Influence of metal stearates on thermal stability of poly(vinyl chloride)
I. Calcium stearate

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The mechanism of stabilizing effect of calcium stearate in thermal dehydrochlorination of poly(vinyl chloride) was studied. Nonstabilized as well as stabilized samples of poly(vinyl chloride) thermally stressed were analyzed by infrared spectroscopy and by determining viscosimetrically their relative molecular mass. A reaction scheme of the processes proceeding in the course of dehydrochlorination was suggested. By comparing the experimental and theoretical kinetic curves, the rate constants of individual kinetic steps of the reaction scheme were determined.

Исследовался механизм стабилизирующего действия стеарата кальция при термическом дегидрохлорировании поливинилхлорида. Нестабилизированные и стабилизированные образцы поливинилхлорида, термически доведенные до различной степени дегидрохлорирования анализировались с помощью инфракрасной спектроскопии, а также вискозиметрически была установлена их относительная молярная масса. На основании полученных экспериментальных результатов предложена реакционная схема процессов, протекающих при дегидрохлорировании. Исходя из сравнения экспериментальных и теоретических кинетических кривых были определены константы скоростей отдельных кинетических стадий реакционной схемы.

Thermal stabilizers are basic additives to poly(vinyl chloride) (PVC) in its technological processing. The role of different types of stabilizers is to bond the eliminated hydrogen chloride [1], to replace the labile chlorine atoms in PVC chain and thus prevent further dehydrochlorination [2], to reduce the length of the arising polyene sequences [3], to preserve colour of the polymer [4—6] or to hinder from the catalytic effect of products of stabilizer decay on dehydrochlorination [7].

At present, the carboxylates of metals of the second group of the periodic system such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, and Ba^{2+} salts of phthalic, sebacic, lauric, stearic and other acids [8—10] come to the fore in the wide series of thermal PVC stabilizers. The synergic mixtures of metal soaps have most frequently been used because they provide for satisfactory thermal and colour properties of PVC, are inexpensive and owing to low toxicity some of them may be used in PVC mixtures for food industry [2]. In the mixtures, calcium stearate frequently occurs; therefore, not only the studies concerned with thermal dehydrochlorination of the PVC stabilized solely by this stabilizer can be encountered [10], but also the studies dedicated to its reactivity with PVC model compounds [11—13]. Nonetheless, despite the extensive study, the kinetic parameters of reactions occurring in the mixture PVC—calcium stearate have not been quantitatively evaluated.

In this study the kinetics of thermal dehydrochlorination of the PVC stabilized by calcium stearate is experimentally investigated and a reaction scheme of the process is proposed. By comparing the experimental and theoretical kinetic curves, the rate constants of individual kinetic steps of the reaction scheme are determined. On the basis of the obtained results the stabilizing effect of calcium stearate in PVC mixtures is discussed.

Experimental

Chemicals

Suspension poly(vinyl chloride) Slovinyl S-621 (Czechoslovakia) was used without purification. The relative molecular mass determined viscosimetrically was 53 400.

Calcium stearate was prepared by precipitating stearic acid with calcium hydroxide. The purity of the product determined by elemental analysis was 99.9 %, m. p. = 140—143 °C.

Montan wax (Wachs E, BASF) used in the amount of 0.5 mass % as lubricant. Anal. grade calcium chloride. Anal. grade stearic acid, m. p. = 69—70 °C, b.p. = 183—184 °C.

Measuring methods

PVC films were prepared from given amounts of PVC, calcium stearate and wax E by 3 min calendering at 180 °C. The width of films was up to 100 μm.

The kinetics of dehydrochlorination was investigated by the continuous potentiometric method [14]. The measurements were carried out in nitrogen atmosphere and in air at 180 °C.

For measuring the infrared spectra the films were pressed to a width of about 60 μm at 180 °C under the pressure of 30 MPa. The infrared spectra were measured by Specord IR 75 spectrometer (Zeiss, Jena).

The viscosities of solutions in cyclohexanone of 2 g dm^{-3} concentration were measured at 25 °C by using the Ubbelohde dilution viscosimeter.

Results and discussion

The relationships between the dehydrochlorination conversion and time for a set of PVC mixtures containing 0—5.0 mass % of calcium stearate and dehydrochlorinated in nitrogen and air are shown in Figs. 1 and 2. The dehydrochlorination conversion x is the ratio of the moles of hydrogen chloride evolved from the sample to moles of monomer links in the sample. Fig. 3

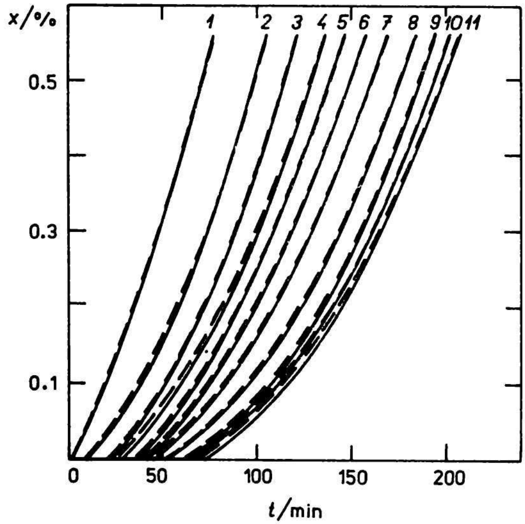


Fig. 1. Kinetic curves of thermal dehydrochlorination of the PVC stabilized by calcium stearate in nitrogen atmosphere at 180 °C. Mass fraction of calcium stearate in mixture: *1.* 0; *2.* 0.005; *3.* 0.01; *4.* 0.015; *5.* 0.02; *6.* 0.025; *7.* 0.03; *8.* 0.035; *9.* 0.04; *10.* 0.045; *11.* 0.05.
——— Experimental kinetic curve;
— — — calculated kinetic curve.

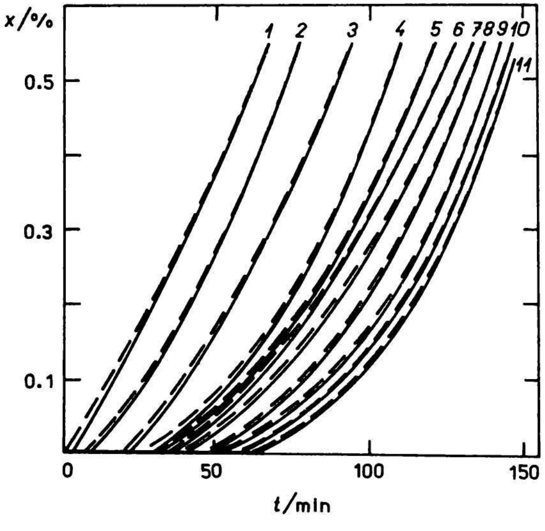


Fig. 2. Kinetic curves of thermal dehydrochlorination of the PVC stabilized by calcium stearate in air at 180 °C. Mass fraction of calcium stearate in mixture: *1.* 0; *2.* 0.005; *3.* 0.01; *4.* 0.015; *5.* 0.02; *6.* 0.025; *7.* 0.03; *8.* 0.035; *9.* 0.04; *10.* 0.045; *11.* 0.05.
——— Experimental kinetic curve;
— — — calculated kinetic curve.

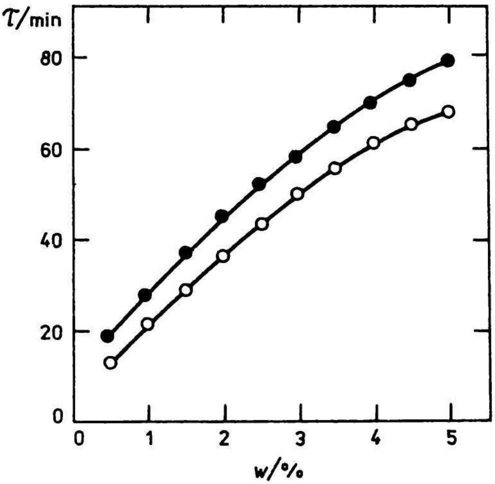
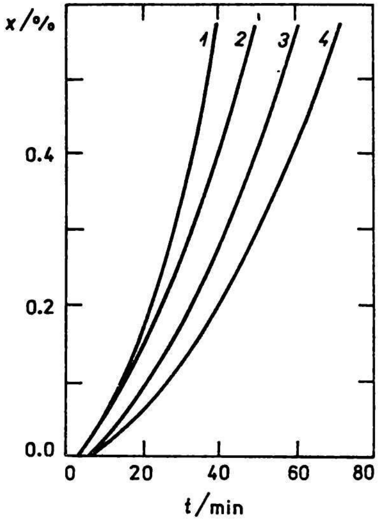


Fig. 3. Dependence of the time of thermal stability τ on the mass fraction of calcium stearate in nitrogen (●) and in air (○).

represents the dependence of the time of thermal stability τ on the content of calcium stearate in the mixture (τ is the time interval in which no hydrogen chloride evolved from the sample is indicated). It results from this figure that τ increases not linearly with the mass fraction of calcium stearate and is lower in air. The times of thermal stability are approximately 1.5—2 times lower when compared with those for the stabilizers based on tin or lead; this indicates that calcium stearate is a less efficient thermal stabilizer. This conclusion is consistent with the published data [15, 16]. The effective rate constants of dehydrochlorination after the time of thermal stability were obtained from the slope of linear section of the curves $x = f(t)$ for time $t > \tau$. Their values almost linearly increase in nitrogen atmosphere from $5.2 \times 10^{-5}\,\text{min}^{-1}$ for PVC containing 0.5 mass % of calcium stearate to $5.9 \times 10^{-5}\,\text{min}^{-1}$ for PVC containing 5.0 mass % of the stabilizer and in air from $8.0 \times 10^{-5}\,\text{min}^{-1}$ to $8.7 \times 10^{-5}\,\text{min}^{-1}$ These values indicate that some of the decomposition products of the stabilizer slightly catalyzes the dehydrochlorination of PVC. The products of the reaction between stabilizer and hydrogen chloride split off during dehydrochlorination are calcium chloride and stearic acid. For examining the influence of these products on further course of dehydrochlorination, we prepared PVC mixtures containing an addition of calcium chloride and an addition of stearic acid, and investigated the kinetics of dehydrochlorination of these mixtures in nitrogen atmosphere and in air. Kinetic curves in Fig. 4 show that stearic acid slightly accelerates the dehydrochlorination of PVC when compared with nonstabilized PVC (Figs. 1 and 2) while the presence of calcium chloride in the quantity of 1—3 mass % practically does not affect the course of dehydrochlorination.

In Fig. 5 the dependence of the relative molecular mass M_r on the time of thermal stress is given for a sample containing 4 mass % of calcium stearate (the

Fig. 4. Influence of stearic acid and calcium chloride on dehydrochlorination of PVC: *1*. PVC + stearic acid ($w = 0.03$); *2*. PVC + stearic acid ($w = 0.02$); *3*. PVC + stearic acid ($w = 0.01$); *4*. PVC + $CaCl_2$ ($w = 0.01$; 0.02; 0.03).



values of constants in the Mark—Houwink equation are: $K = 2.04 \times \times 10^{-4}\,dm^3\,g^{-1}$, $a = 0.56$ [17]). It is obvious from this figure that M_r does not change for 40 min while in the case of pure polymer it increases from the beginning of thermal stress. For the times of degradation over 180 min an insoluble fraction can be observed, which points to PVC crosslinking. The time corresponding to the bending in the relationship $M_r = f(t)$ is close to the time of thermal stability.

For completing the information on the behaviour of the stabilizer in the polymer, the infrared spectroscopy was used. The dependence of absorbance of

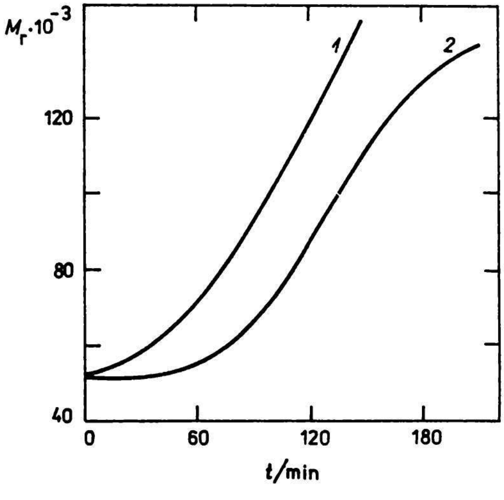


Fig. 5. Dependence of the relative molecular mass of PVC on the time of thermal dehydrochlorination in nitrogen atmosphere: *1*. pure PVC; *2*. PVC with 4 mass % of calcium stearate.

the chosen absorption bands on the time of thermal stress is given in Fig. 6. In line with literature [10], the pair of bands at $\tilde{\nu} = 1540$ and $1580\,\mathrm{cm^{-1}}$ was assigned to antisymmetrical stretching vibration of the stearate anion (COO^-). It is evident from the figure that the absorbance of the band at $\tilde{\nu} = 1580\,\mathrm{cm^{-1}}$ rapidly decreases after initial increase, while the absorbance of the band at $\tilde{\nu} = 1540\,\mathrm{cm^{-1}}$ smoothly decreases with the time of destruction. A partial replacement of the stearate anion by the chloride anion is likely to correspond to the absorbance maximum at $\tilde{\nu} = 1580\,\mathrm{cm^{-1}}$, which points to a successive two-step mechanism of the reaction of calcium stearate with the hydrogen chloride split off from PVC. This is in agreement with the considerations presented in paper [10]. It follows from the analysis of the bands at $\tilde{\nu} = 1540\,\mathrm{cm^{-1}}$ and $1580\,\mathrm{cm^{-1}}$ that the stabilizer is not completely used up even in long-lasting thermal destruction of PVC. The bands at $\tilde{\nu} = 1700\,\mathrm{cm^{-1}}$ and $1750\,\mathrm{cm^{-1}}$ are assigned to stretching vibrations of the monomeric and dimeric form of stearic acid. The dependence of absorbance of the band at $\tilde{\nu} = 1700\,\mathrm{cm^{-1}}$ on time exhibits a maximum, which indicates a decrease in the amount of stearic acid during dehydrochlorination. That may be due to exudation of this acid [18] or to the reverse reaction of stearic acid with the arisen calcium chloride.

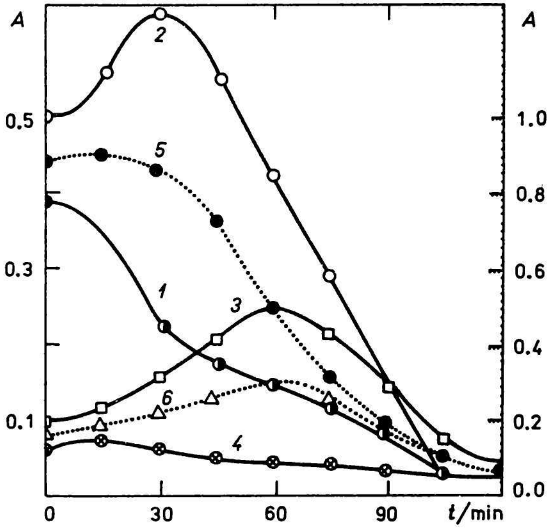


Fig. 6. Dependence of absorbance of vibration bands on the time of thermal dehydrochlorination for the mixture PVC + 3 mass % of calcium stearate in nitrogen atmosphere: *1.* $\tilde{\nu} = 1540\,\mathrm{cm^{-1}}$; *2.* $\tilde{\nu} = 1580\,\mathrm{cm^{-1}}$ (antisymmetrical vibration of the stearate anion); *3.* $\tilde{\nu} = 1700\,\mathrm{cm^{-1}}$; *4.* $\tilde{\nu} = 1750\,\mathrm{cm^{-1}}$ (vibration of the monomeric and dimeric form of stearic acid); *5.* sum of the vibrations of the stearate anion (curves *1* and *2*); *6.* sum of the vibrations of stearic acid (curves *3* and *4*).

The obtained results as well as the published information led us to propose the following scheme of thermal dehydrochlorination of PVC stabilized by calcium stearate:

1. Dehydrochlorination of nonstabilized PVC

$$\mathrm{PVC} \xrightarrow{k_1} \mathrm{dePVC} + \mathrm{HCl}$$

where dePVC stands for dehydrochlorinated PVC.

2. Reaction of calcium stearate with hydrogen chloride in two steps

$$\mathrm{CaSt_2} + \mathrm{HCl} \xrightarrow{k_2} \mathrm{CaClSt} + \mathrm{HSt}$$

$$\mathrm{CaClSt} + \mathrm{HCl} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{CaCl_2} + \mathrm{HSt}$$

where $\mathrm{CaSt_2}$, CaClSt, and HSt stand for $\mathrm{Ca(C_{17}H_{35}COO)_2}$, $\mathrm{CaClC_{17}H_{35}COO}$, and $\mathrm{C_{17}H_{35}COOH}$, respectively.

3. Catalysis of PVC dehydrochlorination by stearic acid

$$\mathrm{PVC} + \mathrm{HSt} \xrightarrow{k_5} \mathrm{dePVC}$$

In this mechanism the catalytic effect of hydrogen chloride on PVC dehydrochlorination is not allowed for because hydrogen chloride accelerates the dehydrochlorination only from a certain critical width of film (about 500 µm) [19] which is much larger than the width of the samples prepared here. The proposed mechanism can be described by a system of four independent kinetic equations. The composition of mixtures is expressed in terms of relative mole fractions as the ratio of moles of the component to moles of monomer links in PVC sample. Individual components are denoted as follows: x_1 — calculated dehydrochlorination conversion, x_2 — HCl in polymer, x_3 — double bonds in polymer, x_4 — $\mathrm{CaSt_2}$, x_5 — HSt, x_6 — CaClSt, x_7 — $\mathrm{CaCl_2}$. We assume that HCl is evolved from the sample after the concentration of HCl in polymer has reached a certain critical value to which the critical relative mole fraction x_c corresponds. Hence, the first two kinetic equations obtain the following forms. Provided $x_2 < x_c$

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = 0\,; \quad \frac{\mathrm{d}x_2}{\mathrm{d}t} = (k_1 + k_5 x_5)(1 - x_3) - k_2 x_2 x_4 - k_3 x_2 x_6 + k_4 x_5 x_7$$

Provided $x_2 = x_c$

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = (k_1 + k_5 x_5)(1 - x_3) - k_2 x_2 x_4 - k_3 x_2 x_6 + k_4 x_5 x_7\,; \quad \frac{\mathrm{d}x_2}{\mathrm{d}t} = 0$$

The change in relative mole fractions x_3 and x_4 in time can be expressed by the kinetic equations

$$\frac{\mathrm{d}x_3}{\mathrm{d}t} = (k_1 + k_5 x_5)(1 - x_3)$$

$$\frac{dx_4}{dt} = -k_2 x_2 x_4$$

The relative mole fractions x_5, x_6, and x_7 can be expressed by material balances

$$x_5 = x_3 - x_1 - x_2 - a$$
$$x_6 = 2(x_4^\circ - x_4) - x_5$$
$$x_7 = x_4^\circ - x_4 - x_6$$

where x_4° is the initial content of $CaSt_2$ in the mixture and a is the amount of HCl which escapes from the sample after calendering.

This system of kinetic equations was solved by the fourth-order Runge—Kutta method [20]. The values of rate constants for particular reaction steps were obtained from the curves $x = f(t)$ by minimizing the sum of squared differences between the experimental and calculated conversions for the whole system of eleven curves simultaneously [21]. We took into account in the calculations that the samples were calendered for 3 min before their destruction was investigated. Of course, the destruction of PVC also takes place during calendering, but the arisen hydrogen chloride is not registered and its part remaining in the polymer escapes from it after a certain time. Then, at the time $t = 0$, $x_1 = 0$ and $x_2 = 0$ and the other relative mole fractions are equal to the values calculated for 3 min thermal stress of the original mixture.

The calculated values of relative mole fractions of the components in the reaction system as functions of time are represented in Fig. 7 for the sample with initial 3 mass % content of calcium stearate subjected to dehydrochlorination

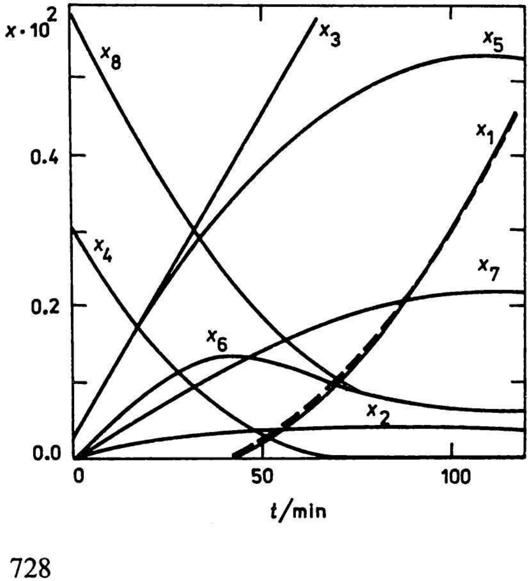


Fig. 7. Calculated dependences of relative mole fractions in mixture ($w = 0.03$) on time for dehydrochlorination in air: x_1 — dehydrochlorination conversion, ——— experimental kinetic curve, — — — calculated kinetic curve; x_2 — HCl in polymer; x_3 — double bonds in polymer; x_4 — $CaSt_2$; x_5 — HSt; x_6 — CaClSt; x_7 — $CaCl_2$; x_8 — $2x_4 + x_6$ (Ca—St bonds).

Table 1

Rate constants of the reactions taking place during thermal stress of the PVC stabilized by calcium stearate

Rate constant	Atmosphere	
	Nitrogen	Air
k_1/min^{-1}	5.8×10^{-5}	8.4×10^{-5}
k_2/min^{-1}	240	232
k_3/min^{-1}	128	69
k_4/min^{-1}	4.3	2.3
k_5/min^{-1}	8.9×10^{-5}	2.6×10^{-5}
x_c	1.8×10^{-4}	3.9×10^{-4}

in air. The reasonability of the proposed mechanism and the successfulness of the method of calculation are documented in Figs. 1 and 2 where the experimental and calculated kinetic curves are compared. The rate constants of the proposed reaction scheme of dehydrochlorination in nitrogen and air are given in Table 1. It can be seen that the main function of calcium stearate in thermal stress of PVC is its reaction with the liberated hydrogen chloride which proceeds in two steps. It can be deduced from the values of rate constants k_2 and k_3 that the dehydrochlorination atmosphere does not have practically any influence on the rate constants of the reaction of calcium stearate with hydrogen chloride. In accordance with experiments, the calculated value of k_5 shows that the accelerating effect of stearic acid on PVC dehydrochlorination is small.

The values of calculated rate constants can be verified by comparing them with the values obtained by experiment. A good agreement has been obtained by comparing the calculated rate constants k_1 and k_5 with the rate constants obtained by evaluation of the kinetic curves of PVC dehydrochlorination in the absence and in the presence of stearic acid. Curve *5* in Fig. 6 which corresponds to the sum of absorbances of the carboxylate anion (sum of curves *1* and *2*) and curve *8* in Fig. 7 which represents the dependence of number of the Ca—St bonds on time exhibit analogous course. The curves for stearic acid, *i.e.* curve *6* in Fig. 6 and curve *5* in Fig. 7 are also similar. The results of calculations enable us to investigate the course of consumption of the stabilizer (Fig. 7, curve *4*). In Fig. 8 the consumption of calcium stearate during calendering is represented. As it is evident, decrease in the content of calcium stearate in the sample is 4—10 %. At the time $t = \tau$ about 90 % of calcium stearate was consumed in dehydrochlorination in both atmospheres in all samples. Furthermore, it results from these calculations that the time of thermal stability and the time necessary

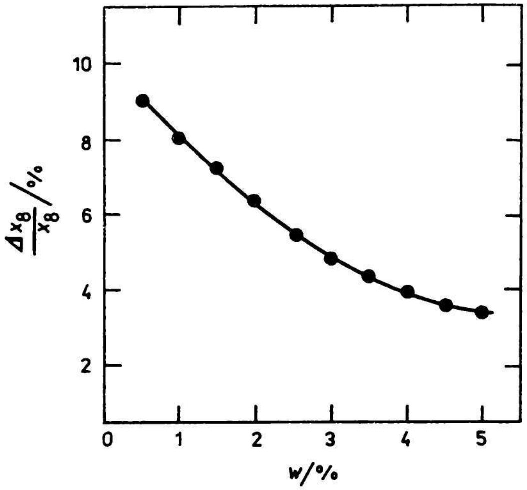


Fig. 8. Decrease in content of stabilizer during calendering as a function of the content of stabilizer in PVC mixture.

for reaching the maximum value of the relative mole fraction of CaClSt are approximately equal.

The effect of calcium stearate in mixtures with PVC can be summarized as follows: Calcium stearate has a low stabilizing effect in thermal stress of PVC. It functions evidently only as a scavenger of hydrogen chloride with which it reacts in two steps. Stearic acid which is a product of these reactions slightly accelerates further elimination of hydrogen chloride from PVC while the other reaction product ($CaCl_2$) has no influence on the dehydrochlorination. The evolution of hydrogen chloride proceeds more rapidly in air, but the atmosphere of dehydrochlorination does not affect the interaction of calcium stearate with HCl. During thermal stress, the polymer continuously changes its colour from white to dark-brown. The good consistence of the experimental and calculated kinetic curves points to the reasonability of the proposed mechanism of thermal dehydrochlorination of the PVC stabilized by calcium stearate.

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