Effect of Solvent (Plasticizers) on PVC Degradation

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Summary: Both plasticized (semi-rigid and flexible) PVC materials as well as PVC in solutions, the rate of their thermal degradation and effective stabilization are caused by essentially different fundamental phenomena in comparison to aging of PVC in absence of the solvent. Both structure and macromolecular dynamics render the significant influence on its stability, i.e. chemical nature of the solvent (plasticizer), its basicity, specific and non-specific solvation, degree of PVC in a solution (solubility), segmental mobility of macromolecules, thermodynamic properties of the solvent (plasticizer), formation of associates, aggregates, etc.

The chemical stabilization of PVC plays a less significant role. The effect of above factors on stability (behavior) of semi-rigid and flexible PVC will be done on quantitative level.

It will be described effect of "echo"-type of stabilization on the stability of PVC in the presence of plasticizers. If we would like to have stable material from PVC we should make stabilization of plasticizers as more reactive chemical compounds.

Keywords: aggregates; associates; basicity; plasticizers; segmental mobility of macromolecules; solubility; solution; solvent; specific and non-specific solvation; thermodynamic properties

Effect of Solvent

At PVC's degradation in solution, one of the basic reasons of change of the process kinetic parameters is the nucleophilic activation of a PVC's dehydrochlorination reaction. The process is described by E_2 mechanism.[1–3] Thus, there is a linear dependence between PVC's thermal dehydrochlorination rate and parameter of solvent's relative basicity B cm^{-1} (Fig. 1).[1–3] (The value B cm^{-1} is evaluated by shift of a characteristic band OH of phenol at $\lambda = 3600$ cm^{-1} in an IR-spectrum at interaction with the solvent[4]). It is essentially important that the rate of PVC's dehydrochlorination in the solvents with relative basicity $B > 50$ cm^{-1} was always above, than the rate of PVC's dehydrochlorination without the solvent, while when $B < 50$ cm^{-1}, PVC's desintegration rate was always less, than at it's destruction without the solvent. The revealed dependence $V_{HCl} = f\ (B)$ is described by the equation:

$$V^*_{HCl} = V_{HCl} + k(B - 50) \qquad (1)$$

An inhibition of PVC's disintegration in the solvents with basicity $B < 50$ cm^{-1} is very interesting and practically important phenomenon. It has received the name "solvatational" stabilization of PVC. Let's notice, however, that ignoring of the fact that PVC solutions even at low concentration (2 wt. %) do not represent solutions with isolated macromolecules but rather with structured systems, results that in a number of cases a deviation from linear dependence of PVC dehydrochlorination rate of the solvent basicity B cm^{-1} is observed. In particular, an abnormal behavior of PVC is observed at destruction in certain ester-type solvents (plasticizers) (Fig. 1, points 25–28), that apparently caused by structural changes of macromo-

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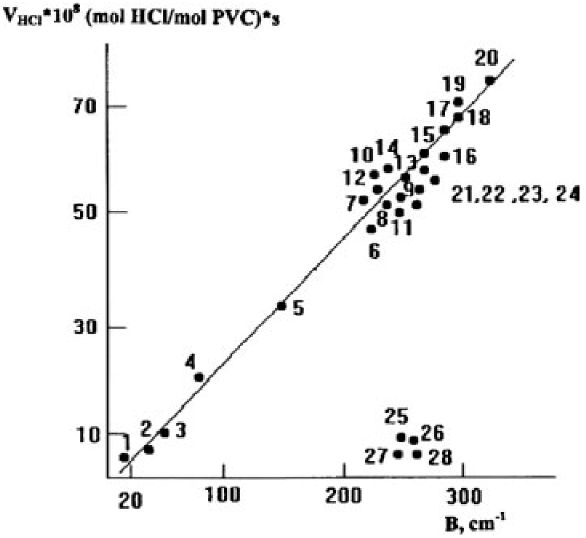

Figure 1.
Influence of the solvent's basicity on the rate of thermal dehydrichlorination in solution: 1 – *n*-dichlorobenzene, 2 – *o*-dichlorobenzene, 3 – naphthalene, 4 – nitrobenzene, 5 – acetophenone, 6 – benzonitrile, 7 – di-*n*-(chlorophenyl-chloropropyl) phosphate, 8 – triphenylphosphite, 9 –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

lecules. This was never before taken into account at work with PVC in solutions.

It was revealed quite unexpectedly that not only interaction ''polymer – solvent'', but also interaction ''polymer – polymer'' in solutions provide significant influence on rate of PVC disintegration. It's known that structure and properties of the appropriate structural levels depend from conformational and configurational nature of macromolecules, including a supermolecular structure of the polymer, which in turn determines all basic (both physical and chemical) characteristic of polymer.

''Polymer – polymer'' interaction results to formation of structures on a supermolecular level. In particular, as getting more concentrated the PVC-solvent system consistently passes a number of stages from isolated PVC macromolecules in a solution (infinitely diluted solution) to associates and aggregates from macromolecules in a solution. At the further increase of PVC concentration in a solution formation of spatial fluctuational net with structure similar to a structure of polymer in the block occurs.

When polymer's concentration in a solution increases, the rate of PVC's dehydrochlorination reaction changes as well, and various character of influence of the solvent on a PVC disintegration rate in solution is observed depending on a numerical value of basicity parameter B cm^{-1}.[5–10] If the relative basicity of employed solvents was $\mathrm{B} > 50\ \mathrm{cm}^{-1}$, the polymer's degradation rate decreases when its concentration increases. If a basicity of the employed solvents was $\mathrm{B} < 50\ \mathrm{cm}^{-1}$, the polymer's degradation rate increases with increased concentration of a polymer. In all cases the rate of HCl elimination from a polymer has a trend in a limit to reach values of PVC dehydrochlorination rate in absence of the solvent $V_{HCl}^{PVC} = 5 * 10^{-8}$(mol HCL/mol PVC)/s. (Fig. 2).

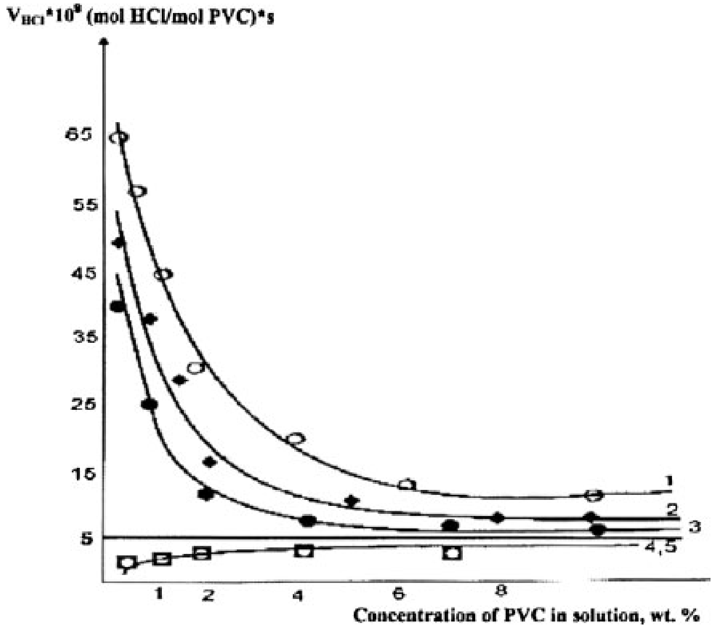

Figure 2.
A change of PVC's dehydrochlorination rate of its concentration in a solution: 1 – cyclohexanol, 2 – cyclohexanone, 3 – benzyl alcohol, 4 – 1, 2, 3 – trichloropropane, 5 – *o*-dichlorobenzene, 6 – no solvent; 423 K, under nitrogen.

Equation (1) turns into an Equation (2) if to take into account that the PVC's degradation rate is determined not only by parameter of relative basicity of the solvent 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 a solution $\Delta C = /C\text{-}C_0/$, where C_0 - concentration of a beginning of PVC macromolecules association in a solution):

$$V_{HCl} = V^0_{HCl} + A_1/(C + /\Delta C/ + d_1) \times (B - 50) \qquad (2)$$

Here factor $A_1 = (0.8 \pm 0.2)^* 10^{-9}$ (mol HCL/mol PVC)/s; d_1 - dimensionless factor reflecting interaction "polymer – solvent" ($d_1 = 0.5 \pm 0.25$). The deviation from the moment of a beginning of macromolecules association in a solution is taken on the absolute value, since it can change in both directions to more concentrated and more diluted solutions of a polymer.

Equation (2) well describes a change of PVC's thermal dehydrochlorination rate of its concentration in a solution in view of parameter of relative basicity of the solvent B, irrespective of the chosen solvent (Fig. 3).

The observable fundamental effect has the significant importance at production of plasticized (in particular, by esters) materials and products made from PVC. Despite of very high basicity of ester-type plasticizers ($B = 150\ cm^{-1}$) in an interval of PVC concentration in solutions more than 2%, a noticeable reduction of PVC degradation rate is observed (Fig. 1, curve, points 25–28), *i.e.* on – 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 formulations of plasticized materials from PVC with the very little contents of metal-containing stabilizers - HCl acceptors, or without their use at all.

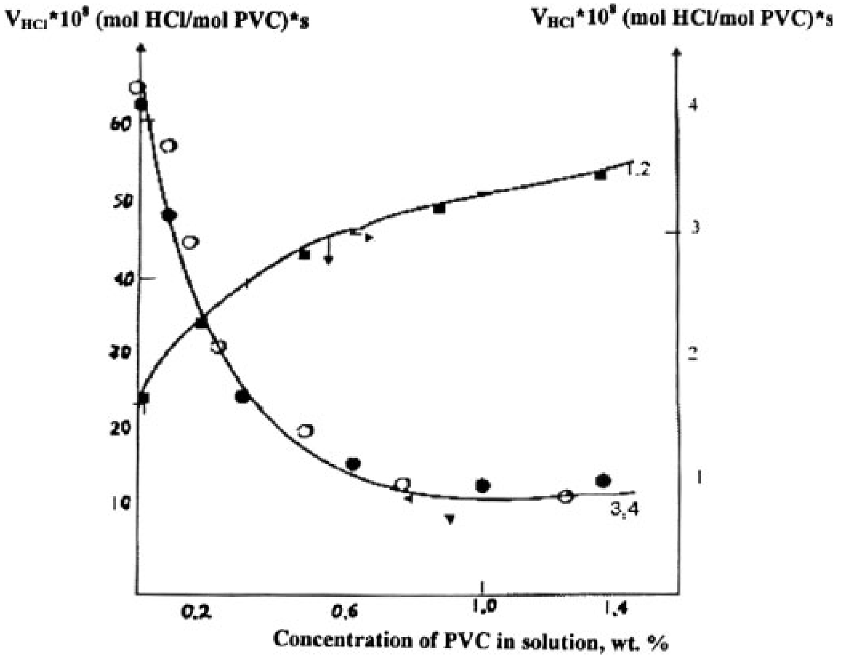

Figure 3.
A change of PVC's dehydrochlorination rate from its concentration in a solution: 1, 2 – 1, 2, 3 – trichloropropane, 3, 4 – cyclohehanol, 1, 3 – experimental data, 2, 4, - calculated data with equation (4) at $A_1 = 10^{-9}$ and $d_1 = 0.8$ and 0.7 correspondingly; 423 K, under nitrogen.

Temperature is very important on 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 retain at temperatures up to 430–445 K. In other words, PVC at plasticization, is capable to keep its structural individuality on a supermolecular level, which is formed during polymer's synthesis. Specifically in these conditions the ester-type plasticizer behaves not as a highly-basic solvent, but as a stabilizer at PVC's thermo-degradation due to formation of associates *etc*. This leads to a reduction of stabilizer's amount, extension of exploitation time of materials and products, *etc*.

It is necessary to note that the change of PVC's degradation rate at association of macromolecules is the general phenomenon and does not depend on how it was achieved. In particular, similar (as well as at concentration of PVC solutions (Fig. 2, 3)), character of change of PVC dehydrochlorination rate in a solution is observed, if the change of PVC's structural - physical condition in a solution is reached upon addition even chemically inert non-solvents, for example, hexane, decane, undecane, polyolefines, polyethylene wax, *etc*.[6,9–12] (Fig. 4). It is interesting to note that the degree of relative change of PVC disintegration rate under action of the second inert polymer (non-solvent) is much higher, than at concentration of a PVC solution, especially in case of use of the low-basic solvents (trichloropropane, dichlorobenzene – a result of formation of more dense formations on a supermolecular level, corresponding associates and aggregates, thanks to whom there is a significant change of a PVC destruction rate.

The more contents of non-solvent (including an inert polymer) in a blend

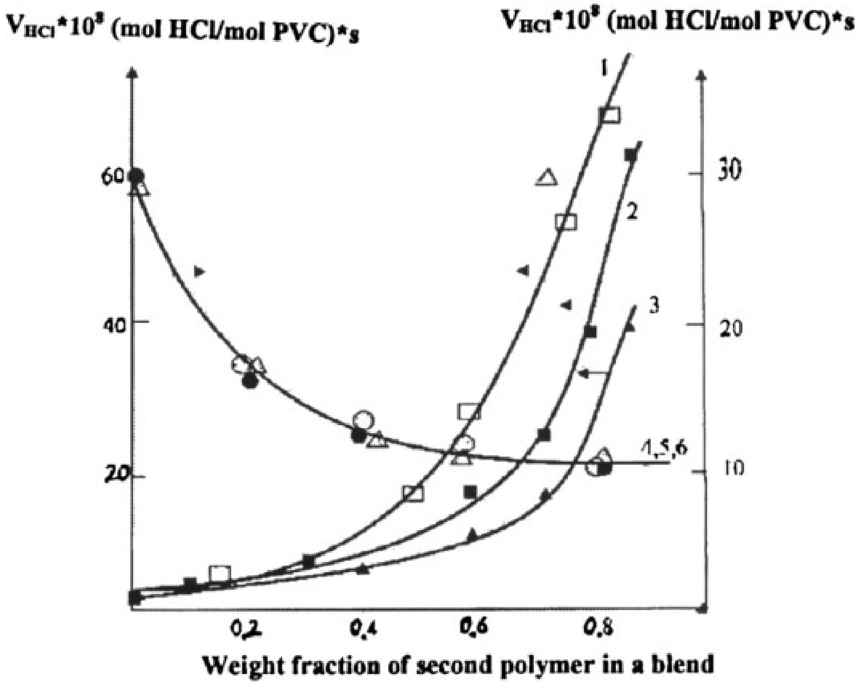

Figure 4.
A change of PVC thermodegradation rate of the contents of the secong inert polymer in solution of trichloropropane (1, 3), dichlorobenzene (2), and cyclohexanol (4–6) for blends of PVC with poly(ethylene) (1, 4), poly(propylene) (2, 5), and poly(isobutylene) (3, 6); 423 K, under nitrogen.

and lower thermodynamic compatibility of components in a solution, the more structural formation takes place in a solution, including one at the presence of a polymer blends (associates, aggregates). Formation of a fluctuational net with participation of macromolecules is probable. Since the reason of change of PVC thermal dehydrochlorination rate in case of its blends with chemically inert thermodynamically incompatible polymers is the same, as at concentration 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, at consideration of PVC thermal destruction a concentration of the second polymer in a blend with PVC, as well as a degree of its thermodynamic affinity to PVC have to be taken in account in addition to an influence of polymer's concentration in a solution, basicity of the solvent B cm^{-1} and forces of interaction "polymer – solvent". In view of these factors the Equation (2) turns into an Equation (3):

$$\begin{aligned} V_{HCl} = V^0_{HCl} & \\ &+ (A_1/c \\ &+ /(c + |\Delta c| + d_1 + \alpha n)) \\ &\times (B - 50) + A_1/B)(d_2\alpha^n/c) \qquad (3) \end{aligned}$$

where α - 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 and varying from zero (in a case of a complete thermodynamic compatibility of the components) up to certain value equals ~10 (in a case of a complete thermodynamic incompatibility of the polymers). Dimensionless coefficient d_2 reflects interaction of the second polymer with the solvent. At destruction of PVC in a blend with poly(ethylene) in a solution of dichlorobenzene, trichloropropane, and cyclohexanol it equals 2.5 ± 0.1.

Observable changes of PVC thermal disintegration rate under action of 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 from macromolecular globules of PVC with transformation to the structure, which it has in absence of the solvent. This evokes unexpected effect of "the solvent action" (a delay or an acceleration depending on the solvent's basicity B cm^{-1}) in relation to PVC's thermal disintegration. The solvent's displacement, which accelerates PVC's disintegration ($B > 50$ cm^{-1}), results to easing of its interaction with PVC and leads to a delay of process of HCl elimination from macromolecules, *i.e.* to stabilization. This occurs both in a case of concentration of PVC's solutions, and in case of addition of second polymer, which is thermodynamically incompatible with PVC. In the solvents slowing down PVC's disintegration ($B < 50$ cm^{-1}) by virtue of low nucleophilicity, an effect of the solvent displacement and the easing of its influence on PVC results in an opposite result – an increase of HCl elimination rate from PVC upon of increase of its concentration in a solution or at use of chemically inert non-solvent. It is obvious that irrespective of the fact how to make changes in PVC's structure in a solution – by increase of its concentration in a solution or by addition of second thermodynamically incompatible with PVC chemically inert non-solvent - the varying structural - physical condition 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 system polymer - solvent, and previously unknown phenomena can be classified as structural - physical stabilization (in case of a reduction of gross - rate of PVC disintegration in highly-basic solvents at $B > 50$ cm^{-1}) and, respectively, structural - physical antistabilization (in case of increase of gross - rate of PVC disintegration in low-basic solvents with $B < 50$ cm^{-1}).

"Echo" - Stabilization of PVC

At last, it is necessary to specify to one more appreciable achievement in the field of aging and stabilization of PVC in a solution. In real conditions the basic reason of the sharp accelerated aging of plasticized materials and products is the oxidation of the solvent by oxygen of air (Fig. 5, curve 3).

$$RO_2^\bullet + RH \xrightarrow{K_2} ROOH + R^\bullet$$

$$ROOH \xrightarrow{K_3} RO^\bullet + HO^\bullet$$

$$RO_2^\bullet + RO_2^\bullet \xrightarrow{K_6} \text{inactive products}$$

Peroxides, formed at oxidation of ester-type plasticizers, initiate disintegration of macromolecules. In these conditions the rate of PVC destruction can increase in two and more orders of magnitude and is determined by oxidizing stability of the solvent to oxygen - parameter $K_{ef} = K_2{}^{*}K_3^{0.5*}K_6^{-0.5}$. Then higher an oxidizing stability of the solvent (in particular, ester-type plasticizer), at which's presence a thermooxidative disintegration of PVC occurs, then lower its degradation rate and longer an exploitation time of semi-rigid and flexible materials on a basis of PVC.[13–18] An inhibition of process of the solvent's oxidation (including plasticizers) due to of incorporation of stabilizers – antioxidants or their synergistic compositions slows a thermo-oxidative disintegration of PVC in a solution (Fig. 5, curve 5).

At effective inhibition of the ester-type plasticizers' oxidation by oxygen of air the rate of PVC thermo-oxidative destruction in their concentrated solutions is getting closer to the rate of polymer's disintegration, what is characteristic for its thermal destruction at plasticizer's (solvent's) presence, *i.e.* slower, than PVC's desintegration without a solvent. This occurs due to a structural - physical stabilization. In these cases an inhibition of reaction of the

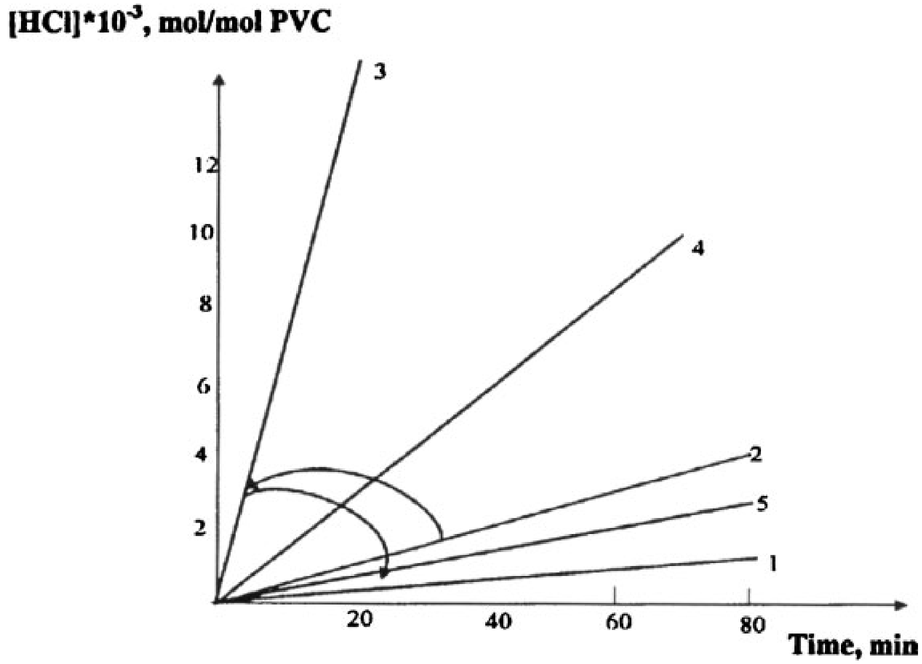

Figure 5.
"Echo"-stabilization of PVC. Elimination of HCl during thermo- (argon) (1, 2) and thermo-oxidative (air) (3–5) destruction of PVC in solution of dioctyl sebacinate: 1–4 unstabilized PVC, 5 – PVC, stabilized with diphenylpropane (0.02 wt. %) – "echo" stabilization; 2, 4 – PVC with no solvent; 448 K.

solvent's oxidation at use of "echo" – type stabilizers - antioxidants causes PVC's stabilization (Fig. 5, curve 5). This fundamental phenomenon of PVC's stabilization in a solution at its thermo-oxidative destruction has received the name of an "echo" - stabilization of PVC.[2,15,16]

Tasks for a Future

Thus, a creation of high-quality and economic semi-rigid and flexible materials and products on a basis of PVC, including ones where solvents are employed, require the specific approach, essentially differing from principles of manufacture of rigid materials and products from PVC. In particular, account and use of the fundamental phenomena: 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's manufacture and processing in the beginning of XXI century, obviously they are following:

Manufacture of an industrial PVC, not containing of labile groups in a backbone. It will provide drastic increase of an intrinsic stability of polymeric products, possibility of PVC processing with the minimal contents or in total absence of stabilizers and other chemicals - additives and opportunity of creation of materials and products on a PVC basis with the essentially increased service life-time;

Wide use of the latest achievements in area of destruction and stabilization of PVC, both at presence and absence the solvents. First of all, 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 minimal contents of chemicals - additives and increased life-time of their service at exploitation in natural and special conditions;

The use of non-toxic, non-flammable products which do not emit toxic and other poison gaseous and liquid products at elevated temperature at manufacture of materials and products from PVC;

Complete elimination of all toxic and even low-toxic (particularly compounds based on Pb, Cd, Ba, *etc*.) chemicals – additives from all formulations;

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’’ may be expected, which undoubtedly will be presented us by this outstanding polymer - puzzle, a plastic’s ‘‘working horse’’ for many decades. Certainly it will give new stimulus in development of scientific bases and practical development with opening of new pathways, conducting to essential delay of PVC’s ageing in natural and special conditions at reduction of amounts of the appropriate chemicals - additives, down to their complete elimination.[18–25]

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