Influence of metal stearates on thermal stability of poly(vinyl chloride)
II. Magnesium stearate

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Influence of magnesium stearate on the kinetics of thermal dehydro-
chlorination of poly(vinyl chloride) is studied. The samples thermally
stressed are analyzed by infrared spectroscopy and by viscosimetric deter-
mination of their relative molecular mass. A reaction scheme of the pro-
cesses proceeding in the course of dehydrochlorination is suggested and the
rate constants of individual kinetic steps are determined by comparing the
experimental and theoretical kinetic curves. On the basis of the results
obtained the mechanism of the stabilizing effect of magnesium stearate is
discussed.

An inherent property of poly(vinyl chloride) (PVC) is its low thermal stabili-
ty. For this reason, thermal stabilizers are the basic additives in PVC technologi-
cal processing. The stabilizers based on lead and tin are extensively used [1—6],
but, due to their price as well as toxicity in the case of lead compounds, great
effort is being made to substitute this class of stabilizers by the stabilizer
mixtures of soaps of metals from the second group of the periodic system.
Before analyzing the mechanism of action of polycomponent stabilizer mix-
tures, it is advisable to study the influence of individual components on PVC
thermal stability.

In our previous paper the influence of calcium stearate on PVC thermal
dehydrochlorination has been studied. The rate constants of the reactions
occurring in the polymer blend have been obtained. In order to increase the
reliability, the rate constants have been determined from a set of eleven experi-
mental kinetic runs by their simultaneous comparison with the theoretical
values [7]. In continuation, this paper is devoted to the study of the influence of
magnesium stearate on PVC thermal dehydrochlorination.

Experimental

Suspension poly(vinyl chloride) Slovinyl S-621 and montan wax have been charac-
terized in Ref. [7].

Magnesium stearate, $M_r = 591.3$, m.p. = 136—138 °C, purity of the stabilizer was 99 %.

Anal. grade cyclohexanone was used, anal. grade magnesium chloride $MgCl_2$ $6H_2O$ was dehydrated by heating to constant mass.

Preparation of PVC films, determination of the HCl evolved from PVC samples, measurement of infrared spectra and viscosimetric determination of relative molecular mass of the polymer have been described in Ref. [7].

Results and discussion

The kinetic curves for a set of PVC blends with relative mole fractions of magnesium stearate $0—5.593 \times 10^{-3}$ dehydrochlorinated in nitrogen and in air at 180 °C are shown in Figs. 1 and 2 (the relative mole fraction is defined as the ratio of moles of the component to the moles of monomeric links in PVC sample). Fig. 3 represents the dependence of the time of thermal stability τ on the content of magnesium stearate in the blend. As it can be seen, τ increases nonlinearly with the relative mole fraction of magnesium stearate and is lower in air. For the time $t > \tau$, the effective rate constants of dehydrochlorination have been determined as the slopes of the linear parts of kinetic runs. Their values are $(5.1—5.9) \times 10^{-5}$ min^{-1} for the nitrogen atmosphere and $(6.1—8.0) \times 10^{-5}$ min^{-1} for the dehydrochlorination under air and they document the well-known fact that PVC loses HCl more rapidly in air than in nitrogen. The effective rate constants of stabilized samples are less than those for the non-
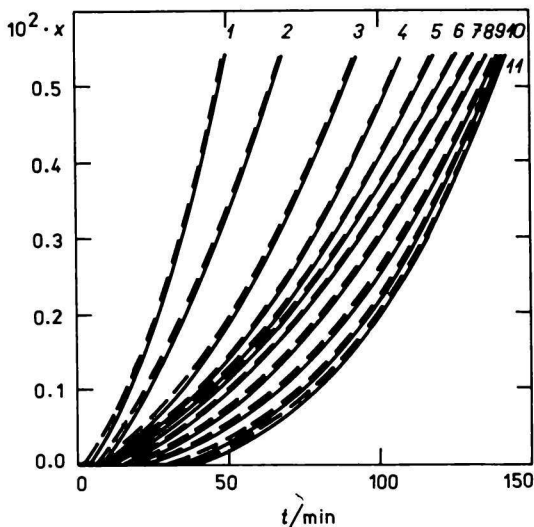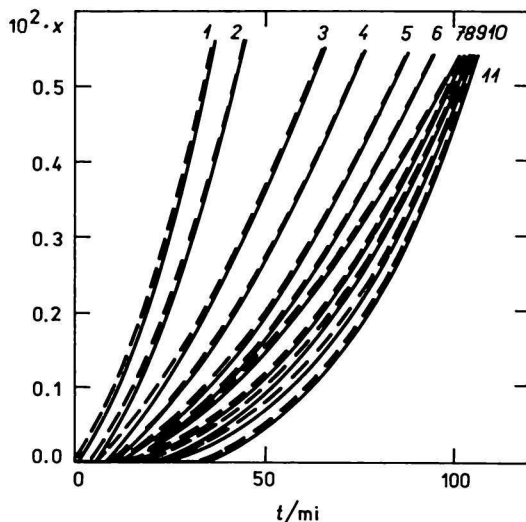

Fig. 1. Kinetic curves of thermal dehydrochlorination (conversion x) of the PVC stabilized by magnesium stearate in nitrogen atmosphere at 180 °C. Relative mole fraction of magnesium stearate in the blend (x 10^3): 1. nonstabilized PVC, 2. 0.539, 3. 1.073, 4. 1.618, 5. 2.168, 6. 2.724, 7. 3.286, 8. 3.854, 9. 4.427, 10. 5.007, 11. 5.593. — Experimental kinetic curve; --- calculated kinetic curve.

stabilized PVC. With increasing the content of magnesium stearate the effective rate constants increase, which suggests that the products of stabilizer decay catalyze the splitting-off of HCl. In the course of the reaction of magnesium stearate with eliminated HCl, stearic acid and magnesium chloride are formed. In Ref. [7] it has been shown that stearic acid slightly catalyzes the PVC dehydrochlorination. The films containing magnesium chloride have been prepared in order to examine its influence on dehydrochlorination. No influence
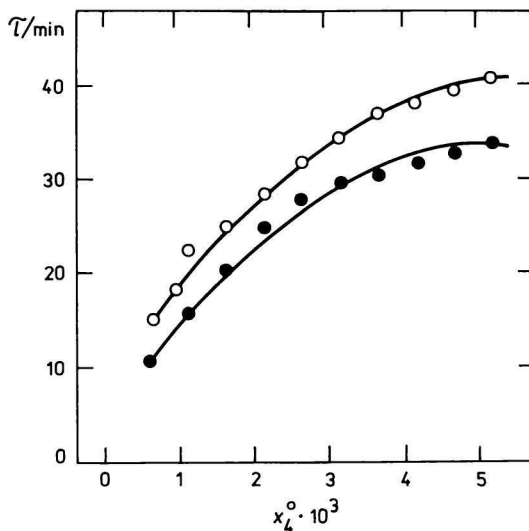
Fig. 3. Dependence of the time of thermal stability τ on the relative mole fraction of magnesium stearate for the atmosphere of nitrogen (O) and air (●).
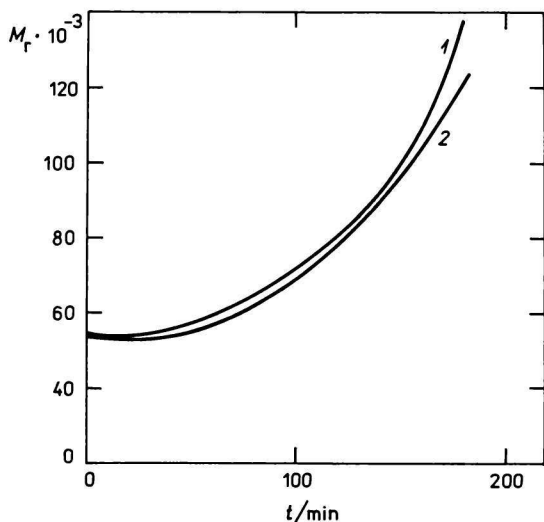
Fig. 4. Dependence of relative molecular mass of PVC on the time of thermal stress in nitrogen atmosphere at 180 °C. *1.* Nonstabilized PVC; *2.* stabilized PVC.

has been observed when the relative mole fraction of $MgCl_2$ was up to 2.0×10^{-2}.

Fig. 4 shows the dependence of relative molecular mass of the polymer M_r on the time of thermal stress for the sample with the initial relative mole fraction of magnesium stearate 3.29×10^{-3} For comparison, also the dependence of M_r for nonstabilized PVC degraded under nitrogen is drawn. At the beginning of thermal stress, the relative molecular mass of the stabilized polymer does not change. After a certain time, M_r increases, which points out the crosslinking of the polymer; the increase of relative molecular mass is in correlation with the time of thermal stability. This indicates that an important role of magnesium stearate (if not the principal one) is to bond the HCl split off from PVC since HCl supports the crosslinking of PVC [8].

Changes of magnesium stearate in the blend during dehydrochlorination were studied by infrared spectroscopy. Fig. 5 represents the dependence of the absorbance of individual bands for the blend with initial relative mole fraction of magnesium stearate 3.29×10^{-3} The most significant changes can be observed in the bands at $\tilde{v} = 1540$ and 1580 cm^{-1} By the analogy with the bands of calcium stearate [9], we assign these bands to antisymmetric vibrations of carboxylate anion. The curve for $\tilde{v} = 1580$ cm^{-1} seems to be the superposition of two curves corresponding to the two-step reaction of magnesium stearate with HCl, where the rate of the first step is considerably higher than the rate of the other one. The band at $\tilde{v} = 1540$ cm^{-1} completely disappears after 60 min of thermal stress. The band at $\tilde{v} = 1580$ cm^{-1} indicates that the stabilizer is not completely used up even after quite a great time of thermal stress. The bands at $\tilde{v} = 1700$ and 1750 cm^{-1} are assigned to stretching vibrations of the monomeric

Fig. 5. Dependence of absorbance of vibration bands on the time of thermal stress for the PVC stabilized in nitrogen atmosphere ($x_q^0 = 3.29 \times 10^{-3}$). $\bar{v}$/cm^{-1}: 1. 1540, 2. 1580, 3. 1700, 4. 1750.
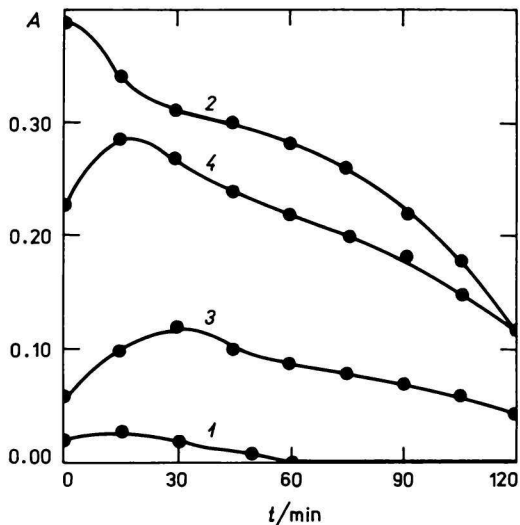
and dimeric form of stearic acid [9]. Both curves exhibit a maximum. The decrease of the absorbance after reaching the maximum may be due to exudation of stearic acid from the sample [5].

Our results as well as the published data lead to the suggestion of the following reaction scheme of thermal dehydrochlorination of PVC stabilized by magnesium stearate:

1. Dehydrochlorination of PVC

$$PVC \xrightarrow{k_1} dePVC + HCl$$
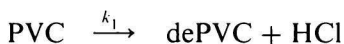
where dePVC means dehydrochlorinated PVC.

2. Reaction of magnesium stearate with HCl in two reaction steps

$$MgSt_2 + HCl \xrightarrow{k_2} MgClSt + HSt$$

$$MgClSt + HCl \xrightarrow{k_3} MgCl_2 + HSt$$
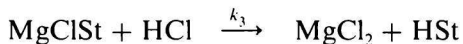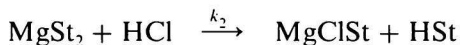
where $MgSt_2$ is $Mg(C_{17}H_{35}COO)_2$, MgClSt is $MgCl(C_{17}H_{35}COO)$, and HSt stands for stearic acid.

3. Catalysis of PVC dehydrochlorination by stearic acid

$$PVC \xrightarrow{HSt, k_4} dePVC + HCl$$

In the reaction scheme the catalytic effect of HCl is not taken into consideration for the same reason as in our previous paper [7]. The reaction scheme can be

described by the system of four independent differential equations. The relative mole fractions of individual components are denoted as follows: x_1 — calculated conversion of dehydrochlorination, x_2 — HCl in the polymer, x_3 — double bonds in the polymer, x_4 — $MgSt_2$, x_5 — HSt, x_6 — MgClSt. We assume that HCl is evolved from the polymer after the mole fraction x_2 has reached the critical value x_c.

Provided $x_2 < x_c$

$$dx_1/dt = 0; \quad dx_2/dt = (k_1 + k_4x_5)(1 - x_3) - k_2x_2x_4 - k_3x_2x_6$$

Provided $x_2 = x_c$

$$dx_1/dt = (k_1 + k_4x_5)(1 - x_3) - k_2x_2x_4 - k_3x_2x_6; \quad dx_2/dt = 0$$

The kinetic equations for the other components are

$$dx_3/dt = (k_1 + k_4x_5)(1 - x_3)$$

$$dx_4/dt = -k_2x_2x_4$$

Relative mole fractions x_5 and x_6 can be expressed by material balances

$$x_5 = x_3 - x_1 - x_2 - a$$

$$x_6 = 2(x_4^o - x_4) - x_5$$

where x_4^o is the initial relative mole fraction of magnesium stearate in the PVC blend and a is the amount of HCl which escapes from the sample after calendering.

The system of differential equations has been solved by the fourth-order Runge—Kutta method, the sum of squares of deviations between theoretical and experimental kinetic curves has been minimized by the simplex method [10] simultaneously for the whole set of eleven runs. Minimization parameters were the rate constants of the process and the critical relative mole fraction x_c. Analogically as in paper [7] the changes occurring in the PVC blend during calendering were taken into account; in the quoted paper also the more detailed description of the calculation procedure can be found. Comparison of theoretical and experimental kinetic runs is shown in Figs. 1 and 2. The agreement between theory and experiment is excellent, which demonstrates that the reaction scheme describes adequately the reactions occurring in PVC blends.

The values of rate constants are listed in Table 1. The calculated rate constants k_1 describing the elimination of HCl from PVC are in accordance with the average values determined by experiment for the stabilized samples which are 5.6×10^{-5} min^{-1} for nitrogen atmosphere and 7.0×10^{-5} min^{-1} for air, respectively. The rate constants k_4 are also in good agreement with the rate constants

Table 1

Rate constants of the reactions occurring in thermal dehydrochlorination of PVC stabilized by magnesium stearate

Rate constant	Atmosphere	
	Nitrogen	Air
k_1/min^{-1}	5.5×10^{-5}	6.8×10^{-5}
k_2/min	258	347
k_3/min	114	18
k_4/min^{-1}	7.3×10^{-5}	9.9×10^{-5}
x_c	$7.0 \times 10^{-}$	$1.1 \times 10^{-}$

found experimentally ($k_4 = 7.4 \times 10^{-5}$ min^{-1} for nitrogen atmosphere and $k_4 = 1.3 \times 10^{-4}$ min^{-1} for air).

Troubles were encountered in the determination of rate constants k_2 and k_3 corresponding to the two-step reaction of HCl with magnesium stearate and in the estimation of the critical relative mole fraction x_c. Near the minimum, the sensibility of the calculation procedure with respect to these parameters was low; they varied in a rather broad interval, but, the products $k_2 x_c$ and $k_3 x_c$ remained approximately constant. This suggests that the parameters k_2, k_3, and x_c are not independent in the region of the minimum. In order to determine them more accurately, additional information would be needed. Nonetheless, the
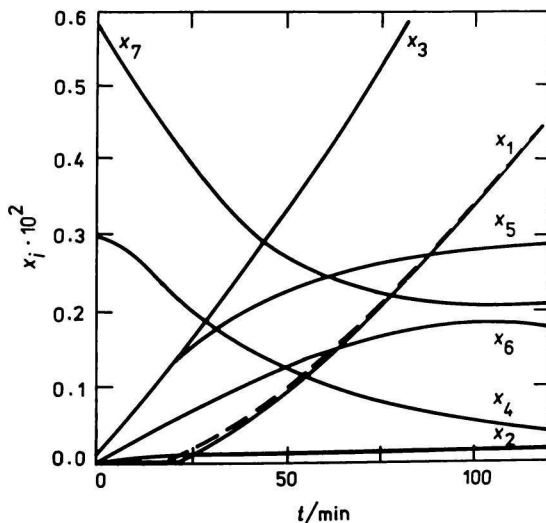

Fig. 6. Calculated dependences of relative mole fractions of individual components in the blend ($x_4^0 = 3.29 \times 10^{-3}$) on time for the dehydrochlorination in nitrogen. x_1 — conversion of dehydrochlorination, experimental kinetic curve (——), calculated kinetic curve (---); x_2 — HCl in polymer; x_3 — double bonds in polymer; x_4 — MgSt$_2$; stearic acid; x_6 — MgClSt; $x_7 = 2x_4 + x_6$ (Mg—St bonds).

values of k_2 and k_3 unambiguously show that the reaction of magnesium stearate with HCl is very quick and in accord with infrared spectra, the rate constant k_2 is considerably higher than k_3. The calculations enable to follow changes in the polymer blend during thermal stress. As an example see Fig. 6. The calculated kinetic curve x_1 resembles perfectly the experimental one. The content of double bonds in PVC is given by the curve x_3. At the time $t = 0$ the content of double bonds is greater than zero due to the degradation processes in the course of calendering. The content of stearic acid x_5 reaches a stationary value. The calculations also show that in the time $t = \tau$, 70—75 % of the stabilizer is consumed (expressed as the content of Mg—St bonds) in both dehydrochlorination atmospheres.

The results obtained show that magnesium stearate is as a thermal stabilizer of PVC little efficient. Its principal task is to bond the eliminated HCl. Neither is the colour of the film favourable for its more extensive employment. The films after calendering are brownish and the colour becomes darker with thermal stress. The reaction of magnesium stearate with HCl occurs in two steps. Stearic acid as a product of this reaction slightly accelerates the dehydrochlorination of PVC, the other product, magnesium chloride, has no effect on the dehydrochlorination.

References

1. Nagy, T and Kelen, T   *Angew. Makromol. Chem. 104,* 67 (1982).
2. Wypych, J., *J. Appl. Polym. Sci. 23,* 39 (1979).
3. Czakó, E., Vymazal, Z., Vymazalová, Z., and Štěpek, J., *Eur. Polym. J. 13,* 847 (1977).
4. Eremina, M. and Fedoseeva, G. T   *Vysokomol. Soedin., B 29,* 619 (1987).
5. Nass, L. I., *Encyclopedia of PVC.* M. Dekker, New York, 1976.
6. Minsker, K. S. and Fedoseeva, G. T., *Degradatsia i stabilizatsia polivinilkhlorida.* Mir, Moscow, 1979.
7. Oremusová, J., Šimon, P   Valko, L., and Kovařík, P., *Chem. Papers 43,* 721 (1989).
8. Marks, G. C., Benton, L. J., and Thomas, C. M., *J. Appl. Polym. Sci. 22,* 2415 (1978).
9. Vymazal, Z., Volka, K., Vymazalová, Z., Mastný, L., and Sabaa, M. W., *Eur. Polym. J. 23,* 331 (1987).
10. Nelder, J. A. and Mead, R., *Comput. J. 7,* 308 (1965).