

# Basic Principles of Thermal Degradation and Thermal Stabilization of Poly(vinyl Chloride). Synergism of Stabilizer Action

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## Synopsis

Changes in the quantities of active stabilizing components during thermal aging of plasticized poly(vinyl chloride) containing a mixture of calcium and zinc stearates were analyzed. A mathematical model of the stabilization process by using the stabilizer mixture and a computer program for analyzing the process of PVC thermal degradation after the beginning of HCl evolution are given.

## INTRODUCTION

Synergism of stabilizer action is a term that describes the as yet undefined properties of a mixture of stabilizers that result in a better total action than expected from a summation of the effects of the individual components. The principles of synergism, in spite of the wide use of excellent mixtures of stabilizers, remain obscure because of a lack of acquaintance with the basic parameters of stabilizers action, their reactivity, and the acceleration of PVC decomposition before the beginning of HCl emission.

Data referring to the behavior of stabilizers in mixtures do exist. Synergism of barium-cadmium stabilizers has been interpreted as the result of the different melting points of the components, which causes cadmium stearate (mp 110°C) to penetrate into PVC particles and owing to this HCl was bonded by it more effectively.<sup>1</sup>

According to other authors,<sup>2,3</sup> synergism of action of stabilizers Ba-Cd and Ca-Zn is caused by early reaction of Ba and Ca. Cadmium and zinc react when barium or cadmium is consumed to a greater extent.

Synergism of action depends on the relation of the weight of the components,<sup>4</sup> and using the mixture leads to better utilization of both reacting components.<sup>5</sup> The possibility of reaction between chemically different stabilizers has been raised; this can be observed when, for example, calcium dislodges zinc from its chlorine derivatives.<sup>5-7</sup>

The above-mentioned results have led to a continuation of the study on this subject.

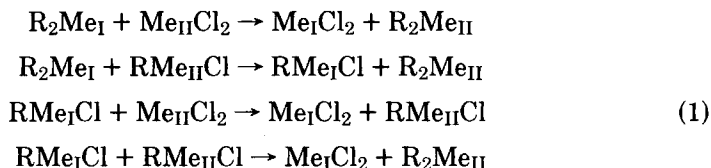
## EXPERIMENTAL

### Materials and Methods

The analytical methods for the determination of values as well as the materials used for the study have been described before.<sup>8-14</sup> Because of the universal character of their relationships, the differences in the tested products does not essentially influence the results.

## RESULTS AND DISCUSSION

Because of the methods of the measurements or methods of calculation of constants of kinetical equations of stabilizers,<sup>8-15</sup> the principles and parameters of the reaction between stabilizing components and their reaction products with HCl are the problems in question. Interaction is consistent with following equations:



Total expression of these reactions may give mistaken data, because the reactivities of the stabilizers in their initial form and those reacted with one molecule of HCl are different; and so is the influence of the reaction products of stabilizers of RMeCl and MeCl<sub>2</sub> type on the PVC decomposition rate. Hence, these reactions should be considered as collateral.

According to the principles of distribution of one reacting component in admixture with some competitive agent, the distribution of emitted HCl during PVC thermal degradation is proportional to the products of their reaction constants and concentrations of the reactive components of both stabilizers. Similar principles in connection with the interaction shown by eqs. (1) have been taken into account. The other principles have been defined in other works.<sup>8-15</sup>

To obtain kinetic data concerning the process of PVC thermal degradation in the presence of a stabilizer mixture, a computer program has been worked out. In this program, the calculation of constant  $k_5$  [constant of rate of reactions (1)] needs more extensive explanation. The value of constant  $k_5$  is chosen from the interval in which the lower limit is zero and the upper limit is the optionally chosen positive number  $K5_r$ .

The first condition causes an automatic decrease in the value of the constant  $k_5$  when the value of the reaction product of one of the stabilizers is smaller than zero in any time  $t_i$ . This condition decreases the inquiry time of the corresponding value of constant  $k_5$  by the elimination of excessively high values.

In time  $t_0$ , the quantity of HCl split off is equal to the quantity of HCl bonded by the stabilizers. In the case of stabilization by an individual stabilizer, the equation of the quantity of HCl bonded is as follows:

$$v_{2t_0} = k_2[RMeCl]a_{t_0}$$

Since

$$v_{2t_0} = a_{t_0}$$

it follows that

$$k_2[\text{RMeCl}] = 1$$

The equation is connected with the reaction between RMeCl and HCl, because bivalent metal carboxylate stabilizers in initial form have sufficiently high reactivity to have completely reacted before time  $t_0$ .

The above-mentioned condition is essential for mixtures of stabilizers, but in that case the quantities of HCl refer to the participation of the individual stabilizing component in the bonding of HCl. Hence, the constant  $k_5$  is selected so that the product  $k_2[\text{RMeCl}]$  is equal to 1 in time  $t_0$  for at least one of the stabilizers.

## DESCRIPTION OF THE COMPUTER PROGRAM INTE

### Symbols

#### Data Input

$v_0$	rate of degradation of PVC without stabilizer
$t_0$	time of initiation of HCl emission
$K5_r$	limiting value of constant of rate of reaction of cation interchange
$PA_l$	stabilizer acceptance ability of HCl
$K1_l$	constant of rate of reaction between $\text{R}_2\text{Me}$ and HCl
$K2_l$	constant of rate of reaction between RMeCl and HCl
$K3_l$	constant of degradation rate in presence of RMeCl
$K4_l$	constant of degradation rate in presence of $\text{MeCl}_2$
$Kd3_{j,l}$	constants $k_3$ and $k_4$ for stabilizers whose products of reaction affect nonlinearly the degradation kinetics, given proportionally to concentrations of these products ( $Sd3_{j,l}$ and $Sd4_{j,l}$ )
$Sd3_{j,l}$	
$Kd4_{j,l}$	
$Sd4_{j,l}$	
$\Delta t$	unit period of time of degradation

#### Data Output

$a_i$	quantity of HCl rising in time $t_{i-1}/t_i$
$UK1_{i,l}$	quantity of HCl reacting with stabilizer $l$ ,
$UK2_{i,l}$	quantity of HCl reacting with partially reacted stabilizer $l$
$U51_i$	quantity of interreacting stabilizer in initial form—chlorine acceptor
$U52_i$	quantity of interreacting partially reacted stabilizer—chlorine acceptor
$U53_i$	quantity of interreacting stabilizer in initial form—chlorine donor
$U54_i$	quantity of interreacting partially reacted stabilizer—chlorine donor
$VK1_{i,l}$	potential rate of HCl bonding by stabilizer $l$ in initial form
$VK2_{i,l}$	potential rate of HCl bonding by partially reacted stabilizer $l$
$V5_i$	total rate of interacting the stabilizers
$S1_{i,l}$	quantity of RMeCl formed
$S2_{i,l}$	quantity of metal chloride formed

$P_{i,l}$	quantity of stabilizer in initial form
$PR_{i,l}$	percent of unreacted stabilizer
$Wt_i$	quantity of HCl emitting in time $t_{i-1}/t_i$
$SWt_i$	quantity of HCl emitted up to time $t_i$

### Comments

Index  $l$  ( $l = 1, 2$ ) represents the stabilizers number; index  $i$  ( $i = 1, 2, \dots, t_0, \dots, 100$ ) marks time  $t_i$ .

When index  $l$  exists in any equation, the value is calculated for both stabilizers, while index 1 or 2 marks values or equations concerning the first or the second stabilizer.

In the program, it is accepted that the stabilizer with index  $l = 1$  is the chlorine acceptor from reaction products with HCl of the stabilizer marked  $l = 2$ .

### Algorithm

Program INTE begins with reading and printing of input data. Next, the program looks for the value of constant  $K5$  in the interval  $[0, K5_r]$  by using a sectional method. First, for  $K5 = 0$  and next for  $K5 = K5_r/2$ , the output data are calculated for each  $t_i \in [1, t_0]$  based on the following equations:

$$a_i = \Delta t \left[ \sum_{l=1}^2 (K3_l S1_{i-1,l} + K4_l S2_{i-1,l}) - v_0 \right] \quad (S1_{0,l} = S2_{0,l} = 0)$$

$$UK1_{i,l} = \frac{a_i K1_l P_{i-1,l}}{\sum_{l=1}^2 (K1_l P_{i-1,l} + K2_l S1_{i-1,l})} \quad \left( P_{0,l} = \frac{PA_l}{2} \right)$$

$$UK2_{i,l} = \frac{a_i K2_l S1_{i-1,l}}{\sum_{l=1}^2 (K1_l P_{i-1,l} + K2_l S1_{i-1,l})}$$

$$VK1_{i,l} = K1_l P_{i-1,l} UK1_{i,l}$$

$$VK2_{i,l} = K2_l S1_{i-1,l} UK2_{i,l}$$

$$V5_i = K5 (P_{i-1,1} + S1_{i-1,1}) (S1_{i-1,2} + S2_{i-1,2})$$

$$U51_i = V5_i \frac{P_{i-1,1} K1_1}{P_{i-1,1} K1_1 + S1_{i-1,1} K2_1} \quad (2)$$

$$U52_i = V5_i \frac{S1_{i-1,1} K2_1}{P_{i-1,1} K1_1 + S1_{i-1,1} K2_1}$$

$$U53_i = V5_i \frac{S1_{i-1,2}}{S1_{i-1,2} + S2_{i-1,2}}$$

$$U54_i = V5_i \frac{S2_{i-1,2}}{S1_{i-1,2} + S2_{i-1,2}}$$

$$S1_{i,1} = S1_{i-1,1} + UK1_{i,1} + U51_i - UK2_{i,1} - U52_i$$

$$S1_{i,2} = S1_{i-1,2} + UK1_{i,2} - U53_i - UK2_{i,2} + U54_i$$

$$S2_{i,1} = S2_{i-1,1} + UK2_{i,1} + U52_i \quad (3)$$

$$S2_{i,2} = S2_{i-1,2} + UK2_{i,2} - U54_i$$

In Eqs. (3), the following limitations are obligatory: If for  $l = 1$  or  $l = 2$   $S1_{i,l} < 0$ , then in Eqs. (3)  $S1_{i,l} = 0$  is taken. If for  $l = 1$  or  $l = 2$   $S2_{i,l} > PA_l/2$ , then in eqs. (3)  $S2_{i,l} = PA_l/2$  is taken. If for  $l = 1$  or  $l = 2$   $VK1_{i,l} < UK1_{i,l}$  or  $VK2_{i,l} < UK2_{i,l}$ , then in eqs. (3)  $UK1_{i,l} = VK1_{i,l}$  or  $UK2_{i,l} = VK2_{i,l}$ .

If for any  $t_i \in [1, t_0]$   $S2_{i,2} < 0$ , then the desired value of constant  $k_5$  is decreased and the program returns to calculation  $a_i$  with  $t_i = 1$ .

After making calculations for time  $t_0$ , the accuracy of constant  $k_5$  is inspected. The constant  $k_5$  is precise when for  $l = 1$  or  $2$ :

$$|K2_l S1_{t_0,l} - 1| < \epsilon \quad (4)$$

for any selected  $\epsilon > 0$ . If condition (4) is not fulfilled, as in the case when  $K2_l S1_{t_0,l} > 1$ ,  $k_5$  is decreased, and in the reverse case,  $k_5$  is increased. Calculations then begin from  $a_i$ .

When the accuracy of the value of  $k_5$  is satisfactory the program calculates all output data in the interval  $t_0 < t_i \leq 100$  and  $Wt_i$  and  $SWt_i$  (up to  $t_0$ ,  $Wt_i = 0$ ):

$$Wt_i = \sum_{l=2}^2 UK1_{i,l} - VK1_{i,l} + \sum_{l=1}^2 UK2_{i,l} - VK2_{i,l} \quad (5)$$

$$SWt_i = SWt_{i-1} + Wt_i$$

If any difference in eq. (5) is negative, then it is replaced by zero.

When the constant  $K3_l$  or  $K4_l$  is a sequence of number pairs ( $Kd3_{j,l}$ ,  $Sd3_{j,l}$ ) or ( $Kd4_{j,l}$ ,  $Sd4_{j,l}$ ), then for each  $t_i$  this constant is calculated by linear interpolation. Constant  $K3_l$  is interpolated for  $Sd3_{j,l} \leq S1_{i-1,l} \leq Sd3_{j+1,l}$ , and constant

rate of HCl rising  $\mu\text{mol HCl/g PVC}$

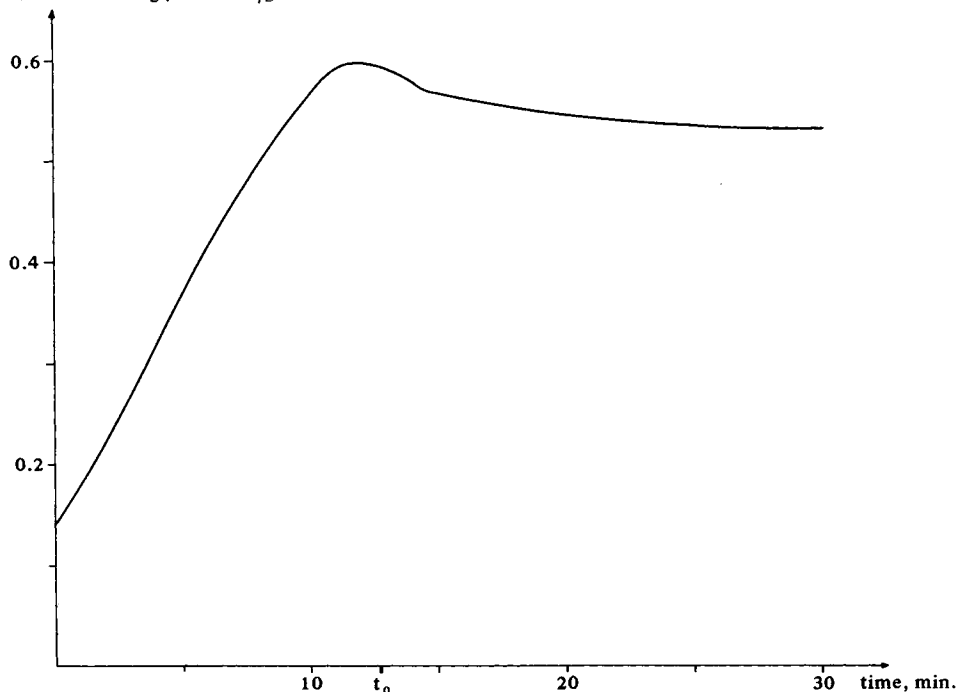


Fig. 1. Rate of HCl emission during heating of PVC composition stabilized by mixture of calcium and zinc stearates.

$K4_l$  for  $Sd4_{j,l} \leq S2_{i-1,l} \leq Sd4_{j+1,l}$ . After completion of the calculations, all output data are printed in periods of 6 sec.

The concept of the model of participation of mixture stabilizers in the process of PVC decomposition and stabilization mentioned above in mathematical form is based on the following principles: (1) Stabilizers react at a rate dependent on the value of constant  $k_2$  (the principles of its determination and calculation were explained earlier<sup>8,15</sup>) and on the actual concentration. (2) Distribution of the product of PVC decomposition, namely, HCl, between the two stabilizers depends on the value of the product  $k_2[\text{RMeCl}]$ . (3) HCl emission is observed at the moment when the product  $k_2[\text{RMeCl}]$  for any stabilizer is lower than unity, i.e., when this stabilizer is not able to bind the quantity of the degradation product formed. According to the assumption (2), both stabilizers jointly are also not able to bind all the HCl split off in time  $t_0$ .

One can see that program INTE fulfills simultaneously two functions: (a) it seeks the real value of constant  $k_5$ ; (b) it analyzes the actual data computed based on the mathematical model.

### MECHANISM OF ACTION OF MIXTURE OF CALCIUM AND ZINC STEARATES

Calcium and zinc carboxylates belong to a basic group of thermal stabilizers. Therefore, the synergism of their action by using the INTE program was analyzed. The figures below are concerned with mixtures of stearates of calcium

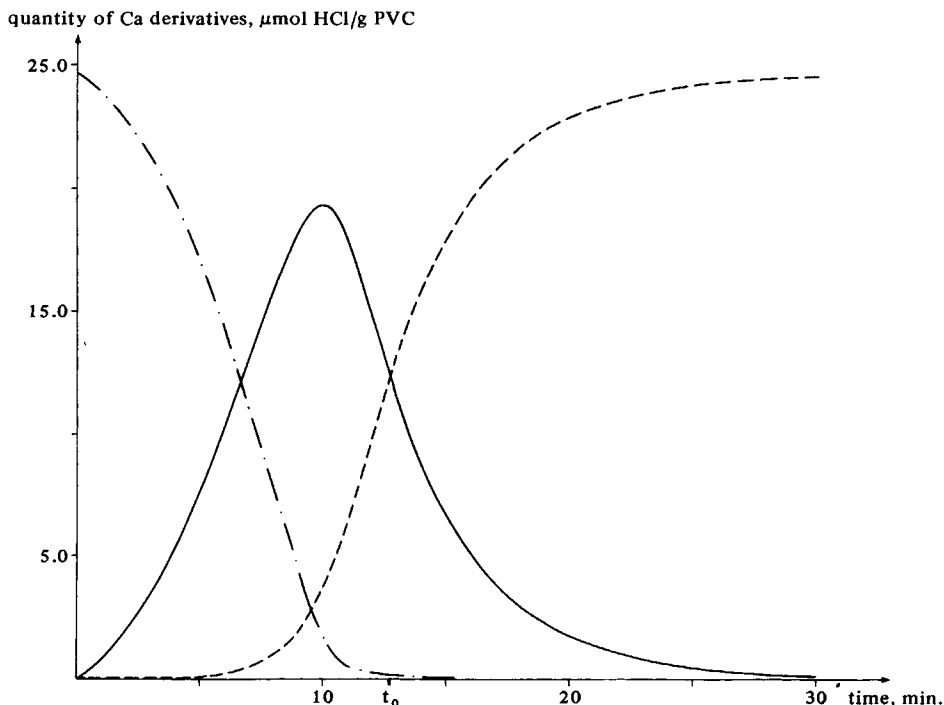


Fig. 2. Changes in quantities of calcium derivatives during thermal degradation of PVC composition stabilized by mixture of calcium and zinc stearates: (---) calcium stearate; (—) calcium stearate reacted with one molecule HCl ( $\text{RCaCl}$ ), (- · - ·) calcium chloride.

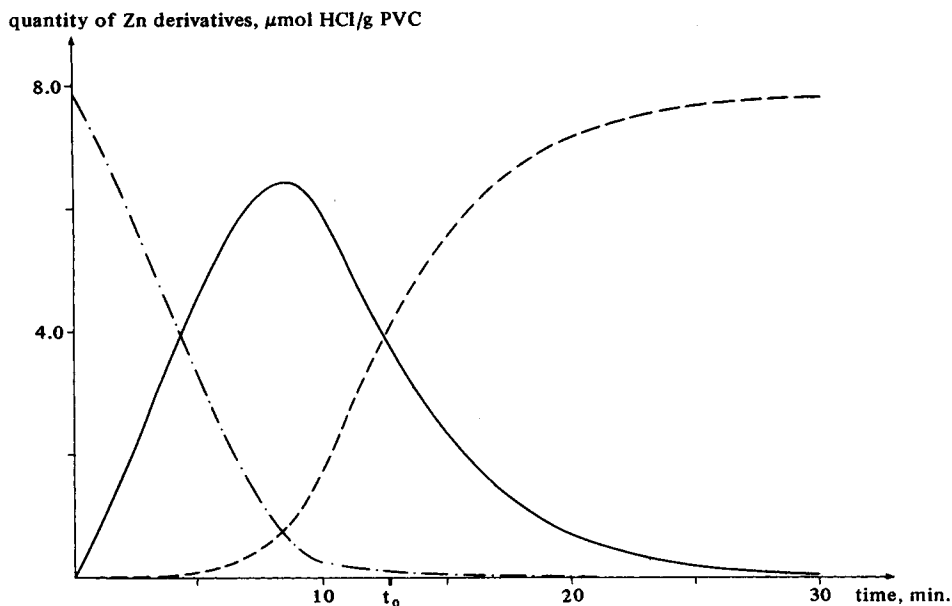


Fig. 3. Changes in quantities of zinc derivatives during thermal degradation of PVC composition stabilized by mixture of calcium and zinc stearates: (---) zinc stearate; (—) zinc stearate reacted with one molecule HCl ( $RZnCl$ ); (---) zinc chloride.

and zinc in a weight proportion of 3:1, but investigations were carried out also for 12:1, 5:1, and 1:1 mixtures.

Based on experimental data and calculations, it was found that the rate constant of interreaction between derivatives of calcium and zinc,  $k_5$ , differs from zero and its value is equal to  $0.000450 \mu\text{mole HCl}^{-1}\cdot\text{g PVC}\cdot\text{min}^{-1}$ . At the same time results of earlier works<sup>5-7</sup> were confirmed by the other method. Interreaction between the stabilizing derivatives of both metals could in no case be disputed. This reaction could be confirmed by simple and exact experiments. When heating the dispersion of calcium stearate in plasticizer (for example, DOP), it was found that by moderately increasing the temperature, calcium stearate is changed from a white powder to a brown-colored gluey substance which is insoluble at  $180^\circ\text{C}$ . By pouring into the mixture at this temperature some quantity of zinc chloride, complete dissolution of the gluey substance takes place in a few minutes.

Taking into consideration the temperature of the dissolution of zinc stearate (near  $110^\circ\text{C}$ ) under this condition, this phenomenon can be explained only by the presence of interreaction of the derivatives of these metals. This reaction has definite consequences during the thermal degradation of PVC compositions. Changes in chemical compounds of PVC composition stabilized by mixtures of calcium and zinc stearates are shown in Figures 1, 2, and 3.

The rate of HCl emission increases rather rapidly at the beginning of the heating process, and after a maximum it slowly decreases. The beginning of HCl emission follows after a maximal rate of splitting off.

The initial increase in the rate of PVC degradation is caused by  $RZnCl$  and  $MeCl_2$  products formed owing to the great reactivity of zinc stearate with HCl, but this rate and its increase are not so high as in the case of zinc stearate alone, because the reverse reaction takes place simultaneously; and as a result of this

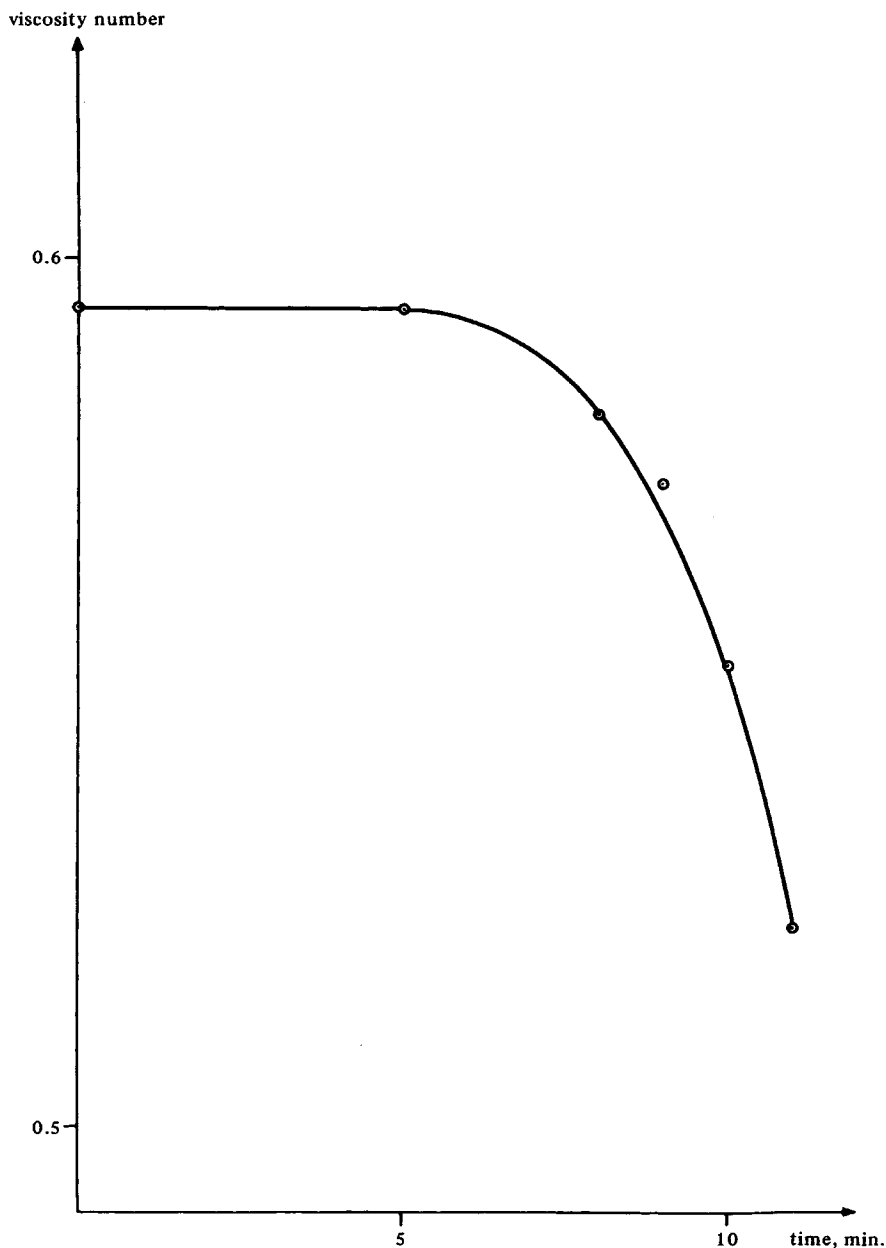


Fig. 4. Change in viscosity number during thermal degradation of PVC composition stabilized by mixture of calcium and zinc stearates.

reaction, products catalyzing the decomposition of PVC ( $\text{RZnCl}$  or  $\text{ZnCl}_2$ ) are deposited as harmless chlorine derivatives of calcium. At the same time, the active stabilizer taking part in the stabilization process is dissolved.

Later, the increase in the rate of PVC thermal degradation is connected with the progressive diminution in the mixture of the reaction products catalyzing the decomposition. The beginning of HCl emission depends on reciprocal relationship between the quantity of HCl formed and the concentration of the active stabilizing components.



The curves of the concentration of calcium stearate derivatives are more precipitous. It is connected with the type of action. This stabilizer plays an important role in the HCl acceptance process. The main stabilizing products of the first stage of heating are initial stearates, both metals. By the reaction of HCl acceptance, chlorine derivatives of metal stearates are formed. Consequently, in this step of degradation crosslinking reactions should not take place, nor should changes in color owing to the action of zinc stearate.

In the next stage of degradation, zinc chloride is slowly formed, hence the crosslinking process can begin. After a certain time the quantities of zinc chloride formed are proportional to the duration of the degradation process.

Figure 4 confirms the above-mentioned character of the changes. The beginning of HCl emission was, in the case of the composition tested, near the point of intersection of the  $RMeCl$  and  $MeCl_2$  curves, i.e., at equal concentrations of these two products. This is not the usual, but an accidental coincidence connected with the quantities of the components.

The above-reported principles of analysis of the action of stabilizing composition, beside the cognitive aspects, have practical applications, especially in the sphere of the production of stabilizers, their adequate selection for any compositions of poly(vinyl chloride), and for determining the quantity of stabilizer addition.

Although in the present and earlier works<sup>8-10</sup> only a few stabilizers were discussed, the selected method is also efficient for other compositions, i.e., all metal carboxylates. The method should be adapted for application to determining mixtures containing organozinc stabilizers.

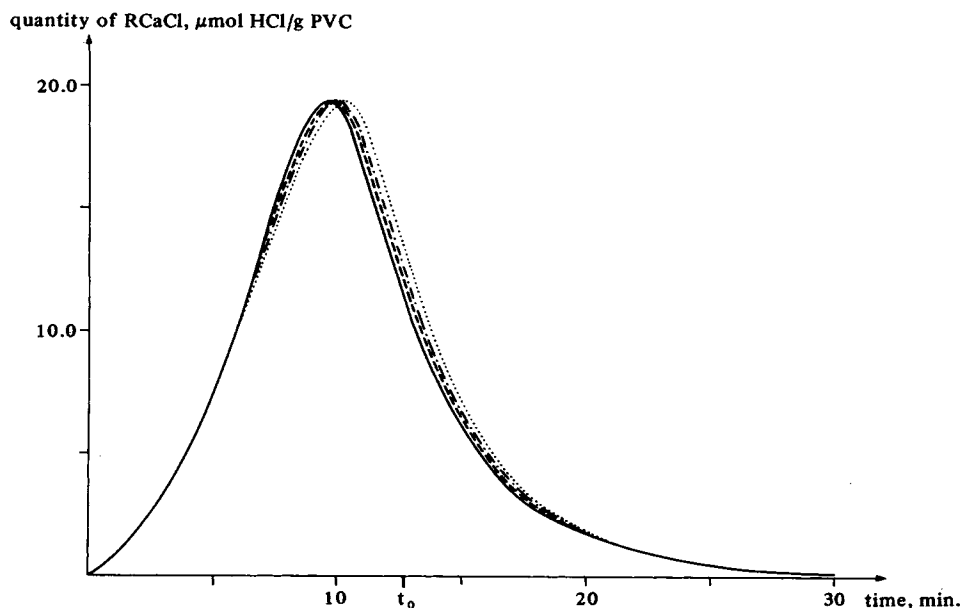


Fig. 5. Relation between quantity of partially reacted calcium stearate and value of constant  $k_5$ : (—) 0.0001; (---) 0.0003; (- · - · -) 0.00045; (···) 0.0007.

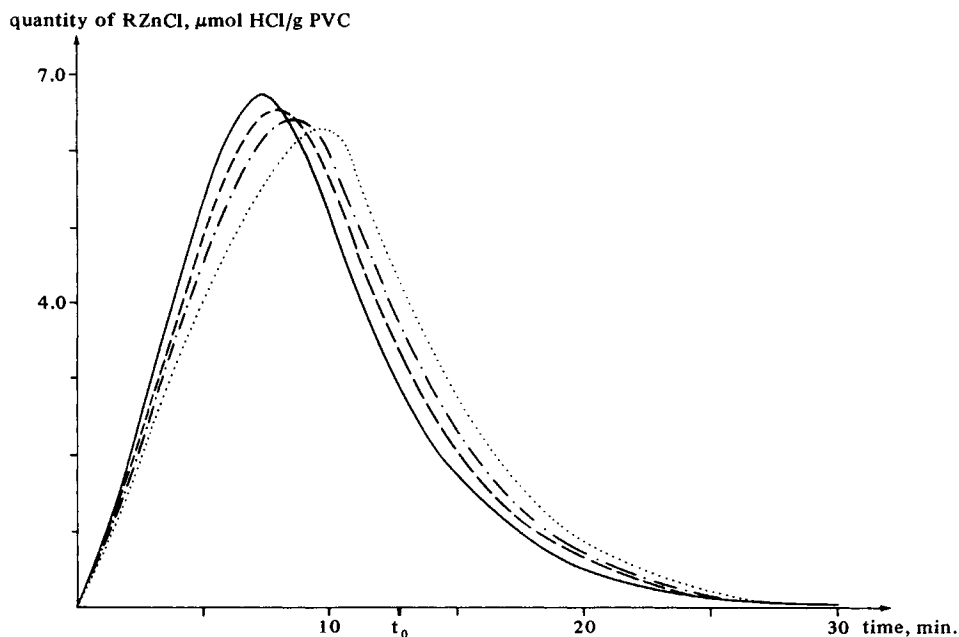


Fig. 6. Relation between quantity of partially reacted zinc stearate and value of constant  $k_5$ : (—) 0.0001; (---) 0.0003; (- · - · -) 0.00045; (···) 0.0007.

#### Value of Constant $k_5$ and Results of Calculations

For an experimental explanation of the significance of the value of constant  $k_5$  in the calculations, an arbitrary value of this constant has been chosen for analyzing the results. Figure 5 demonstrates the results of the calculations of the quantity of calcium stearate reacted with one molecule of HCl during thermal degradation. It can be seen that differences in the value of  $k_5$  do not cause more changes in the quantity of  $\text{RCaCl}$ , because the HCl formed in most parts reacts with calcium stearate directly or through mediation of zinc stearate (Fig. 6).

Greater changes could be noted with reference to analogous data for zinc stearate.

Just as by increasing the constant  $k_5$  the maximal quantity of  $\text{RZnCl}$  moves to the right, so the quantity of hydrogen chloride formed decreases.

When constant  $k_5$  is correct,  $k_2[\text{RCaCl}] = 1$  in time  $t_0$ . When

$$k_5 < k_{5 \text{ real}} \quad k_2[\text{RCaCl}] < 1 \quad \text{for } t_i = t_0$$

and

$$k_5 > k_{5 \text{ real}} \quad k_2[\text{RCaCl}] > 1 \quad \text{for } t_i = t_0$$

Thus, in time  $t_0$ , the quantity of active stabilizer is changed, as shown by Figure 7.

When the value of  $k_5$  is too low, it is found that the calculated beginning of the degradation of the composition containing the mixture of stabilizers occurs too early, and vice versa when the value is too high.

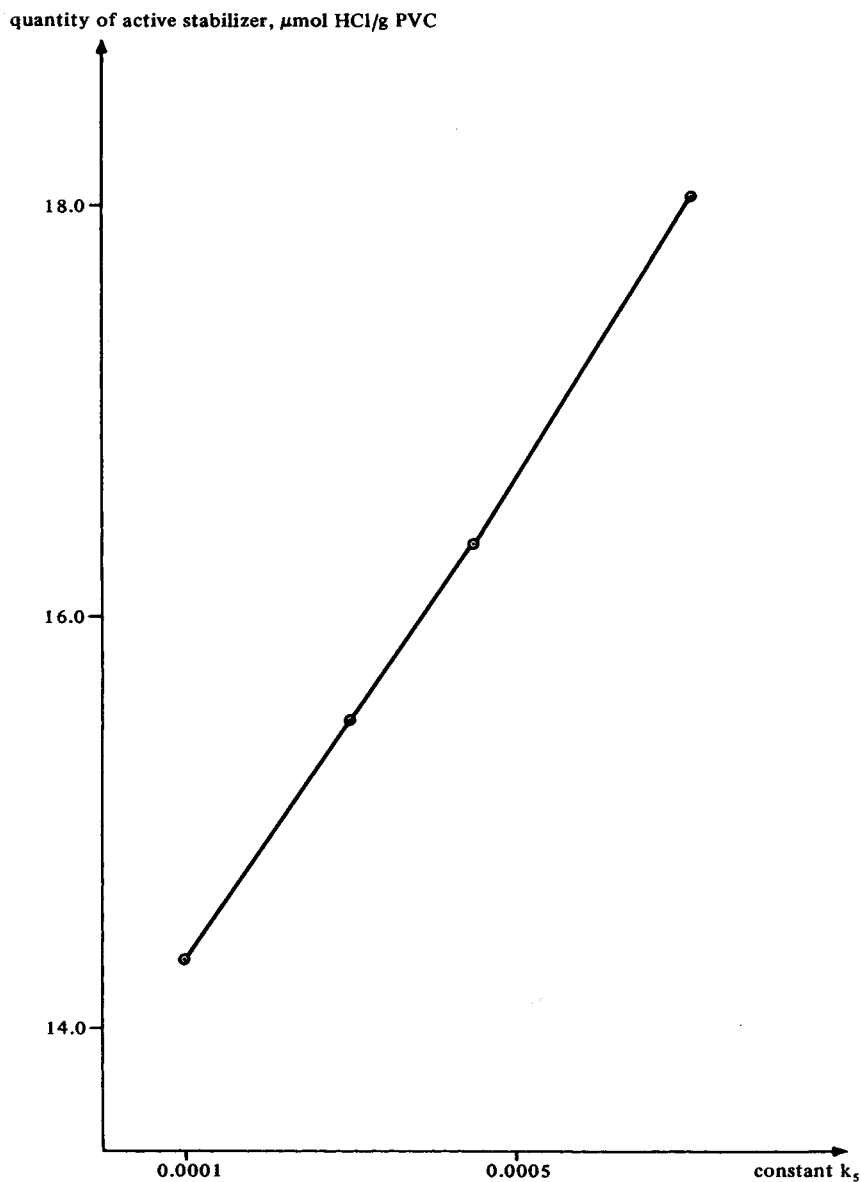


Fig. 7. Quantity of active stabilizer in time  $t_0$  in relation to value of constant  $k_s$ .

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