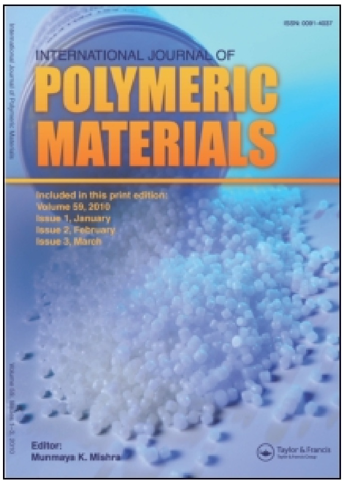

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Principles of Poly(vinyl)chloride Stabilization

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Principles of the stabilization of the hard and plasticized (solvents including) PVC are basically different. The stabilization of the PVC used in hard materials and products is based on the fundamental principles of chemical stabilization of the PVC. The stabilization of the plasticized PVC material and products (solvent including) is based on the principles of solvation and "echo" stabilizations.

KEY WORDS PVC, hard PVC, plasticized PVC, stabilization.

More than 3000 materials and products are based on poly(vinyl)chloride. It is important that the principles of stabilization of stiff and plasticized (solvents including) PVC are basically different.

A. THE STABILIZATION OF PVC AT CREATION OF THE STIFF MATERIALS

Poly(vinyl)chloride stability and HCl-elimination rate are practically determined by the effect of long range neighbouring groups, i.e., by the content of inner oxovinylene (carbonylallyl) groups—CAG $({}_{\sim}\underset{(1)}{C(O)}—\underset{(2)}{(CH{=}CH)_n}—\underset{(3)}{CHCl}—CH_{2\sim}, n = 1)$—with the sufficient validity—the only significant labile groups within PVC macromolecules[1-7] (Figure 1).

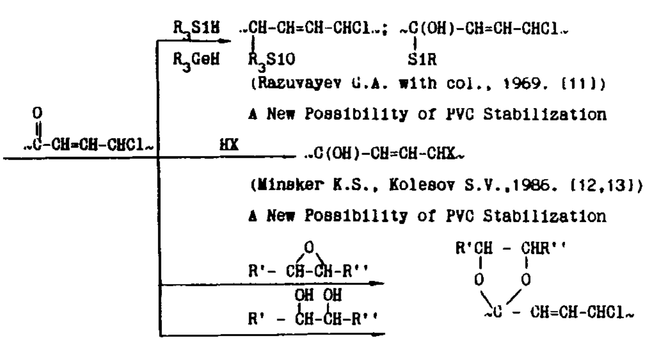
$$V_{HCl} = k_s a_0 + k_p \bar{\gamma}_0$$

k_s and k_p are the rate constants of statistic dehydrochlorination of macromolecules PVC (reaction rate constants in formation of isolated C═C bonds at random in homotriads ${}_{\sim}VCVCVC_{\sim}$) and the rate constants elimination of the HCl activated by CAG (γ_0), a_0 is the Cl content in the starting polymers (mol/basis-mol PVC).

The effective stabilization of PVC is based on the principle of increasing its self-stability under the influence of various chemical and physical factors at the expense of the directional change of chemical structures of the active centres (CAG) when they chemically interact with various chemical additives (stabilizers). Note that these additives result from the polymer-analogous reactions, which represent a new approach for chemical stabilization of macromolecules.[6-10] Since this is a fundamental principle, the ways based on using the compounds (chemical stabilizers) interacting with at least one of the CAG reaction centres; C═O (1), ~CH═CH~ (2), $\rangle$C—Cl (3) prove to be fruitful for practical stabilization of PVC.

The conjugation O═C—CH═CH~ in CAG is necessary to be destroyed in the oxovinylene group and/or a labile chlorine atom in CAG—to be substituted for more stable frame group.

1) Polymer-analogous reactions on C═O-groups of CAG are:

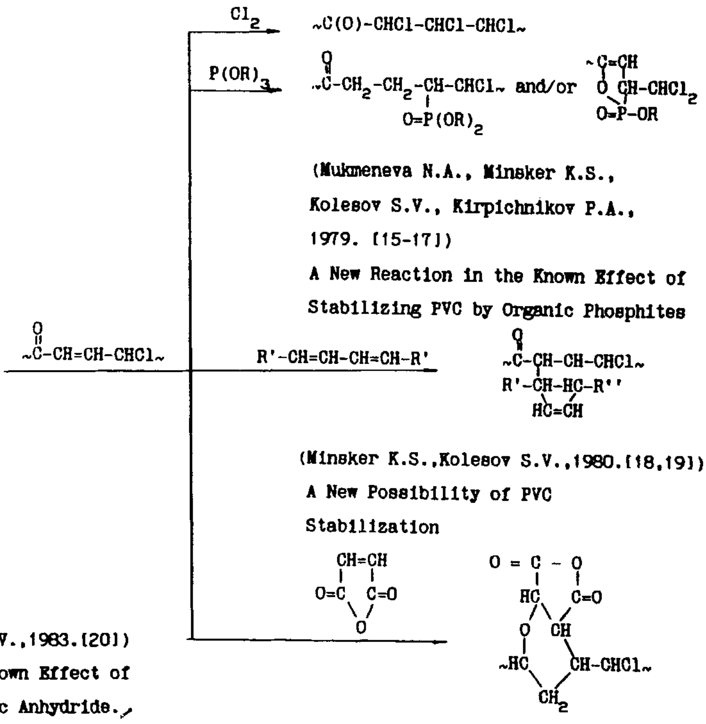


(Razuvayev G.A. with col., 1969. [11])
A New Possibility of PVC Stabilization

(Minsker K.S., Kolesov S.V., 1986. [12,13])
A New Possibility of PVC Stabilization

(Minsker K.S., Ivanova S.R., 1978, [14])
A New Reaction in the Known Effect of
Stabilizing PVC by Epoxycompounds.

2) Polymer-analogous reactions on ~CH═CH~ bonds are:



(Mukmeneva N.A., Minsker K.S.,
Kolesov S.V., Kirpichnikov P.A.,
1979. [15-17])
A New Reaction in the Known Effect of
Stabilizing PVC by Organic Phosphites

(Minsker K.S., Kolesov S.V., 1980. [18,19])
A New Possibility of PVC
Stabilization

(Minsker K.S., Kolesov S.V., 1983. [20])
A New Reaction in the Known Effect of
Stabilizing PVC by Maleic Anhydride.

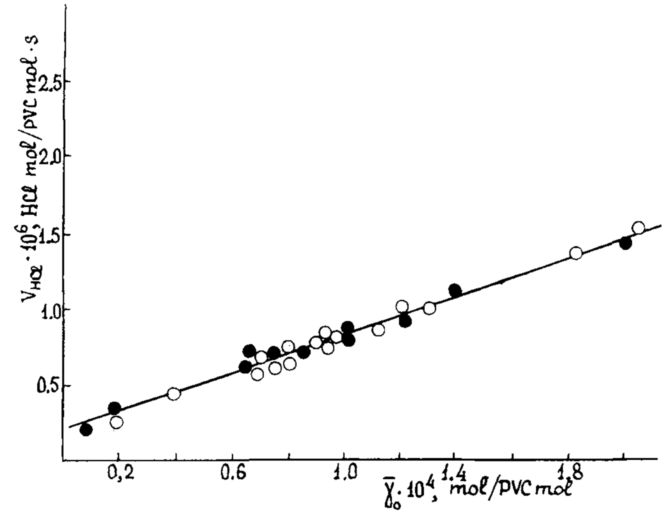
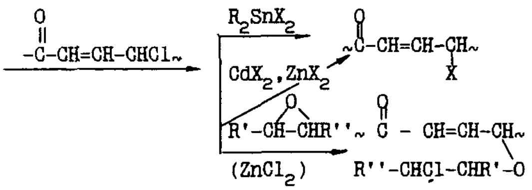


FIGURE 1 The dependence of PVC dehydrochlorination rate on the content of carbonylallyl groups within macromolecules (448 K, 10^{-2} Pa); Commerical specimens ($\bar{M}_n^0\cdot10^3$; $\bar{\gamma}_0$ mol/PVC mol × 10^4) (x): Thervyl (Czeckoslovakia) (160; 0.2); PVC-50 USA (167; 0.41); B/N 1-8000 Japan (139; 0.70); C-70, CIS (137; 0.70); Sicron 548 FM Italy (143.5; 0.75); Ravenyl RR-100 170 F, Italy (136; 0.80); M-64 CIS (108.5; 0.80); TK-1300, Japan (163; 0.88); Nicavinyl SG-1300, Japan (137.5; 0.92); C-63 CIS (104; 0.93); Solvic 223, Belgium (65.5; 0.96); Vestolyt S 6057 Germany (90; 1.10); Hostalyt, Germany (108.5; 1.19); Lucovil GB-1150, France (133; 1.31); PVC-S-64, Poland (109; 1.80); PVC-K-60-65, Korea (109; 2.02); Laboratory specimens (0): Thervyl, Czeckoslovakia (160; 0.10); (150; 0.13); CIS (83; 0.2); (215.5; 0.67); (146; 0.68); (137.5; 0.77); (119; 0.87); (89; 1.02); (89; 1.02); (124.5; 1.18); (94.5; 1.41); (61.5; 1.97).

3) Polymer-analogous reactions on $>\!C\!-\!Cl$ labile bonds are:



(Minsker K.S.,Kolesov S.V., Ivanova S.R., 1982. [21])

A New Reaction In the known Effect of Stabilizing PVC by Epoxycompounds.

The discovered polymer-analogous reactions of various classes of chemical additives with PVC, where the rate of HCl elimination from polymer products is determined by the content of oxovinylene groups ($\bar{\gamma}_0$), and obtained kinetic Equations (1)[10] allowed us to exactly interpret the chemism of stabilizing effect of many famous classes of PVC stabilizers (organic phosphites,[15-18] epoxy compounds,[14,21] dienophiles,[20] new possible ways of PVC chemical stabilization being discovered at the

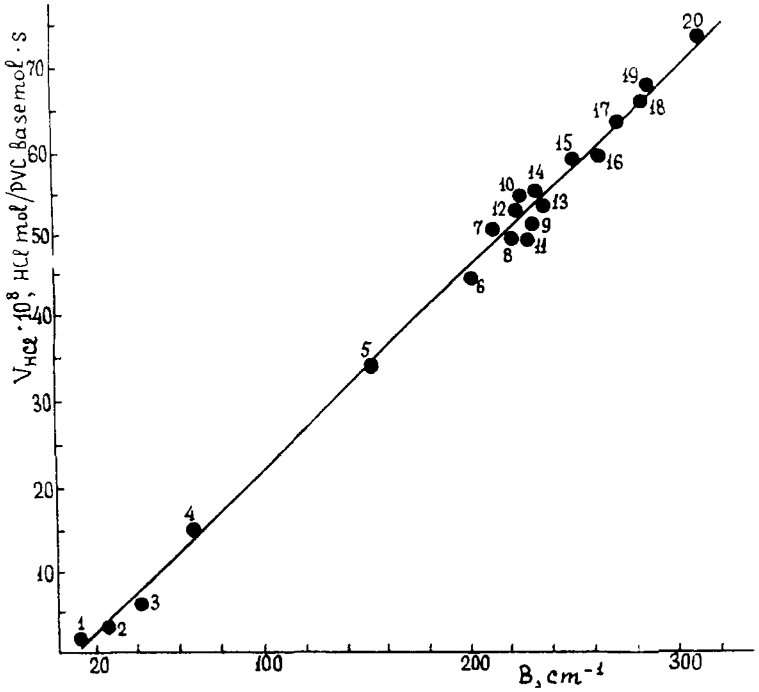


FIGURE 2 The effect of the solvent basicity on the PVC thermal dehydrochlorination (423 K, N_2) in the solution: 1—*n*-dichlorbenzene; 2—*o*-dichlorbenzene; 3—naphthalene; 4—nitrobenzene; 5—acetophenone; 6—acetophenone; 7—di-*n*-(chlorphenyl-chlorpropyl)phosphate; 8—triphenylphosphate; 9—phenyl-bis-(β-chlorethyl)phosphate; 10—tri-(*n*-chlorphenylphosphate); 11—2-ethylhexylphenylphosphate; 12—tricresylphosphate; 13—cyclohexanone; 14—phenylbis-(β-chlorpropyl)phosphate; 15—tri-β-chlorethylphosphate; 16—tri-β-chlorpropylphosphate; 17—di(2-ethylhexyl)phosphate; 18—2-ethylhexyldinonylphosphate; 19—tri-(2-ethylhexyl)phosphate; 20—tributylphosphate.

same time (conjugated diene compounds,[19,20] Dils-Alder adducts, α,β-dicarbonyl compounds,[22–24] proton acids[12,13] etc.

The dependence of additives effectivity on their chemical structure allows one to substantiate from the scientific point of view the selection of chemical stabilizer for VC polymers for formulation of stiff PVC materials and products.

It is of importance that chemical stabilization is not limited only by VC polymer dehydrochlorination inhibition. Polymer-analogous conversions of oxovinylene (CAG) groups and polyene groups lead to the increase of colour stability of polymer products[25,26] and inhibition of macromolecule crosslinking.[25–27] Consequently, the operating characteristics of PVC materials are improved if the fundamental phenomenon-chemical stabilization of polymer products is applied to VC polymers, the decomposition rate of which is determined by the CAG content (γ_0). In this case dienophiles, conjugated dienes, Dils-Alder adducts are especially efficient.

Another highly important consequence of VC polymers chemical stabilization is the increase of their photostability[25,26] (Figure 2).

CAG conversion into cyclohexane, dioxalane, dihydropirane etc. groups improves the ultraviolet stability of a polymer. New groups, forming in the polymer-analogous reactions of chemical stabilizers (dienes, dienophiles, organic phosphites, epoxy compounds, diols) with CAG, appear to be inner color stabilizers,[25] that in principle corresponds to the formation of VC-based selfstabilizing polymer products. All that allows us to speak about a new effect—the result of polymer product stabilization—selfphotostabilization of VC polymers.[25]

B. STABILIZATION OF PVC AT CREATING OF THE PLASTICIZED MATERIALS AND IN THE SOLUTIONS

The destruction and stabilization of solvent containing PVC differs from that of individual polymer products and is determined by basically different fundamental principles. This is because the elimination of HCl from PVC may proceed in a general case faster or slower, depending on the solvation effects of the "polymer-solvent" interaction.[28-37] There is a clear linear dependence between the rate of elimination of HCl from PVC in solution and the basicity of the solvent B (Figure 2), (with exception of ester plasticizers[38,39]).

There exists a linear dependence of PVC brutto-dehydrochlorination rate (V_{HCl}) on the parameter B—the solvent basicity (or its donor number D_N) with a high correlation coefficient ($r = 0.986$) (Figure 2).

It should be mentioned that for the cases of degradation of pure PVC and PVC in the presence of phosphates or other solvents with $B = 55 \pm 5$ cm^{-1} the V_{1p} rates are close, where as the rate of the random process V_{1r} increases in parallel to the variation of B, although no chemical interaction with normal vinyl chloride units of the chain or with carbonyl-allylic, fragments is observed. For the case of $B < 55 \pm 5$ cm^{-1}, where the effect of the solvational stabilization of PVC is clearly manifested, the V_{1r} is constant. The growth rate of polyene sequences initiated with CAG (V_{1p}), however, decreases.[29]

Thus, the rate of elimination of HCl from PVC in solution is described by the equation:

$$V_{HCl} = (V_{1r} + V_{1p}) + V_3 = (V_{1r} + V_{1p}) + k_{eff}(B - 50)m,$$

where m is a coefficient (cm·mol HCl/mol·PVC).

The values of the effective rate constants of elimination of HCl from PVC in solutions k_{eff} calculated from experimental data are equal to $(0.2 \pm 0.03) \times 10^8$ s^{-1} at 423 K, except for the ester plasticizers which do not conform to this rule.[8]

Thus, we can speak about another new fundamental phenomenon for the PVC-solvation stabilization,[31] taking place when polymer product undergo destruction not only in the solutions with the basicity less than 55 ± 5 cm^{-1}, but in several classes of organic compounds with essentially high basicity ($B = 150 \pm 2$ cm^{-1}) as well (this is particularly observed in presence of ester plasticizers).[8]

In the presence of air oxygen the decomposition of solvated VC polymers is always sharply accelerated.[40-44] The HCl-elimination rate being able to rise two orders or more (for instance PVC destruction in presence of ester plasticizers) (Figure 3, curve 4).[40-43] Furthermore, such fundamental phenomena, as the long range neigh-

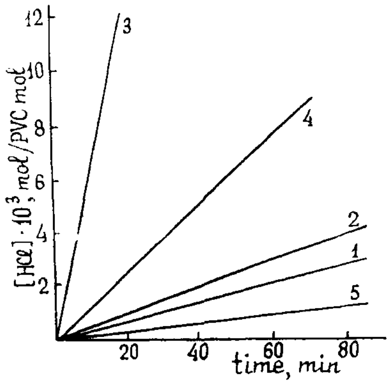


FIGURE 3 The PVC "echo"-stabilization. HCl-elimination in the process of thermal (1; 2) and thermoxidative (3; 4) degradation (448 K, Argon) of the PVC: in the solution of dioctylsebacate: 1,3—unstabilized PVC; 5—the PVC stabilized with 2,2-bis(4-hydroxyphenyl)propanol; (0.2 mass%) without the solvent (2, 4).

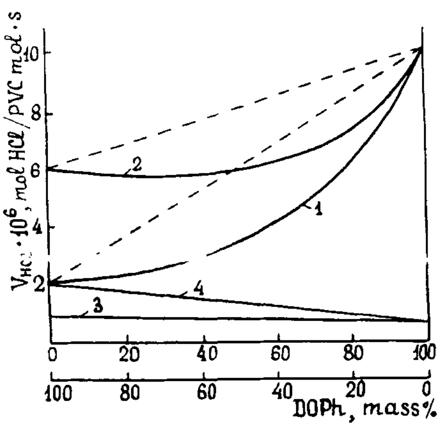


FIGURE 4 "Auto-echo"-stabilization of the PVC in thermoxidative degradation of the PVC in the solution of the mixed solvents (448 K); 1—dioctylphthalate + tricresylphosphate; 2—dioctylphthalate + tri(2-ethylhexyl)phosphate; 3, 4—thermal degradation of the PVC in the solution of mixed solvents (448 K, Argon), 1, 2—respectively.

bouring group effect and solvation stabilization of VC copolymers are in this case rather insignificant. The thermal oxidation rate of VC polymers is determined by oxidability of the organic solvent compound (plasticizer) by air oxygen (Figure 4)[43-46]:

$$k_{\rm eff} = k_2 \cdot k_6^{-0.5} \cdot k_3^{0.5}$$

in the chain oxidation scheme of an organic compound:

$$RO_2^{\bullet} + RH \xrightarrow{k_2} ROOH + R^{\bullet}$$

$$\mathrm{ROOH} \xrightarrow{k_3} \mathrm{RO}^{\cdot} + \mathrm{HO}\cdot$$

$$\mathrm{RO}_2^{\cdot} + \mathrm{RO}_2^{\cdot} \xrightarrow{k_6} \mathrm{R{-}O{-}O{-}R} + \mathrm{O}_2$$

The process proceeds according to the mechanism of free radicals; the free radicals formed during, the solvent oxidation promote the dehydrochlorination of VC polymers. This fact requires a new specific approach to stabilizing solvated polymers during the manufacture of soft and semiductile VC based materials. In this case the use of solvation stabilization of PVC is required. This is achieved by protecting the solvent (plasticizer) from the oxidation by air oxygen using stabilizers-antioxidants or their synergetic combinations. In this case, as a result of the reaction inhibition leading to formation of hydroperoxides on the basis of solvent (plasticizer molecules), the thermal destruction rate of PVC in liquid phase V_{HCl} is reduced by 1.5–2 orders of magnitude. In a limiting case, where the solvent oxidation by air oxygen is completely eliminated, the HCl-elimination rate from polymer products can reach the value of V_{HCl}, characteristic of the thermal destruction in solutions. The V_{HCl} values are in this case comparable to those of solvents with $B < 55 \pm 5$ cm^{-1}, and essentially lower than the value of V_{HCl} under the analogous conditions of decomposition of individual polymer products (Figure 4).

This fundamental phenomenon, characteristic of the stabilization of PVC in solution, has been called "echo-stabilization."[47] In this case effective stabilization of PVC during thermal destruction in solutions where the fundamental effect-solvation stabilization of PVC takes place, is performed through the solvent (plasticizer) stabilization under the conditions of oxidation by air oxygen. Solvation stabilization of polymer products is "echoed" due to the specific interaction "polymer-solvent" causing lower mobility of allyl chloride in CAG.

Hence, the "echo"-stabilization of PVC which represents a new approach for creating soft and semiductile materials, is basically different from the principles of stiff PVC stabilization.

So far we are unable to develop precise guidelines for PVC stabilization using solvents with the basicity $B > 55 \pm 5$ cm^{-1}. Therefore, traditional methods such as; introduction of stabilizing-HCl-acceptors, antioxidants etc. are used in this case to suppress the thermal destruction of PVC, and hence, the HCl elimination rate in destruction of PVC in solution increases in comparison with the rate of thermal destruction of the starting polymer products. Note that this excludes ester stabilizers.

If the mixtures of phosphate ($B = 210$–315 cm^{-1}) and ester plasticizers are used, as for example in production of materials with low flammability, a marked reduction of brutto-dehydrochlorination rate is observed. This includes PVC with ester plasticizer content up to 80–90%, without specially introducing stabilizers-antioxidants (Figure 4), and despite the fact that phosphates contribute to the acceleration of PVC decomposition not only in thermal but also in thermoxidative destruction of polymer products. This fundamental characteristic phenomenon has been called "auto-echo" stabilization[48] and represents a new possibility of VC-based soluted polymers stabilization. The rate of thermoxidative destruction of polymer products is reduced not by means of specially introduced corresponding stabilizers-antioxidants, but through "in situ" formation of phenols and alcohols inhibiting ester plasticizers oxidation by air oxygen, which are products of phosphate plasticizer oxidation.

This new possibility, namely the "auto-echo" stabilization of PVC in solutions, as the above "echo" stabilization of PVC provides guidelines for effective and economical selections of chemical additives in creating soft and semiductile materials and products, and also in processing PVC in solution.

In summary, the effects of neighbouring groups of long range and the principles of chemical, solvation, "echo"- and "auto-echo"-stabilizations form the basis for development of high-quality cost effective, and hard, semiductile and soft (plasticized) PVC materials and products.

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