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ACHIEVEMENTS AND RESEARCH TASKS
FOR POLYVINYLCHLORIDE AGEING AND STABILIZATION

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Abstract. Perspectives of polyvinylchloride (PVC) production without labile groups in a backbone have been considered. It has been shown that such production provides drastic increase of an intrinsic stability of polymeric products, possibility of PVC processing with the minimum amounts or in total absence of stabilizers and other chemicals-additives and the opportunity of creation materials and products on a PVC basis with the essentially increased life time. Data allowing to create rigid, semi-rigid and flexible (plasticized) materials and products with the minimum amounts of chemicals-additives and prolonged life time of their service at exploitation under natural and special conditions are presented.

Key words: labile groups, chemical, structural-physical, solvatation, "echo" stabilization, non-toxic chemicals-additives, zeolites, modified clays.

1. Introduction

Polyvinylchloride (PVC) is one of the most known multi-tonnage and important polymeric products. Thousands of rigid, semi-flexible, and flexible (plasticized) materials and products based on PVC are widely used practically in all spheres of national economy and everyday life. First PVC was synthesized by E. Baumann in 1872, but its industrial production had begun much later – since 1935 in Germany according to literature data and in 1930 in the USA according to the DuPont company data.

The global PVC production is impressive: 220 thousand tons in 1950, about 1.5 million tons in 1960, more than 3 million tons in 1965, more than 5 million tons in 1970; now its production is estimated for more than 15 million tons.

The basic PVC problem is its low stability. Under the action of heat, UV-light, oxygen, radiations *etc.* it easily disintegrates according to the law of framing groups transformation with elimination of hydrogen chloride and formation of double carbon-carbon bonds in macromolecules with the appearance of undesirable coloration (from yellow up to black). Therefore, it is

necessary to apply the set of methods increasing PVC stability against action of various factors during its storage, processing and exploitation as well as during synthesis, storage and use of materials and products on its basis [1, 2].

It is logical to assume that among many aspects causing PVC low stability and rather short life time of materials and products on its basis, the knowledge of the reasons of abnormally high rates of its macromolecules disintegration compared with low-molecular weight models is of primary importance. This problem has appeared to be rather complex for understanding and, in essence, is still being discussed. To the present time the researchers of industrial centers of different countries can not find the mutual point of view concerning identification of a weak point in the structure of PVC macromolecule which determines its abnormally low stability. However, sometimes it is believed to be done purposely, though it is not so clear – what for?

2. Results and Discussion

2.1. What is responsible for PVC low stability?

The PVC low stability used to be connected with possible presence of labile groups in the macromolecules structure, which activate polymer disintegration. These labile groups are distinct from the sequences of regular vinyl chloride repeating units $\sim CH_2-CHCl-CH_2-CHCl-CH_2-CHCl\sim$. The overwhelming majority of researchers believe that such groups are: a) chlorine atoms bonded with tertiary atoms of the C-Cl (A_t) carbon; b) vicinal chlorine atoms in the macromolecule structure $\sim CH_2-CHCl-CHCl-CH_2\sim$ (A_v); c) unsaturated end-groups such as $\sim CH=CH_2$ and/or $\sim CCl=CH_2$; d) β-chloroallyl groups $\sim CH_2-CH=CH-CHCl\sim$ (A_c); e) oxygen-containing hydroxy- and peroxy groups (A_0) [1-8]. Meanwhile, even after brief consideration of PVC disintegration it becomes obvious that there is much less amount of labile groups (which can be considered as the reason of low PVC stability) in the macromolecules, because tertiary chlorine (A_t) and vicinal (A_v) groups turn

into the *b*-chloroallyl ones and the hydroperoxide groups are transformed into carbonyl groups during PVC dehydrochlorination:
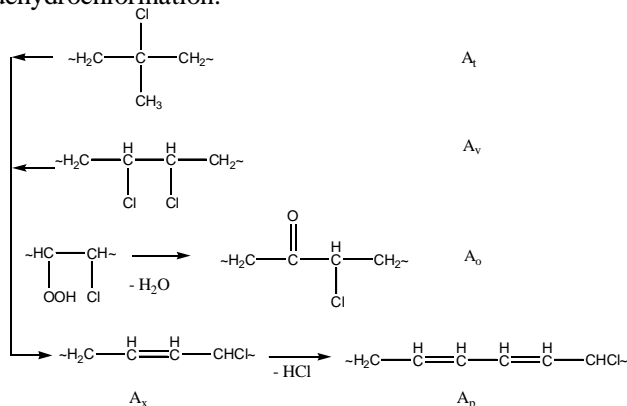
Moreover, the world practice of PVC investigations has shown that initial (freshly synthesized) PVC macromolecules do not contain di-(A_2), tri-(A_3) and/or polyene (A_p) groups [2, 3, 9-14]. Internal peroxide groups ~CH_2–CHCl–O–O–CH_2–CHCl~ are not found as well. So if they are formed during PVC synthesis they would quickly collapse as a result of hydrolysis and/or homolytic break of O–O bonds. There are reliable experimental results, including those received during studying the thermal destruction of fractioned PVC, showing that although unsaturated end-groups are present in the structure of polymeric molecules, they do not affect the PVC disintegration rate [10, 13-15].

Thus, PVC gross-dehydrochlorination of V_{HCl} with sufficient proximity can be described by Scheme 1, where a_0- the content of regular vinyl chloride ~CH_2–CHCl~ groups; K_{Cl}, K_t, K_v, K_c, K_p – rate constants of the corresponding PVC dehydrochlorination reactions; K_{tr} – rate constant of polyene chains destruction.

Following the scheme: $V_{HCl} - K_{Cl}a_0 + K_cA_c + K_pA_p$ with real values of $K_{Cl} = 10^{-8}–10^{-7}$ s^{-1} and $a_0 = 1$ mol/mol PVC; $K_t = 10^{-4}$ s^{-1} and $[A_t] = 10^{-3}$ mol/mol PVC; $K_c = 10^{-4}–10^{-5}$ s^{-1} and $[A_c] = 10^{-4}$ mol/mol PVC; $K_v = 10^{-3}–10^{-4}$ s^{-1} and $[A_v] = 10^{-5}$ mol/mol PVC; $K_p = 10^{-2}$ s^{-1} (448 K).
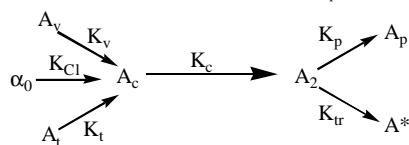
Scheme 1

One can see that Scheme 1 assumes the concept of *b*-chloroallyl activated disintegration of PVC accepted by the majority of researchers, but without convincing proofs [1-5]. However, this postulate is in the contradiction with many experimental facts [16, 17]. In particular:

1. Calculated values of V_{HCl} drastically differ from the experimental ones.

2. The *b*-chloroallyl activation of PVC disintegration assumes an autoacceleration of PVC gross-dehydrochlorination process in time [16-18]. The linear dependence is observed experimentally (Fig. 1). A gross-rate constant of PVC disintegration, according to experimental data and Fig. 1 at $K_c = 10^{-4}–10^{-5}$ s^{-1} should contain the expression with $K_p \cong 10^{-2}$ s^{-1} (at 448 K) from the very beginning of PVC thermal destruction. However, according to the data of thermodisintegration of low molecular weight model compounds [19-21] this is observed only at destruction of the model compounds containing a chlorine atom in a *b*-position to conjugated $(C=C)_n$ bonds (at n ≥ 2), *i.e.* at occurrence of the effect of the adjacent group of the long-range order (Table 1).
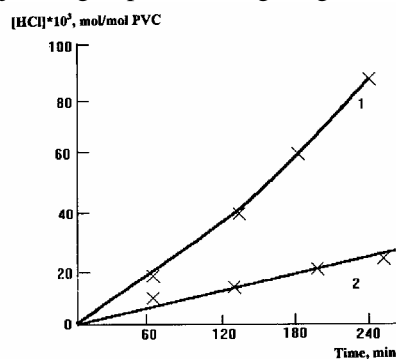

Fig. 1. Kinetic curves of PVC dehydrochlorination. *b*-chloroallyl activation: calculated data (1), experimental data (2), (448 K, 10^{-2} Pa)

Thus, even the primary analysis of experimental results concerning the concept of *b*-chloroallyl activation of the PVC dehydrochlorination, does not sustain criticism and has no right for existence. It is the erroneous point of view.

On the basis of theoretical consideration of PVC thermal disintegration and taking into account all available experimental data it should be noted that if internal *b*-chloroallyl groups (as well as tertiary chlorides and vicinal ones) are present in the macromolecules structure, they do not contribute much to the process of PVC gross-dehydrochlorination due to their sufficient relative stability. It was assumed and proved that an oxovinylen (carbonylallyl) conjugated dienophile group is such a group, in which the unsaturated bond is activated by the adjacent electrophilic group C=O (–C(O)–CH=CHCl–CH_2–) apparently present in PVC macromolecules in rather small amounts $g \cong 10^{-4}$ mol/mol PVC, but disintegrates at the rather high rate ($K_p \cong 10^{-2}$ s^{-1}) with HCl elimination [14, 17, 22-24].

It is extremely important to emphasize that the concept of oxovinylene activation of PVC disintegration does not contradict any known experimental facts. Meantime, new (including the original ones) proofs of existence of the basic groups in the structure of PVC

Table 1
Dehydrochlorination rate constants at thermal destruction of low molecular weight model compounds

No.	Compound	Temperature area where the compounds start to degrade with a noticeable rate, K	Groups index	Decomposition rate constant, K, s^{-1}
1	2,4-dichloro-pentane	563–593	α_0	2.6×10^{-9}
2	*meso*-2,4-di-chloropentane	563–593	α_0	1.9×10^{-9}
3	3-ethyl-3-chloropentane	488–553	A_t	7.9×10^{-6}
4	4-chlorohexene-2	433–463	A_c	5.1×10^{-4}
5	4-chlorodecene-2	438–468	A_c	5.0×10^{-5}
6	7-chloronona-diene-3,5	343–369	A_p	3.4×10^{-2}
7	6-chloroocta-diene-2,4	360–386	A_p	2.6×10^{-2}

macromolecules have been recently received. In particular, oxovinylene groups present in PVC macromolecules are easily disintegrated during alkaline hydrolysis (5 % aqueous solution KOH, 5 % solution of PVC in cyclohexanone) under mild conditions [13, 14]. It is a characteristic reaction for α, b-unsaturated ketones [25]:

$$\sim CH=CH-C(O)\sim \xrightarrow[KOH]{H_2O} \sim C\underset{H}{\overset{O}{\lesseqgtr}} + H_3C-\overset{O}{\underset{}{C}}\sim \quad (1)$$
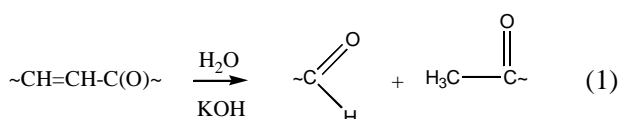
Using this reaction it is easy to estimate the contents of labile oxovinylene groups in the macromolecules structure (g_0) by a decrease of PVC average viscous molecular weight [13-17].

2.2. How can we identify carbonylallyl groups?

It is important to specify that both b-chloroallyl and polyene groups are inert to an alkaline hydrolysis but they easily decomposed during oxidative ozonolysis in the presence of hydrogen peroxide [13]. The ozonolysis method allows to estimate a complete amount of internal unsaturated (b-chloroallyl, chloropolyenyl, and oxovinylene) groups in the PVC macromolecules structure by a decrease of PVC molecular weight. Thus, it is experimentally shown that practically all internal unsaturated groups present in PVC initial macromolecules are oxovinylene ones and PVC dehydrochlorination rate is linearly connected with the content of the internal labile oxovinylene groups in polymeric molecules [14, 26], determined by the alkaline hydrolysis (Fig. 2). It is significant that the polymeric products synthesized in the absence of oxygen were always noticeably more stable than PVC produced in industry in the first case due to the presence of rather stable internal b-chloroallyl (not oxovinylene) groups (oxidative ozonolysis) in PVC macromolecules structure. Generally, the real process of HCl elimination during PVC disintegration *via*

transformation of framing groups is complex, since all abnormal groups contained in the macromolecules structure contribute to the process. However, the contribution of different reactions varies and in some cases may be neglected.
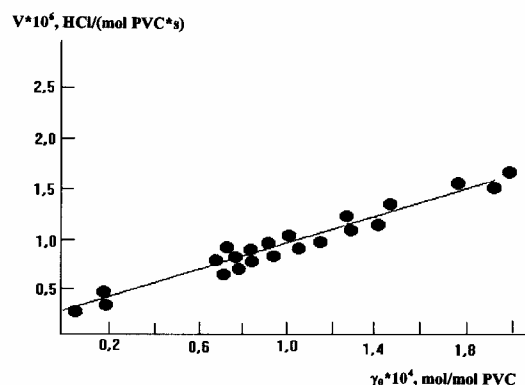

Fig. 2. Dependence of PVC dehydrochlorination rate on the content of carbonylallyl groups in polymer molecules (448 K, 10^{-2} Pa)

The kinetic analysis, when taking into account the real content of characteristics, including abnormal groups in PVC and rate constants of their disintegration (Table 2), has shown [14, 17, 24, 27] the ratio of rate constants $K_{Cl}:K_c:K_t:K_p$ is 1:100:100:100000. For this reason PVC own thermal stability is determined by an effect of the adjacent group of the long-range order (conjugation effect) and the total elimination rate of HCl from PVC is described by the simple equation with sufficient accuracy:

$$V_{HCl} = \frac{dHCl}{dt} = K_{Cl}a_0 + K_p g_0 = V_{Cl} + V_p \quad (2)$$

Taking into account PVC disintegration with participation of tertiary chloride (A_t) and b-chloroallyl (A_c) groups the contribution of the expression $V_p = K_p g_0$ is about 90 % and more of total gross-rate of PVC dehydrochlorination, that precisely points to oxovinylene (not b-chloroallyl) activation of the gross-process of PVC thermal disintegration.

Table 2

Rate constants of dehydrochlorination of haracteristic groups and their content in the initial PVC structure

Group	Content in PVC			Disintegration rate constants at 448 K		
	Index	Amount, mol/mol PVC	Authors	Index	Value, s^{-1}	Authors
~CO–CH=CH–CHCl~	γ_0	~10^{-4}	K.Minsker, 1978 E.Sorvik, 1984 G.Zimmerman, 1984	Kp	10^{-1}–10^{-2}	K.Minsker, 1977 W.Starnes, 1985
(~CH$_2$)CCl–CH$_2$– CH$_2$Cl~	A_{Cl0}	0	K.Minsker, 1978 G.Zimmerman, 1984	K_{Cl}	10^{-5}–10^{-4}	Z.Meyer, 1971 B.Troitsky, 1973 W.Starnes, 1983
–CCl–CH2CH2Cl	A_{t0}	~10^{-3}	E.Sorvik, 1984 A.Caraculaku, 1981 V.Zegelman, 1985	Kt	10^{-4}	W.Starnes, 1983 Z.Meyer, 1971
~CH$_2$–(CH=CH)n>1– CHCl~	A_p	0	K.Minsker, 1976	Kp	~10^{-2}	Z.Meyer, 1971 K.Minsker, 1984
~CH$_2$–CHCl–CH$_2$– CHCl~	α_0	1	–	K_{Cl}	10^{-7}–10^{-8}	Z.Meyer, 1971 K.Minsker, 1972

The development of the concept of oxovinylene activation of PVC thermodestruction appeared to be an important mark in the theory and practice of PVC chemistry and objectively defines the necessity of the new specific approach to the investigation of various aspects of PVC destruction and stabilization.

In particular, new characteristic reaction for unsaturated ketones, confirming the presence of oxyvinylene groups in PVC structure, is the interaction of ~C(O)–CH=CH–CHCl~ groups with organic phosphites P(OR)$_3$ [29-33] and dienes [34, 35].

2.3. Principal ways for PVC stabilization

Organic phosphites under mild conditions (290–330 K) easily react with oxovinylene groups in the presence of proton donors with formation of stable ketophosphonates:

(3)
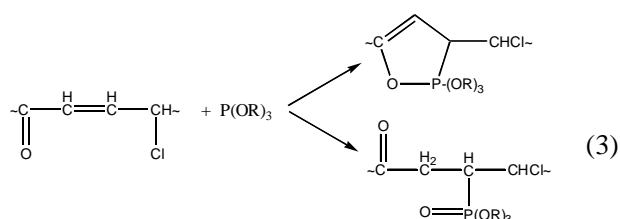
Reaction kinetics of organic phosphites interaction with oxovinylene groups are shown in Fig. 3. The formation of ketophosphonate structures according to the reaction (3) results in disappearance of internal unsaturated C=C bonds in a PVC structure. As a result, neither oxidizing ozonolysis of a polymeric product nor alkaline hydrolysis in particular results in disintegration of macromolecules and decrease of PVC molecular weight.
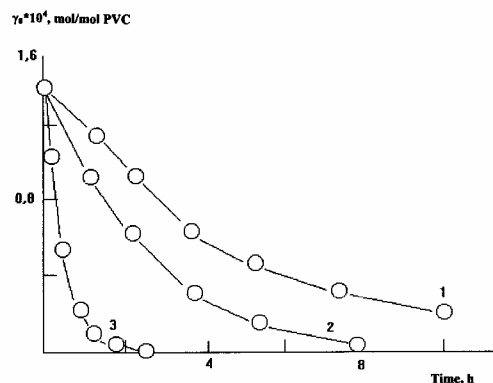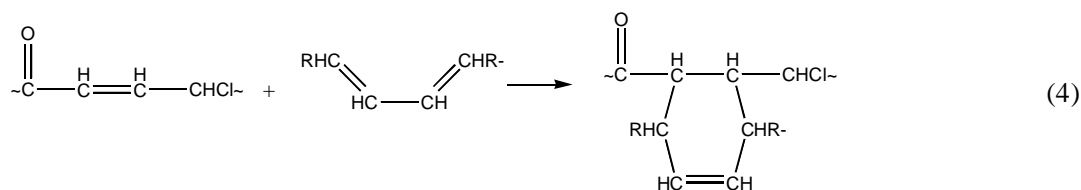

Fig. 3. The change of ~C(O)–CH=CH~ groups content in PVC during its interaction with tri-(2-ethylhexyl)phosphite (1-3). C$_0$ = 10^{-2} mol/mol PVC. Temperatures: 289 K (1), 298 K (2), 448 K (3)

It is important to specify that organic phosphites do not react with *b*-chloroallyl groups that is confirmed by the method of competing reactions of organic phosphites (trialkyl-, arylalkyl- and triarylphosphites) with a mixture (1:1, mol/mol) of methylvinylketone (model of an oxovinylene group) and 4-chloropentene-2 (model of a *b*-chloroallyl group) at 353 K. An organic phosphite practically quantitatively (regarding to proton donors) selectively reacts with methylvinylketone, while 4-chloropentene-2 is practically quantitatively segrerated after the reaction without changes, not counting some amount of its dehydrochlorination products (less than 7 wt %). The CH$_3$–C(O)–CH$_2$–CH$_2$–P(OR)$_2$ is the main reaction product (up to 75 wt %). In this reaction trialkyl- and alkylarylphosphites are more active than triarylphosphites.

Dienophylic oxovinylene groups react with conjugated dienes according to the Diels-Alder reaction:

$$\sim\!\!C(O)\text{-}CH\!=\!CH\text{-}CHCl\!\sim \;+\; RHC\!=\!CH\text{-}HC\!=\!CHR\text{-} \;\longrightarrow\; \text{(cyclohexene adduct)} \qquad (4)$$

This new, not known earlier reaction for PVC proceeds under mild conditions (353 K) with cyclopentadiene, piperylene, isoprene, 5-methylheptatriene-1,3,6 *etc.* and results (see reaction 4) in liquidation of internal unsaturated C=C groups in PVC chains similarly to organic phosphites.

PVC stabilization, *i.e.* a complex of methods used for the increase of polymer stability to the action of various factors (heat, light, oxygen *etc.*) during storage, processing and exploitation, is closely connected with a level of PVC development disintegration theory. Therefore, it is clear that significant change of theoretical developments about the reasons of PVC thermal instability (a presence of oxovinylene groups in the backbone), mechanism of the process (fundamental influence of the adjacent groups of the long-range order) and kinetics of their disintegration have shown the necessity and have given the possibility to create a new view while determing of new effective ways of PVC stabilization.

According to the reaction (3) it is impossible and not necessary to increase stability of PVC macromolecules due to the reduction of rate V_{Cl} because this process is rather slow. According to the experimental data, the rate of PVC statistical dehydrochlorination V_{Cl} (according to the random law) is constant and does not depend on the method of polymer synthesis and its molecular weight. Hence, it is the fundamental characteristic of PVC, showing that all parts in ~BXBXBX~ clusters participate in the process of HCl elimination according to the random law, whereas the rate of the conjugated systems formation V_p may differ as a result of its linearly dependence on the content of oxovinylene groups in PVC initial macromolecules (g_0) (Fig. 2).
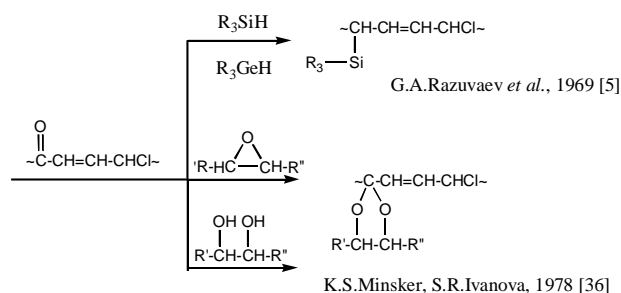
Thus, the basis of effective PVC stabilization which determines both operational properties and durability of rigid materials and products from PVC is the principle of self-stability increase of PVC macromolecules [17, 40-43]. This can be achieved first of all due to a chemical stabilization of PVC – destruction of labile oxovinylene groups present in initial PVC macromolecules *via* specific polymer-analogous reactions with even one reaction center (1)-(3):
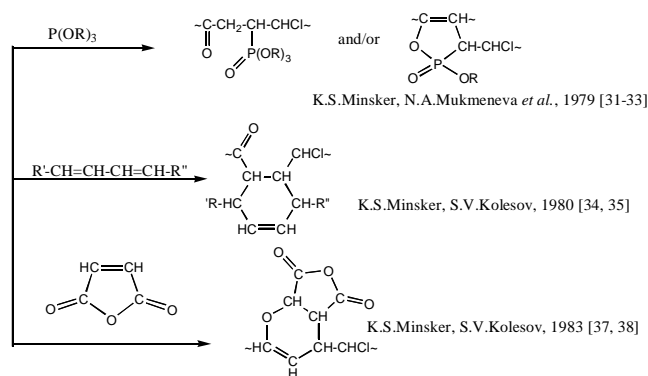
$$\underset{\underset{1\;\;O}{\|}}{\sim}\!C\text{-}\overset{2}{CH}\!=\!CH\text{-}\underset{\underset{3\;\;Cl}{|}}{CH}\!\sim$$
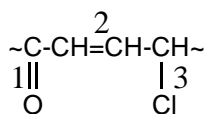
The conjugation ~C(O)CH=CH~ has to be destroyed and/or labile chlorine atom has to be replaced with a more stable framing group during interaction with the corresponding chemicals-additives (stabilizers). This principle is a basis of PVC stabilization in real composition during manufacturing rigid materials and products.
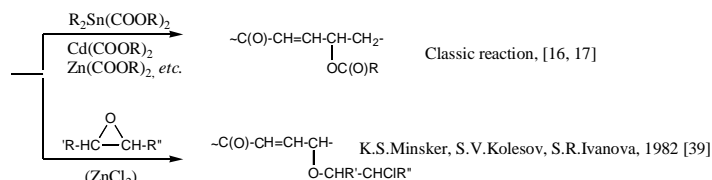
1. Polymer-analogous reactions with >C=O fragments of oxovinylenchloride groups:

(scheme with R_3SiH, R_3GeH → $\sim$CH-CH=CH-CHCl~ with R_3—Si, G.A.Razuvaev *et al.*, 1969 [5]; and with epoxide 'R-HC—CH-R" and OH OH R'-CH-CH-R" → K.S.Minsker, S.R.Ivanova, 1978 [36])

2. Polymer-analogous reactions with >C=C< fragments of oxovinylene groups:

(scheme with $P(OR)_3$ → ~C-CH2-CH-CHCl~ with P(OR)3 and/or cyclic phosphonate, K.S.Minsker, N.A.Mukmeneva *et al.*, 1979 [31-33]; with R'-CH=CH-CH=CH-R" → K.S.Minsker, S.V.Kolesov, 1980 [34, 35]; with maleic anhydride → K.S.Minsker, S.V.Kolesov, 1983 [37, 38])

3. Polymer-analogous reactions with labile ≥C–Cl groups:

(scheme with $R_2Sn(COOR)_2$, $Cd(COOR)_2$, $Zn(COOR)_2$ *etc.* → ~C(O)-CH=CH-CH-CH2- with OC(O)R, Classic reaction, [16, 17]; with 'R-HC—CH-R" ($ZnCl_2$) → ~C(O)-CH=CH-CH- with O-CHR'-CHClR", K.S.Minsker, S.V.Kolesov, S.R.Ivanova, 1982 [39])

This method is called "chemical stabilization" of PVC [17, 40, 41].

It is important that the concept of oxovinylene activation of macromolecules disintegration during PVC destruction allows to reveal new unexpected possibilities of thermal, as well as light-stabilization of this polymer. This also allows to use previously unknown classes of chemical compounds for its stabilization, namely conjugated

diene hydrocarbons, adducts of Diels-Alder reaction, protonic acids, *α*, *b*-dicarbonic compounds, *etc.* [34-38, 44-46]. New reactions proceeding during PVC chemical stabilization, including the application of known chemicals-additives, which are used for a long time for PVC stabilization (for instance, organic phosphites, epoxy compounds, proton-donating compounds *etc.*), allow to manage PVC aging process more effectively (Scheme 2). The connection between the chemical structure of chemicals-additives and their efficiency as stabilizers for PVC determines an opportunity of scientifically based and economically expedient selection of the corresponding stabilizers and their synergistic combinations at production of rigid materials based on PVC.

2.4. Light stabilization of PVC

Polymer-analogous transformations of oxovinylene groups in PVC macromolecules during its

chemical stabilization with the corresponding chemicals-additives lead not only to the increase of PVC self-stability and inhibition of macromolecules crosslinking, but also to a noticeable increase of PVC color stability.

The transformation of oxovinylene groups as a result of polymer-analogous transformations with chemicals-additives into ketophosphonate-, cyclohexane-, dioxolane-, dihydropyrane, *etc.* groups in structure of PVC macromolecules and "curing" of labile oxovinylenchloride groups increases PVC optical density in the UV-area of the spectrum. Therefore, these groups act as internal light stabilizers resulting in the PVC self-photostabilization [47] (Fig. 4).

Thus, the determining factors causing high rate of PVC disintegration and necessity of its stabilization are the presence of abnormal groups in the structure of polymeric molecules, mainly oxovinylene ones, *i.e.* macromolecule chemical structure.
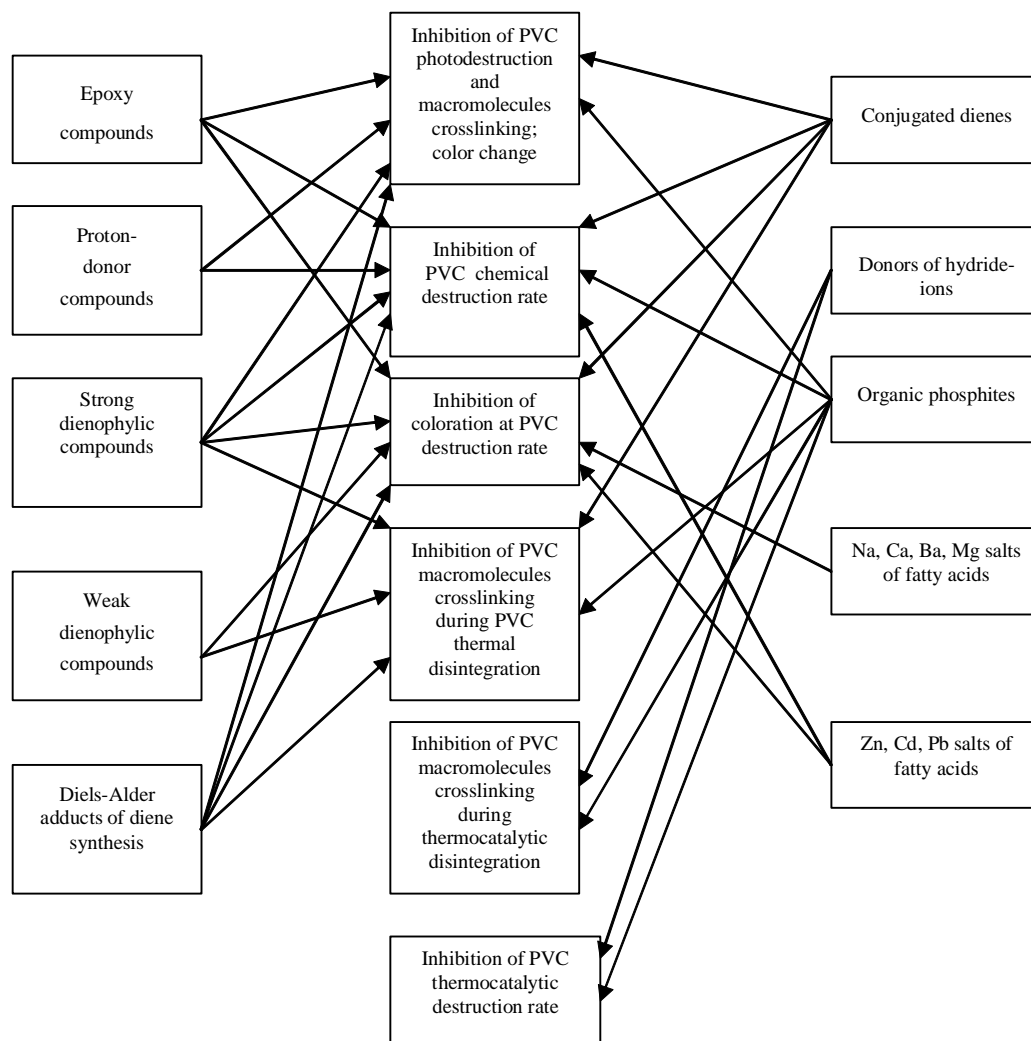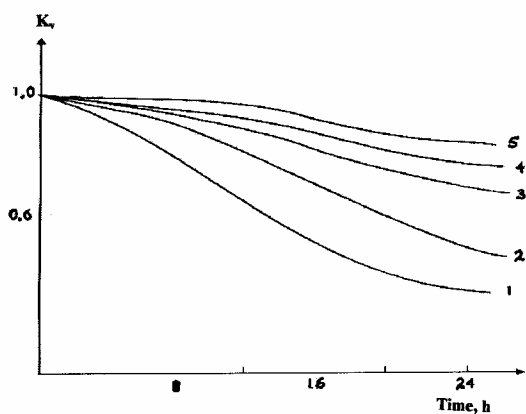

Scheme 2

Fig. 4. Dependence of whiteness coefficient K_w in PVC films upon exposure time: unstabilized PVC (1) and polymers treated with: 2-*tri*-(2-ethylhexyl)phosphate (2), 2-ethylhexyl-9,10-epoxy stearate with ZnCl$_2$ (3), piperylene (4), cyclopentadiene (5). Conditions: T = 295 K, λ – 254 nm, 1 – 1; 5·10^{15} quantum/s·cm^2

2.5. PVC disintegration in solutions. Effect of placticizers

As to plasticized (semi-rigid and flexible) PVC materials as well as PVC in solutions, the rate of their thermal destruction and effective stabilization are caused by essentially different fundamental phenomena in comparison with aging of PVC in the absence of the solvent. Macromolecules structure and dynamics, *i.e.* chemical nature of the solvent, its basicity, specific and non-specific solvatations, PVC content in a solution, segmental mobility of macromolecules, thermodynamic properties of the solvent, formation of associates, aggregates *etc.* are the main affecting factors. The chemical stabilization of PVC plays a less significant role.

The nucleophilic activation of PVC dehydrochlorination reaction is one of the basic reasons of changing the process kinetic parameters during PVC destruction in a solution. The process is described by E$_2$ mechanism. Thus, there is a linear dependence between PVC thermal dehydrochlorination rate and parameter of solvent relative basicity B (Fig. 5) [48–50]. The value B, cm^{-1} is evaluated by the shift of OH characteristic band of phenol with $\lambda = 3600$ cm^{-1} in IR-spectrum at the interaction with the solvent [51].

It is essentially important that the rate of PVC dehydrochlorination in the solvents with relative basicity $B > 50$ cm^{-1} is always higher than the rate of PVC dehydrochlorination without the solvent. At the same time when $B < 50$ cm^{-1}, PVC disintegration rate is always less, than that without the solvent. The revealed dependence $V_{HCl} = f(B)$ is described by the equation (5)

$$V_{HCl}^* = V_{HCl} + k(B - 50) \qquad (5)$$

An inhibition of PVC disintegration in the solvents with the basicity $B < 50$ cm^{-1} is a very interesting and
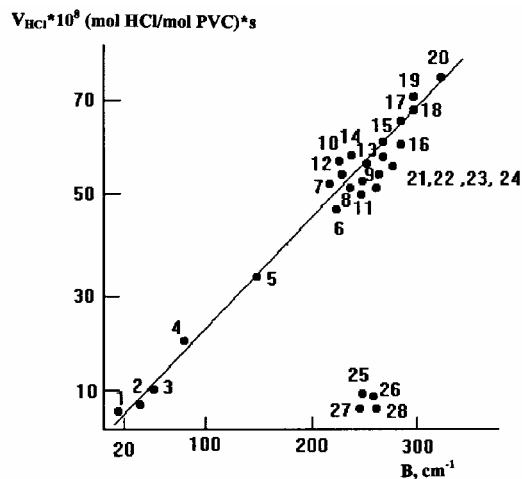

Fig. 5. The influence of the solvent basicity on the rate of PVC thermal dehydrichlorination in a solution: *n*-dichlorobenzene (1), *o*-dichlorobenzene (2), naphthalene (3), nitrobenzene (4), acetophenone (5), benzonitrile (6), di-*n*-(chlorophenyl-chloropropyl) phosphate (7), triphenyl phosphite (8), phenyl-*bis*-(*b*-chloroethyl) phosphate (9), tri-(*n*-chlorophenyl phosphate) (10), 2-ehtylhexylphenyl phosphate (11), tricresyl phosphate (12), cyclohexanone (13), phenyl-*bis*-(*b*-chloropropyl) phosphate (14), tri-*b*-chloroethyl phosphate (15), tri-*b*-chloropropyl phosphate (16), di-2-(ethylhexyl) phosphate (17), 2-ethylhexylnonyl phosphate (18), tri-(2-ethylhexyl) phosphate (19), tributylphosphate (20), dibutyl phthalate (21, 25), di-2-ethylhexyl adipinate (22, 26), dioctyl phthalate (23, 27), dibutyl sebacinate (24, 28). Concentration of PVC in solution: 0.2 wt % (1–24), 2 wt % (25–28). T = 423 K, under nitrogen

important phenomenon. It is so called "solvatational" stabilization of PVC. However, ignoring the fact that even at low concentrations (2 wt %) PVC solutions do not represent solutions with isolated macromolecules but rather with structured systems, in some cases a deviation from linear dependence of PVC dehydrochlorination rate on the solvent basicity B is observed. In particular, an abnormal behavior of PVC is observed during destruction in certain ester-type solvents (plasticizers) (Fig. 5, points 25–28), that is apparently caused by structural changes of macromolecules. This was never taken into account before while working with PVC in solutions.

It was found quite unexpectedly that not only the interaction "polymer – solvent", but also the interaction "polymer – polymer" in solutions provide significant affects the rate of PVC disintegration. It is known that the structure and properties of the corresponding structural levels depend on conformational and configurational nature of macromolecules, including a supermolecular structure of the polymer, which in its turn determines all basic (both physical and chemical) characteristics of the polymer.

"Polymer–polymer" interaction results in the formation of structures at supermolecular level. During concentration, in particular, PVC-solvent system consistently passes a number of stages from the isolated PVC macromolecules in a solution (extremely diluted

solution) to associates and aggregates from macromolecules in a solution. At the further increase of PVC concentration in a solution the formation of spatial fluctuational net with a structure similar to that of polymer in the block occurs.

When polymer concentration in a solution increases, the rate of PVC dehydrochlorination reaction changes as well, and various character of solvent influence on a PVC disintegration rate in solution is observed depending on a numerical value of basicity parameter B [52–57]. If $B > 50$ cm^{-1} the polymer disintegration rate decreases with the increase of its concentration. If $B < 50$ cm^{-1} the polymer disintegration rate increases with the increase of polymer concentration. In all cases the rate of HCl elimination from a polymer has a trend to reach values of PVC dehydrochlorination rate in the absence of the solvent $V_{HCl}^{PVC} = 5 \cdot 10^{-8}$ (mol HCl/mol PVC)/s. (Fig. 6).
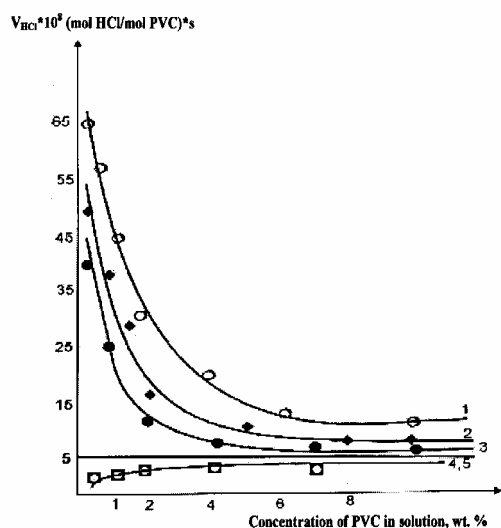

Fig. 6. Dependence of PVC dehydrochlorination rate on its concentration in a solution: cyclohexanol (1), cyclohexanone (2), benzyl alcohol (3), 1,2,3 – trichloropropane (4), *o*-dichlorobenzene (5), without solvent (6).
T = 423 K, under nitrogen.

Equation (5) turns into the equation (6) taking into account the fact that the PVC disintegration rate is determined not only by the parameter of solvent relative basicity B, but also by its concentration in a solution (C, mol PVC/l), as well as by degree of "polymer – polymer" interaction (degree of macromolecules structurizarion in the solution $DC = /C\text{-}C_0/$, where C_0 - concentration of the beginning of PVC macromolecules association in a solution):

$$V_{HCl} = V_{HCl}^0 + A_1 /(C + /\Delta C/ + d_1)(B - 50) \quad (6)$$

where factor $A_1 = (0.8 \pm 0.2) \cdot 10^{-9}$ (mol HCl/mol PVC)/s; d_1 - dimensionless factor representing interaction "polymer – solvent" ($d_1 = 0.5 \pm 0.25$). The deviation from the moment

of the beginning of macromolecules association in a solution is taken as an absolute value, since it can change in both directions: to more concentrated and more diluted solutions of a polymer.
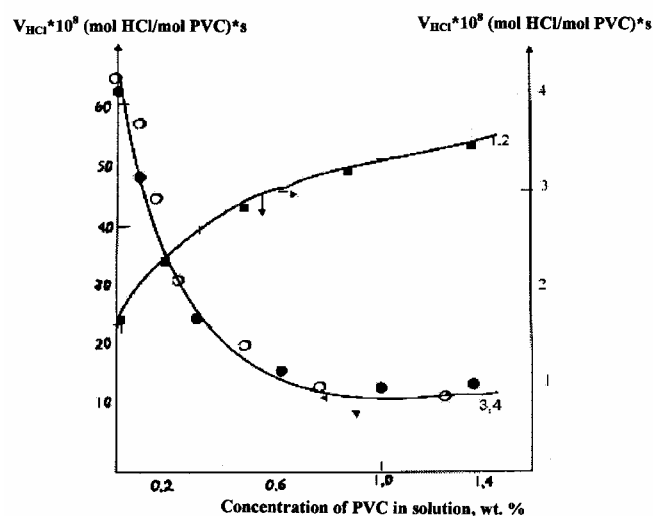

Fig. 7. Dependence of PVC dehydrochlorination rate on its concentration in a solution: 1,2,3–trichloropropane (1, 2), cyclohehanol (3, 4), experimental data (1, 3), calculated data (2, 4) according to the equation (7) at $A_1=10^{-9}$ and $d_1=0.8$ and 0.7 correspondingly. T = 423 K, under nitrogen

Equation (6) correctly describes the change of PVC thermal dehydrochlorination rate depending on its concentration in a solution taking into account the parameter of relative basicity B, irrespective of the chosen solvent (Fig. 7).The observable fundamental effect has the significant importance during production of plasticized (in particular, by esters) materials and products based on PVC. Despite the very high basicity of ester-type plasticizers ($B = 150$ cm^{-1}) at PVC concentration in solutions more than 2 %, a noticeable reduction of PVC disintegration rate is observed (Fig. 4, points 25-28), *i.e.* in essence, stabilization of PVC occurs. This effect is caused by formation of dense globules, associates *etc.* in the system PVC–plasticizer. Practically this allows to create economic composition of plasticized materials from PVC with the very little content of metal-containing stabilizers – HCl acceptors or without them at all.

The temperature is very important in formation of the heterophase system. Even at low concentration of PVC in ester-type plasticizer (for example, in dioctyl phthalate at $C > 0.1$ mol/l) the true solutions are formed only at temperatures above 400 K. Globular structure of suspension PVC and formation of associates takes place at temperatures up to 430–445 K. In other words, PVC during plasticization is capable to keep its structural individuality at supermolecular level formed during polymer synthesis. Just under these conditions the ester-type plasticizer behaves not as a highly-basic solvent, but as a

stabilizer during PVC thermo-disintegration due to formation of associates *etc*. It leads to a reduction of stabilizer amount, extension of exploitation time of materials and products *etc*.

It should be noted that the change of PVC disintegration rate during macromolecules association is the general phenomenon and does not depend on the way it was achieved. In particular, the similar character (as well as at concentrating of PVC solutions (Figs. 6 and 7)) of change of PVC dehydrochlorination rate in a solution is observed if the change of PVC structural-physical condition in a solution is achieved with the addition of even chemically inert non-solvents, for example, hexane, decane, undecane, polyolefines, polyethylene wax *etc*. [53, 56-59] (Fig. 8).
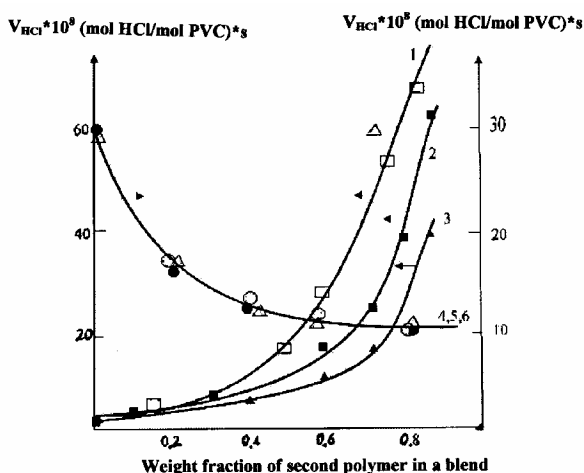

Fig. 8. Dependence of thermal destruction rate on the content of the second inert polymer in a solution of trichloropropane (1, 3), dichlorobenzene (2), and cyclohexanol (4–6) for PVC with polyethylene (1, 4), polypropylene (2, 5), and polyisobutylene (3, 6); T = 423 K, under nitrogen

It is interesting to note that the degree of relative change of PVC destruction rate under the action of the second inert polymer (non-solvent) is much higher, than at concentration of a PVC solution, especially in the case of low-basic solvents (trichloropropane, dichlorobenzene) – the result of formation of more dense formations at a supermolecular level corresponding associates and aggregates, due to which there is a significant change of a PVC destruction rate. The more content of non-solvent (including an inert polymer) in a mixture and lower thermodynamic compatibility of components in a solution, the more structural formation takes place in a solution, including that in the presence of polymer blends (associates, aggregates). Formation of a fluctuational net with the participation of macromolecules is probable. Since the reason of PVC thermal dehydrochlorination rate change in the case of its mixtures with chemically inert and thermodynamically incompatible polymers is the same, as at concentrating of a PVC solution (structural-chemical

changes of a polymer in a solution), the parameters determining the rate of PVC disintegration will be, obviously, similar. Therefore, while considering PVC thermal destruction rate a concentration of the second polymer in a blend with PVC and a degree of its thermodynamic affinity to PVC have to be taken into account in addition to an influence of polymer concentration in a solution, basicity of the solvent *B* and interaction "polymer–solvent" forces. In view of these factors the equation (6) turns into an equation (7):

$$V_{HCl} = V_{HCl}^0 + (A_1/c + /(c + |\Delta c| + d_1 + an))(B - 50)$$

$$+ A_1/B)(d_2 a^n/c) \tag{7}$$

where *a* - fraction of the second polymer, varying from 0 to 0.99; *n* – dimensionless parameter describing a degree of thermodynamic affinity of PVC to the second polymer, varying from zero (in the case of a complete thermodynamic compatibility of the components) up to 10 (in the case of a complete thermodynamic incompatibility of the polymers). Dimensionless coefficient d_2 reflects interaction between the second polymer and the solvent. During PVC destruction in a mixture with polyethylene in a solution of dichlorobenzene, trichloropropane, and cyclohexanol d_2 is equal to 2.5±0.1.

Observable changes of PVC thermal disintegration rate under the action of the second thermodynamically incompatible with PVC polymer (or owing to an increase of PVC concentration in a solution) are caused by a displacement of the solvent out of macromolecular globules of PVC with transformation to the structure, which it has in the absence of the solvent. This phenomenon stimulates unexpected effect of "the solvent action" (a retardation or an acceleration depending on the solvent basicity *B*) relatively to PVC thermal disintegration. The displacement of the solvent accelerating PVC disintegration ($B > 50$ cm^{-1}) weakens its interaction with PVC and leads to a retardation of HCl elimination from macromolecules. It means stabilization occurs both in the case of PVC solutions concentrating, and in the case of second polymer addition, which is thermodynamically incompatible with PVC. In the solvents retarding PVC disintegration ($B < 50$ cm^{-1}) due to the low nucleophilicity, an effect of the solvent displacement and weakening of its influence on PVC have the opposite result – an increase of HCl elimination rate from PVC with the increase of its concentration in a solution or using chemically inert non-solvent. It is obvious that irrespective of the ways of PVC structure changes – by increase of its concentration in a solution or by addition of the second thermodynamically incompatible with PVC, chemically inert non-solvent – the varying structural-physical state of the polymer results in a noticeable change of its thermal dehydrochlorination rate in a solution. These effects are caused by structural-physical changes in the system polymer – solvent, and previously unknown

phenomena can be classified as a structural-physical stabilization (in the case of PVC disintegration gross-rate reduction in highly-basic solvents at $B > 50$ cm^{-1}) and respectively, structural-physical antistabilization (in the case of PVC disintegration gross-rate increase in low-basic solvents with $B < 50$ cm^{-1}).

2.6. "Echo"-stabilization of PVC

At last, it is necessary to specify one more remarkable achievement in the field of aging and stabilization of PVC in a solution. Under real conditions the main reason of the sharp accelerated aging of plasticized materials and products is the oxidation of the solvent by air oxygen (Fig. 9, curve 3).
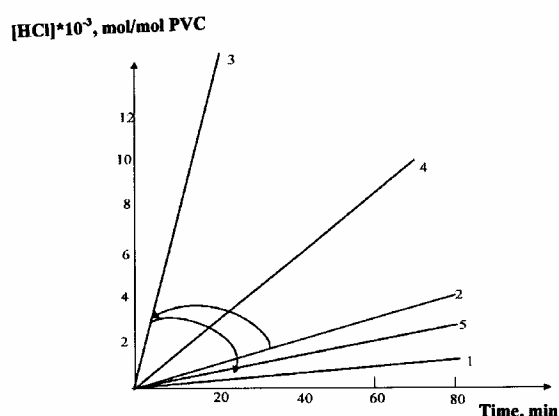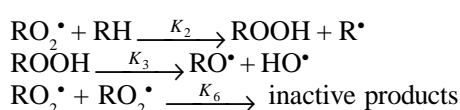
$$RO_2^\bullet + RH \xrightarrow{\quad K_2 \quad} ROOH + R^\bullet$$
$$ROOH \xrightarrow{\quad K_3 \quad} RO^\bullet + HO^\bullet$$
$$RO_2^\bullet + RO_2^\bullet \xrightarrow{\quad K_6 \quad} \text{inactive products}$$

Fig. 9. "Echo"-stabilization of PVC. HCl elimination during thermo- (argon) (1, 2) and thermo-oxidative (air) (3–5) PVC destruction in the solution of dioctyl sebacinate: unstabilized PVC (1–4), PVC stabilized with diphenylpropane (0.02 wt %) – "echo" stabilization (5), PVC without a solvent (2, 4); T = 448 K

Peroxides, formed during oxidation of ester-type plasticizers, initiate macromolecules disintegration. Under such conditions the PVC destruction rate may be increased in two and more orders of magnitude and determined by oxidizing stability of the solvent to oxygen – by parameter $K_{ef} = K_2 \cdot K_3^{0.5} \cdot K_6^{-0.5}$. The higher an oxidizing stability of the solvent (in particular, ester-type plasticizer), in the presence of which PVC thermooxidative disintegration occurs, the lower its destruction rate and the longer life time of semi-rigid and flexible materials based on PVC [60, 61, 63]. An inhibition of the solvent oxidation process (including plasticizers) due to introduction of stabilizers-antioxidants or their synergistic compositions inhibits PVC thermo-oxidative disintegration in a solution as well (Fig. 9, curve 5).

During effective inhibition of the ester-type plasticizers oxidation by air oxygen the rate of PVC thermo-

oxidative destruction in their concentrated solutions approach the rate of polymer disintegration, which is characteristic for its thermal destruction in the plasticizer (solvent) presence, *i.e.* slower, than PVC disintegration without a solvent. In these cases an inhibition of the solvent oxidation using "echo"-type stabilizers-antioxidants causes so-called PVC "echo"-stabilization (Fig. 9, curve 5) [49, 62, 63].

3. Conclusions

Thus, creation of high-quality and economic semi-rigid and flexible materials and products based on PVC, including those with the solvents, requires the specific approach, essentially differing from principles of manufacturing rigid materials and products from PVC. The main principles are: solvatational, structural-physical and "echo"-stabilization of a polymer in a solution.

As to paramount tasks of fundamental and applied research in the field of PVC manufacturing and processing at the beginning of XXI century, obviously they are the following:

• Manufacture of an industrial PVC without labile groups in a backbone. It will provide drastic increase of polymeric products self-stability, possibility of PVC processing with the minimum content or in total absence of stabilizers and other chemicals-additives and the opportunity of creating materials and products on a PVC basis with increased life time.

• Wide use of the latest achievements in the area of PVC destruction and stabilization, both in the presence and absence of the solvents. First of all, the phenomena of chemical, solvatational, structural-physical, self- and "echo"-stabilization of PVC will allow to create rigid, semi-rigid and flexible (plasticized) materials and products with the minimum content of chemicals-additives and increased life time of their service at exploitation under natural and special conditions.

• The use of non-toxic, non-flammable products which do not emit toxic and poison gaseous and liquid products at elevated temperature.

• Complete elimination of all toxic and even low-toxic chemicals-additives from all compositions (namely, compounds based on Pb, Cd, Ba, *etc.*).

• Search of non-toxic and highly effective inorganic chemicals-additives, first of all, stabilizers of a zeolite type, modified clays *etc.*

At the same time new "surprises" presented to us by this unusual polymer may undoubtedly be expected. Certainly it will give a new stimulus for development of scientific bases and practical development with opening of new pathways, conducting to essential retardation of PVC ageing under natural and special conditions at reduction of the correspoding chemicals-additives amounts, until their complete elimination.

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ДОСЯГНЕННЯ ТА ЗАДАЧІ ДОСЛІДЖЕННЯ СТАРІННЯ І СТАБІЛІЗАЦІЇ ПОЛІВІНІЛХЛОРИДУ

Анотація. Розглянуто перспективи виробництва полівінілхлориду (ПВХ) за відсутності лабільних груп у головному ланцюгу. Показано, що таке виробництво забезпечує значне підвищення внутрішньої стабільності полімерних продуктів, можливість обробки ПВХ за мінімальної кількості або відсутності стабілізаторів та інших хімічних додатків. Це також дозволяє створювати матеріали і продукти на основі ПВХ з продовженим терміном експлуатації. Наведені результати дозволяють створювати жорсткі, напівжорсткі та гнучкі (пластичні) матеріали і продукти з мінімальним вмістом хімічних додатків та продовженим терміном експлуатації за природних та спеціальних умов.

Ключові слова*: лабільні групи, хімічна, структурно-фізична, сольватація, "ехо"-стабілізація, нетоксичні хімікати-додатки, цеоліти, модифіковані глини.*