phosphite (VIII) with trinaphthyl phosphite proved effective for polyolefins. The mechanism of the stabilising action under these conditions can be explained by the fact that one of the phosphites, for example compound (I), (VII), or (VIII), for which the oxidation chain termination pathway is dominant, accepts the $RO_2^{\cdot}$ radicals, while the other, for example, trinaphthyl phosphite prevents degenerate branching by decomposing hydroperoxides.

This has been demonstrated kinetically by the displacement of the critical concentrations of the corresponding phosphites (free-radical inhibitors) towards lower values in the presence of trinaphthyl phosphite under the conditions of the inhibited oxidation of low-density polyethylene (473 K, 250 mmHg).

The finding that the replacement of trinaphthyl phosphite by dilauryl thiodipropionate (a typical hydroperoxide decomposing agent) and correspondingly of the polyphosphite (I) by 2,2'-methylenebis(6-t-butyl-4-methylphenol) (a typical inhibitor) leads to analogous results conserve as confirmation of the above mechanism. It is of interest that, when a number of phosphite inhibitors are used in compositions with powerful phenolic inhibitors, a synergistic effect is also observed[100]. This shows that, together with the termination of kinetic oxidation chains, such phosphites can also suppress degenerate branching. A particular tendency in their stabilising behaviour is determined by the competitive strength of the compound with synergistic activity.

Thus the elucidation of the complete phenomenological picture of the mechanism of the action of organophosphorus stabilisers, i.e. of the fundamental decisive pathways leading to the stabilisation of polymers by phosphites and systems based on them, permits a well-founded prediction of the structures of phosphites and their compositions most effective as inhibitors of chain initiation and propagation in the ageing process and as colour stabilisers for polymers and of the pathways leading to the enhancement of the key functions of phosphites as stabilisers.

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