

## Basic Principles of Thermal Degradation and Thermal Stabilization of Poly(vinyl Chloride). Mathematical Model of the Action of PVC Thermal Stabilizers

KRZYSZTOF PROCHASKA and JERZY WYPYCH, *University of Lodz, Computer Centre, Łódź, and Central Laboratory for Technical Products, Chem. Dept., Łódź, Poland*

### Synopsis

A model of the action of chemically homogeneous thermal stabilizers of poly(vinyl chloride) is shown. Based on the described computer program and experimental data, the proposed model is confirmed and rate constants of the reaction of stabilizers with HCl and the effect of the products of this reaction on the kinetics of PVC degradation are calculated.

### INTRODUCTION

First attempts for a common interpretation of experimental data have been made by Yamada,<sup>1</sup> who applied an equation for the determination of the effectiveness of the action of the stabilizers. Further work<sup>2-5</sup> on synergic mixtures of stabilizers contain some experimental data, but do not lead to a mathematical formulation of the problem.

Extensive theoretical analysis of the stabilization process has been made by Minsker.<sup>6,7</sup> Based on widely known kinetic equations, Minsker took into consideration the influence of some factors on the effectiveness of the action of stabilizers.

Though the above-mentioned works tended toward scientific description of the fundamental principles of analysis and choice of stabilizers, the task, however, has not been achieved for the very complex character of the phenomenon. On the other hand, the direction of further works, which should bring into relationship the features of stabilizer (reactivity with HCl, the influence of reaction products of stabilizer with HCl on the rate of thermal degradation of polymer, and the quantity of HCl accepted by the thermal stabilizers) with the effect of PVC stabilization, was delineated.

Mathematical analysis of kinetic parameters of PVC thermal stabilizers in connection with their chemical structure and the mathematical model of PVC thermal degradation and stabilization are the main subjects of the present paper.

## EXPERIMENTAL

### Materials

Poly(vinyl chloride): Industrial types of PVC—Vestolit B 7021, Hostalit PVP 5470.

Plasticizer: Di(2-ethylhexyl) phthalate, purified technical products.

Stabilizers: Ca, Cd, and Zn stearates, dibasic lead stearate, and tribasic lead sulfate, pure chemical reagents.

### Methods

The methods of determination of the rate of HCl splitting off from unstabilized composition,  $v_0$ , of the induction period  $t_0$ , of the rate of HCl emitted from PVC composition including stabilizer,  $v_4$ , and of the quantity of HCl accepted by the stabilizer, PA, are in conformity with methods described in a recent work.<sup>8</sup>

## MODEL OF THERMAL DEGRADATION OF POLY(VINYL CHLORIDE) IN PRESENCE OF STABILIZERS

The rate of PVC thermal degradation in mixtures containing various auxiliary agents was investigated in earlier works.<sup>8,13,14</sup> It was found that the polymer in these mixtures (without any thermal stabilizer) is decomposed at a constant rate ( $v_0$ ) characteristic for the decomposition temperature and quantity and kind of additions. A variable rate of PVC thermal degradation was observed only in the initial stage of HCl splitting off, which was connected with the catalytical action of hydrogen chloride.

Similar results were reached in further investigations<sup>15</sup> of the mixtures including stabilizers.

The above-mentioned processes disturbing the character of the first-order reaction occur immediately after the most of the stabilizer is being reacted, i.e., when it cannot completely bind the increasing HCl.

Based on data obtained, one can state that the poly(vinyl chloride) in mixtures without stabilizers is decomposed at a constant rate, which is easy to determine using the well-known analytical methods.

Introducing the stabilizer into the mixture causes an increase in the length of the induction period owing to the reaction between stabilizer and HCl, which leads to chemical binding of the hydrogen chloride being formed during PVC degradation. So, the length of the induction period ( $t_0$ ) depends on the entire quantity of HCl bound by stabilizer (PA) and also its reactivity with HCl depending on the quantity of unreacted stabilizer in time  $t_0$ .

Determining the rate of reaction of stabilizer with HCl in alcoholic dispersion,<sup>9</sup> it was found that the reaction of the divalent metallic carboxylates proceeds at a considerably higher rate with the first molecule of HCl than with the next one. Similarly, lead stabilizers do not react at a constant rate, but lead carboxylate is more reactive than lead oxide.

Therefore, the rate of reaction between stabilizers and HCl is defined by more than one equation. The reaction rates of divalent metal carboxylates are given by two kinetic equations:

$$v_{1i} = k_1 \cdot [R_2Me]_i \cdot [HCl]_i \quad (1)$$

$$v_{2i} = k_2 \cdot [RMeCl]_i \cdot [HCl]_i \quad (2)$$

where  $[R_2Me]_i$ ,  $[RMeCl]_i$ , and  $[HCl]_i$  are the concentrations of reacting components at time  $t_i$ .

The presence of stabilizers in the mixtures increases the induction period  $t_0$ , but at the same time it complicates the character of changes during degradation because of the influence of reaction products of stabilizers with HCl on the rate of PVC decomposition well known from many works. At the same time, considering the model of thermal stabilization of PVC, the catalytic effect of these products on the decomposition rate of polymer is to be developed. The character of this influence corresponds with the principles of autocatalytic process, in accordance with results presented in a recent work.<sup>8</sup>

The rates of the catalyzed decomposition of PVC are shown by the following equations:

$$v_{3i} = k_3 \cdot [RMeCl]_i \cdot [C-Cl]_i + v_0 \quad (3)$$

$$v_{4i} = k_4 \cdot [MeCl_2]_i \cdot [C-Cl]_i + v_0 \quad (4)$$

As the number of C—Cl bonds in the examined decomposition range is practically unchanged, eqs. (3) and (4) take the form of pseudo-monomolecular reactions of the first order:

$$v_{3i} = k_3[RMeCl]_i + v_0 \quad (5)$$

$$v_{4i} = k_4[MeCl_2]_i + v_0 \quad (6)$$

Before the mathematical description of the above-mentioned processes, all variables are to be reconsidered for the differentiation of the values, which can be only calculated based on a precise mathematical analysis of the PVC thermal degradation process from the values to be determined.

Reaction between stabilizer and HCl, being resolved theoretically, could be shown as in Figure 1. The straight line 1 shows a stabilizer which has no influence on the rate of PVC thermal degradation. Curve 2 characterizes a stabilizer that increases the decomposition rate of PVC, whereas curve 3 describes a stabilizer that decreases its degradation rate.

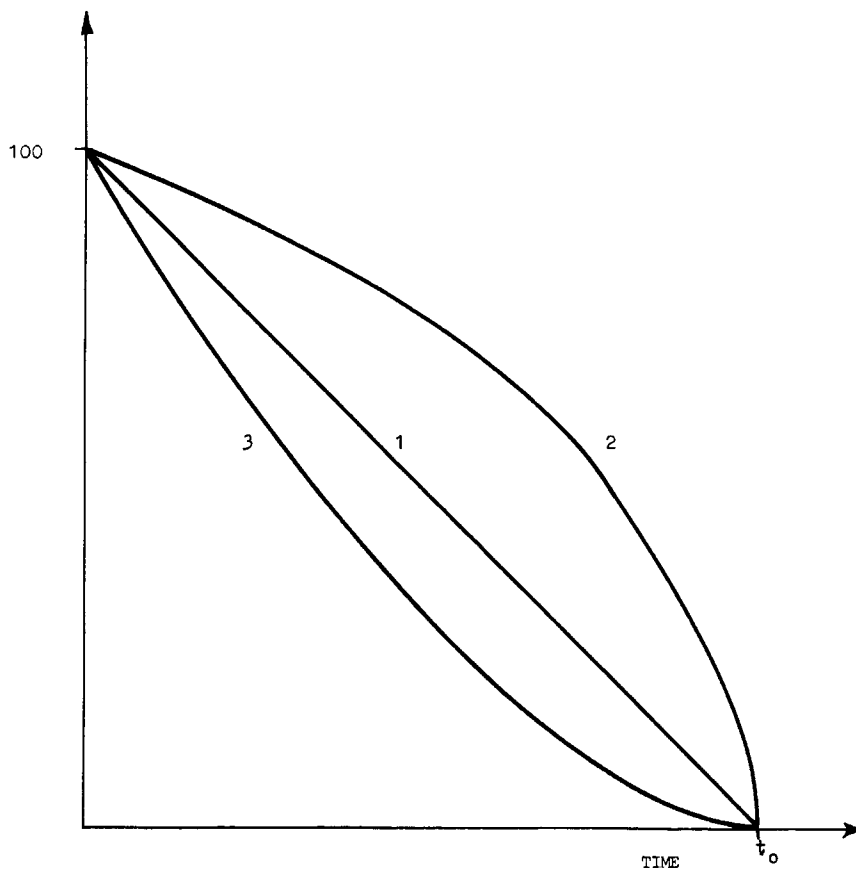
Taking into account the fact that up to time  $t_0$ , stabilizers may be partially unreacted, the courses of reactions of stabilizers with HCl are the same as the curves shown in Figure 2. The curves for individual stabilizers are not known because of lack of data of their reaction rates  $v_0$ ,  $v_1$ ,  $v_2$ ,  $v_3$ , and  $v_4$ . The methods of determination of rates  $v_0$  and  $v_4$  are well known.

The constant  $k_4$  of some stabilizers (e.g., Pb stabilizers, stearates of Ca and Ba) equals zero, while the constant  $k_4$  of other tested stabilizers depends on the concentration of  $MeCl_2$  (Fig. 3).

Besides the above-mentioned values, the methods of the determination of the induction period of rising HCl and its quantity for each time  $t_n > t_0$  are also known. In such a case, the determination of the rates  $v_1$ ,  $v_2$ , and  $v_3$  is the problem to be resolved.

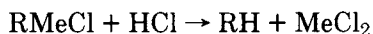
The rates  $v_1$  and  $v_2$  depend on the chemical structure of the reacting components, their concentrations, and type of solvent.<sup>9</sup> If one of these rates is determined, the other one can be calculated from measurements under model con-

Quantity of active stabilizer, %

Fig. 1. Change of active stabilizer concentration when  $v_2 = a_i$ .

ditions (e.g., in alcoholic dispersion). Thus, finding the rates  $v_3$  and  $v_1$  or  $v_2$  is the problem to be resolved.

In continuing,  $v_2$  has been taken as unknown. The  $v_2$  value is the rate of the following reaction:



It is possible to find both values ( $v_2$  and  $v_3$ ) using detailed and precise mathematical analysis of the degradation process.

Based on experimentally measurable values, computer programs for the calculation of the constants  $k_2$  and  $k_3$  for any chemically homogeneous stabilizer have been elaborated.

#### COMPUTER PROGRAM FOR CALCULATING THE REACTION CONSTANTS $k_2$ AND $k_3$ BASED ON TIME $t_0$

The principle of this program consists in using the relation between  $v_2$  and  $a_i$  at the beginning of HCl emission (time  $t_0$ ). In time  $t_0$ , the following relation is

Quantity of active stabilizer, %

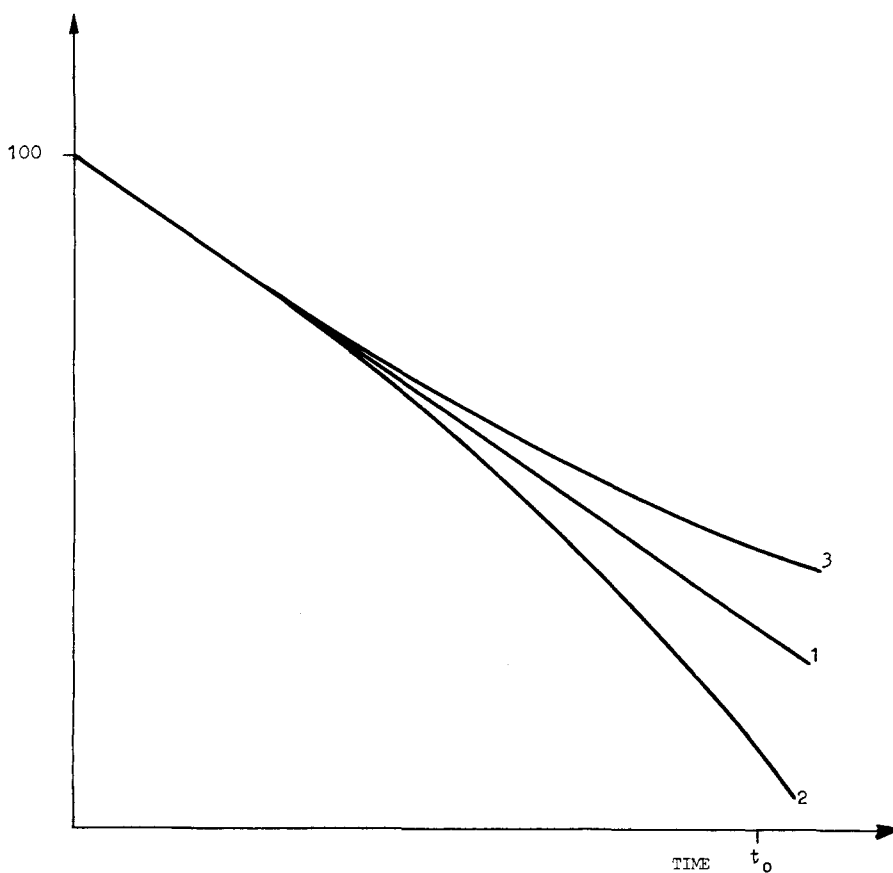


Fig. 2. Change of active stabilizer concentration when, in time  $t_0$ , stabilizer is unreacted.

fulfilled:  $a_{t_0} = v_{2t_0}$ , i.e., the quantity of rising HCl at this moment has been completely bonded by the stabilizer.

At other times  $t_i$ , this relation has the following forms:

$$a_i < v_{2i} \text{ for } t_i < t_0$$

and

$$a_i > v_{2i} \text{ for } t_i > t_0$$

For time  $t_0$ ,

$$v_{2t_0} = k_2(PA - S_{t_0})(a_{t_0})$$

Hence,

$$a_{t_0} = k_2(PA - S_{t_0})(a_{t_0})$$

$$k_2 = \frac{1}{PA - S_{t_0}} = \frac{1}{\Delta}$$

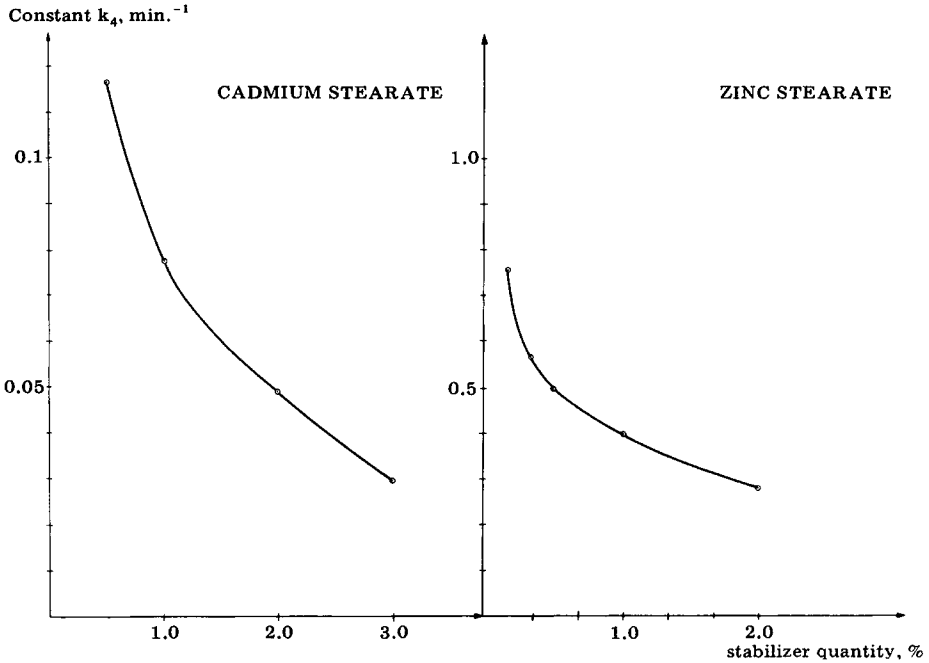


Fig. 3. Relation between constant  $k_4$  and quantity of introduced stabilizer.

Consequently, the value under question in time  $t_0$  is  $\Delta$ , for which

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

So for the time  $t_0$ , the corresponding value of constant  $k_3$  should be chosen in order that the quantity of HCl formed fulfills the relation

$$S_{t_0} = PA - \Delta$$

### Description of Program CON1

Input data for the program are: name of sample,  $t_0$ ,  $v_0$ ,  $PA$ ,  $\Delta r$ , and  $k_4$  (single value or sequence of a number of pairs  $kd_{4j}$ ,  $Sd_{4j}$ ).

After reading of input data, the program proceeds with counting. If  $k_4 = 0$ , then

$$k_2 = \frac{1}{PA - t_0 v_0}$$

and for each  $t_i$ , the following equations are fulfilled:

$$v_{2i} = k_2(PA - S_{i-1})v_0 \cdot \Delta t \quad (S_0 = 0)$$

$$S_i = S_{i-1} + v_0 \cdot \Delta t$$

$$Wt_i = 0 \quad \text{for } v_{2i} \geq v_0$$

$$S_i = S_{i-1} + v_{2i}$$

$$Wt_i = v_0 - v_{2i} \quad \text{for } v_{2i} < v_0$$

Next,  $P_i$  and  $SW_i$  are calculated down to the complete consumption of stabilizer:

$$P_i = \frac{PA - S_i}{PA} \cdot 100\%,$$

$$SW_i = SW_{i-1} + Wt_i, \quad (SW_0 = 0) \quad (7)$$

For  $k_4 \neq 0$ , the method of calculation is more complicated. Firstly,  $\Delta = \Delta r/2$  is taken ( $0 < \Delta \leq \Delta r$ ), and

$$k_2 = \frac{1}{\Delta} \quad (8)$$

Based on these values of  $k_2$  and  $\Delta$ , the constant  $k_3$  is selected in the range  $0 < k_3 \leq 4k_4$  just as

$$|S_{t_0} - (PA - \Delta)| < \epsilon \quad (9)$$

for any  $\epsilon > 0$ . Value  $S_{t_0}$  is calculated by the following method. Firstly,  $k_3 = 2k_4$  is taken, and for each  $t_i$  ( $1 \leq t_i \leq t_0$ ),  $a_i$  and  $S_i$  are calculated:

$$a_i = (k_3 S_{i-1} + \nu_0) \cdot \Delta t \quad \text{for } 0 \leq S_{i-1} \leq PA/2 \quad (10)$$

$$a_i = [S_{i-1}(k_4 - k_3) + PA(k_3 - 0.5k_4) + \nu_0] \cdot \Delta t \quad \text{for } PA/2 < S_{i-1} \leq PA$$

$$a_i = (0.5k_4 PA + \nu_0) \cdot \Delta t \quad \text{for } PA < S_{i-1}$$

$$S_i = S_{i-1} + a_i$$

If the constant  $k_4$  is given by sequence of  $kd_{4j}$ ,  $Sd_{4j}$  the constant  $k_4$  is calculated for each  $t_i$  by line interpolation for  $Sd_{4j} \leq S_{i-1} \leq Sd_{4j-1}$  or  $Sd_{4j} \leq S_{i-1} \leq PA$ . If the above calculations  $S_{t_0}$  do not fulfill the condition (9), the next value  $k_3$  is chosen from the range  $(0, 2k_4]$  or  $[2k_4, 4k_4]$ , and  $S_{t_0}$  is calculated from eqs. (10). This scheme is repeated till the condition (9) is fulfilled.

Then, the pair of numbers  $k_2$  and  $k_3$  is verified. For each  $t_i$ , ( $1 \leq t_i \leq t_0$ ) are calculated:

$$\begin{aligned} \nu_{2i} &= k_2(PA - S_{i-1}) \cdot (a_i) & \text{for } 0 \leq S_{i-1} \leq PA \\ \nu_{2i} &= 0 & \text{for } PA < S_{i-1} \end{aligned} \quad (11)$$

If the condition

$$|\nu_{2t_0} - a_{t_0}| < \epsilon \quad (12)$$

for any  $\epsilon > 0$  is not fulfilled, the next  $\Delta$  is chosen from the range  $(0, \Delta r/2]$  or  $[\Delta r/2, \Delta r]$ , and calculations start from point (8). If the condition (12) is fulfilled, the constants  $k_2$  and  $k_3$  are accurate, and the program next calculates  $P_i$ ,  $S_i$ ,  $SW_i$ ,  $\nu_{2i}$ , and  $Wt_i$  according to eqs. (7), (10), and (11) up to the moment when the active stabilizer becomes completely used up:

$$\begin{aligned} S_i &= S_{i-1} + \nu_{2i} & \text{for } t_i > t_0 \\ Wt_i &= 0 & \text{for } t_i \leq t_0 \\ Wt_i &= a_i - \nu_{2i} & \text{for } t_i > t_0. \end{aligned}$$

#### COMPUTER PROGRAM FOR CALCULATING THE REACTION CONSTANTS $k_2$ AND $k_3$ BASED ON TIME $t_0$ AND QUANTITY OF HCl SPLIT OFF, $Pt_n$

There is another possibility of counting the constants  $k_2$  and  $k_3$  of reaction rates based on experimental data.  $Pt_n$  is the value permitting the fixation of

those constants. It is a quantity of HCl split off up to time  $t_n$ , where  $t_n$  is the time at which stabilizer has been completely used, that is to say, after the experimentally found constant rate of HCl splitting off.

If in time  $t_0$  the stabilizer was completely exhausted, the quantity of HCl would be in accordance with the equation

$$W_1 = \left( \frac{k_4}{2} PA + v_0 \right) \cdot (t_n - t_0)$$

The difference ( $W_1 - Pt_n$ ) determines the limit of the quantity of active stabilizer.

The Symbols in the program description are the same as those used in program CON1.

### Description of Program CON2

Data input are: name of sample,  $t_0$ ,  $t_n$ ,  $Pt_n$ ,  $PA$ ,  $v_0$ , and  $k_4$  (single value or sequence of pairs  $kd_{4j}$ ,  $Sd_{4j}$ ).

Calculations at  $k_4 = 0$  are the same as in program CON1. For  $k_4 \neq 0$ , firstly,  $W_1$  is calculated as above and

$$\Delta r = W_1 - Pt_n.$$

Then, value  $k_3$  is chosen as in program CON1, and

$$W = \sum_{i=t_0+1}^{t_n} Wt_i. \quad (13)$$

If

$$|W - Pt_n| < \epsilon \quad (14)$$

for any  $\epsilon > 0$  (where  $\epsilon$  depends on the chosen accuracy of counting), constants  $k_3$  and  $k_2$  are right; if condition (14) is not fulfilled, the calculations are repeated.

After that, the program calculates  $P_i$ ,  $S_i$ ,  $SW_i$ ,  $v_{2i}$ ,  $Wt_i$ , and  $a_i$ .

### ANALYSIS OF PROGRAMS CON1 AND CON2

The differences between the programs consist mainly in the various input data.

In program CON2, the value  $Pt_n$  is one of the input data. Owing to that, the analyzed curves of quantity of the active stabilizer and quantity of HCl split off are defined by a greater number of known points, and constants  $k_2$  and  $k_3$  could be calculated with more accuracy. In the case of utilization of program CON2, however, the possibility of exact measurement of the  $Pt_n$  value must exist.

In the earlier paper,<sup>8</sup> the typical curve of degradation of PVC was discussed. Attention was paid to the fact that the PVC degradation rate did not run monotonically, being connected with the action of viscosity and surface tension forces. By these processes, HCl together with other products, for example, formed from stabilizer metal chlorides, considerably accelerates PVC degradation.



High concentration of HCl in tested sample causes, at the same time, consumption of active stabilizer, so the experimentally determined value of  $Pt_n$  is disputable.

It was found by experiment that actually applied methods of determination of quantity of HCl splitting off are imprecise for the exact counting of constants  $k_2$  and  $k_3$  according to program CON2.

### INFLUENCE OF ACCURACY OF ANALYTICAL METHODS OF INPUT DATA DETERMINATION FOR THE PROGRAM CON1 ON VALUES OF CALCULATED CONSTANTS $k_2$ AND $k_3$

The program was tested mathematically by separate changing of experimental values of  $v_0$ ,  $t_0$ , and  $k_4$ . Results of calculations are shown in Table I. As can be seen, especially important for the exact calculation of constant  $k_2$  is the accuracy of measurements of the beginning of HCl rising (time  $t_0$ ).

Based on calculations given in Table I, it could be said that for the real value of constant  $k_2$  with an accuracy of 3%, time  $t_0$  should be determined at low  $t_0$  with an accuracy of 0.1 min.

It should be emphasized that rate  $v_0$  has a considerable influence on the result of calculation of constant  $k_2$ . At the same time, it can be stated that the quantity of active stabilizer in time  $t_0$  depends on the types of polymer and plasticizers used. This is connected with experimental data.

The unchanging value of constant  $k_3$  also seems to be an important observation, which for cadmium stearate was equal to zero in spite of using the inaccurate data. This testifies that the appearance of constant  $k_3 = 0$  could not be under any circumstances connected with inaccurate determinations.

### REASON OF VALIDITY OF ACCEPTED MODEL

From the mathematical point of view, the model is correct when only one result fulfills the following criterion:

$$|v_{2t_0} - a_{t_0}| < \epsilon.$$

Therefore, the function  $\Delta = f(v_{2t_0} - a_{t_0})$  was determined (Table II). Results of calculations confirm the existence of only one solution fulfilling the above-mentioned criterion, that is, only one pair of constants exists for which, in time  $t_0$ , the quantity of HCl rising and bonding by stabilizer is equal.

### CONSTANTS $k_2$ AND $k_3$ OF SOME DIFFERENT PVC THERMAL STABILIZERS

Results of calculations, based on experimental data, for some stabilizers are shown in Table III. Irrespective of the kind of stabilizer, a portion of active stabilizer is to be found in time  $t_0$ . This is in opposition to an earlier work,<sup>10</sup> but this fact has been confirmed by experimental data.

The data, including lead stabilizers, are especially easy to explain because of their poor reactivity,<sup>11</sup> but the value was immeasurable.

When dibasic lead stearate is used, hydrogen chloride is emitted after consuming one third part of the addition. It could be said that this was connected

TABLE I  
Values of Constants  $k_2$  and  $k_3$  for Cadmium Stearate Depending on Input Data<sup>a</sup>

Change of $t_0$										
$t_0$	$k_2$	$\bar{i} - t_0$	$\frac{ \bar{t}_0 - t_0 }{\bar{t}_0}$	% $\bar{t}_0$	$\bar{k}_2 - k_2$	$\frac{ \bar{k}_2 - k_2 }{\bar{k}_2}$	% $\bar{k}_2$	% $\frac{\bar{k}_2}{\bar{t}_0}$	Average step of change	$k_3$
5.0	0.02951	2.0	0.2856	28.6	0.02128	0.4189	41.9	1.46		0.0000
6.0	0.03687	1.0	0.1428	14.3	0.01392	0.2740	27.4	1.91		0.0000
8.0	0.08041	-1.0	0.1428	14.3	-0.02962	0.5832	58.3	4.07	8.05	0.0000
9.0	0.41069	-2.0	0.2856	28.6	-0.35990	7.0860	708.6	24.77		0.0000
Change of $v_0$										
$v_0$	$k_2$	$\bar{v}_0 - v_0$	$\frac{ \bar{v}_0 - v_0 }{\bar{v}_0}$	% $\bar{v}_0$	$\bar{k}_2 - k_2$	$\frac{ \bar{k}_2 - k_2 }{\bar{k}_2}$	% $\bar{k}_2$	% $\frac{\bar{k}_2}{\bar{v}_0}$	Average step of change	$k_3$
0.623	0.04205	0.057	0.0838	8.4	0.00874	0.1720	17.2	2.05	2.47	0.0000
0.712	0.05771	-0.032	0.0470	4.7	-0.00692	0.1362	13.6	2.89		0.0000
Change of $k_4$										
$k_4$	$k_2$	$\bar{k}_4 - k_4$	$\frac{ \bar{k}_4 - k_4 }{\bar{k}_4}$	% $\bar{k}_4$	$\bar{k}_2 - k_2$	$\frac{ \bar{k}_2 - k_2 }{\bar{k}_2}$	% $\bar{k}_2$	% $\frac{\bar{k}_2}{\bar{k}_4}$	Average step of change	$k_3$
0.1699	0.05000	0.0629	0.2702	27.0	0.00079	0.0155	1.5	0.06		0.0000
0.1998	0.05037	0.0330	0.1417	14.2	0.00042	0.0082	0.8	0.06	0.06	0.0000
0.2598	0.05116	-0.0270	0.1159	11.6	-0.00037	0.0072	0.7	0.06		0.0000

$${}^a \bar{t}_0 = 7.0, \bar{v}_0 = 0.68, \bar{k}_4 = 0.2328, \bar{k}_2 = 0.05079, \bar{k}_3 = 0.0000.$$

TABLE II  
Function  $\Delta = f(v_2 t_0 - a_{t_0})$

$\Delta$	$a_{t_0} - v_2 t_0$
3	-0.00891
6	-0.00683
9	-0.00594
12	-0.00448
15	-0.00248
18	-0.00105
21	0.00034
24	0.00088
27	0.00196
30	0.00315

TABLE III  
Constants  $k_2$  and  $k_3$  of Some PVC Thermal Stabilizers

Stabilizer	$k_2$	$k_3$	$k_4(t_0)$	% of active stabilizer in time $t_0$
Zinc stearate	0.07619	0.4365	0.4460	20.77
Cadmium stearate	0.05079	0.0000	0.2168	33.40
Calcium stearate	0.04039	0.0000	0.0000	37.57
Dibasic lead stearate	0.01528	0.0000	0.0000	68.40
Tribasic lead sulfate	0.00682	0.0000	0.0000	87.91

with completely used lead stearate, which is about 2000 times more reactive than lead oxide, as was determined in alcoholic dispersion.<sup>9</sup>

The same results were obtained for tribasic lead sulfate, which, in time  $t_0$ , contained 88% of the active form. This was connected probably with anion in-

terchange between  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , because this reaction is relatively of a higher rate than the reaction of  $\text{PbO}$  with  $\text{HCl}$  (similar results were obtained in alcoholic dispersion<sup>9</sup>).

Results for stearates of  $\text{Ca}$ ,  $\text{Cd}$ , and  $\text{Zn}$  could be explained by comparison of their places in the electromotive sequence of those metals, but this relation does not apply for calcium stearate.

Results obtained for calcium stearate cannot be connected with experimental errors or model inconsistency, because they can be explained by considering the physical properties of calcium stearate. In the test temperature ( $180^\circ\text{C}$ ), calcium stearate was only partially dissolved. At the same time, its practical concentration in solution was lower than appeared from the quantity of the addition. The same explanation has been published earlier<sup>12</sup> for barium stearate.

Finally, constant  $k_3$  can be explained. As can be seen from the results shown in Table I, this constant cannot be a value calculated incorrectly because of imprecise experimental data, because for cadmium stearate constant  $k_3$  was always equal to zero in spite of large deviations from experimental values. At the same time, it could not be stated that the value of  $k_3$  was the result of experimental error.

These data are compatible with the theoretical considerations of Minsker,<sup>7</sup> who stated that products of the  $\text{RMeCl}$  type do not catalyze the process of PVC degradation, which is in any case true for all stabilizers except zinc stearate.

The catalytical effect of  $\text{RZnCl}$  is confirmed by the short duration times of the induction period, hence it is improbable that only zinc chloride accelerates PVC decomposition to such a degree that the degradation process follows so rapidly.

It seems that the catalytic effect of  $\text{RZnCl}$  is connected with the mechanism of its action.

### Symbols

- $t_i$  duration time of degradation, min  
 $\Delta t$  unit period of time, min  
 $t_0$  beginning of  $\text{HCl}$  emission, min  
 $v_0$  rate of  $\text{HCl}$  emitted from composition without stabilizers,  $\mu\text{mole HCl/g PVC min}^{-1}$   
 $t_n$  duration time of PVC degradation after full consumption of stabilizer, min  
 $v_{2i}$  rate of stabilizer reaction with second molecule of  $\text{HCl}$ ,  $\mu\text{mole HCl/g PVC min}^{-1}$   
 $k_2$  constant of reaction rate  $v_{2i}$ ,  $\text{g PVC } \mu\text{mole HCl}^{-1} \text{ min}^{-1}$   
 $k_3$  constant of rate of PVC degradation under the influence of  $\text{RMeCl}$ ,  $\text{min}^{-1}$   
 $k_4$  constant of rate of PVC degradation under the influence of metal chloride,  $\text{min}^{-1}$   
 $kd_{4j}$  experimentally determined values of constants of rates of PVC degradation under the influence of different quantities of metal chloride  $Sd_{4j}$ ,  $\text{min}^{-1}$ ;  $\mu\text{mole HCl/g PVC}$   
 $S_i$  quantity of  $\text{HCl}$  created and bonded by stabilizer up to time  $t_i$ ,  $\mu\text{mole HCl/g PVC}$   
 $a_i$  quantity of  $\text{HCl}$  rising in time  $t_{i-1} \div t_i$ ,  $\mu\text{mole HCl/g PVC}$

$Wt_i$  quantity of HCl split off in time  $t_{i-1} \div t_i$ ,  $\mu\text{mole HCl/g PVC}$

$SW_i$  quantity of HCl emitted up to time  $t_i$ ,  $\mu\text{mole HCl/g PVC}$

$P_i$  % of active stabilizer in time  $t_i$ , %

$\Delta r$  limit of quantity of active stabilizer in time  $t_0$ ,  $\mu\text{mole HCl/g PVC}$

$PA$  quantity of introduced stabilizer,  $\mu\text{mole HCl/g PVC}$

$\Delta$  real quantity of active stabilizer in time  $t_0$ ,  $\mu\text{mole HCl/g PVC}$

### References

1. T. Yamada, *Bull. Electrotechn. Lab.*, **20**, 256 (1956).
2. R. Nagatomi and Y. Saeki, *Jpn. Plast. Age*, **5**, 51 (1967).
3. C. Jirkal and J. Stepek, *Plast. Mod. Elastom.*, **21**, 109 (1967).
4. J. Stepek, F. Godenzi, and C. Alcouffe, *Plast. Mod. Elastom.* **18**, 25 (1966).
5. R. D. Deanin and J. F. Landers, *Polym. Eng. Sci.*, **13**, 35 (1973).
6. K. S. Minsker, V. P. Malinnskaya, and V. V. Sayapina, *Vysokomol. Soedin., Seriya A*, **14**, 560 (1972).
7. K. S. Minsker and G. T. Fedoseyeva, *Destrukcyia i stabilizacyia polivinylchlorida*, Kchimia, Moskva, 1972.
8. J. Wypych, *Angew. Makromol. Chem.*, **48**, 1 (1975).
9. J. Wypych, *J. Appl. Polym. Sci.*, **20**, 553 (1976).
10. R. Nagatomi and Y. Saeki, *Kogyo Kagaku Zasshi*, **65**, 393 (1962).
11. K. S. Minsker and L. D. Bubis, *Vysokomol. Soedin.*, **9A**, 646 (1967).
12. L. S. Troickaya and B. B. Troicky, *Plast. Massy*, **7**, 46 (1966).
13. W. Jerzykiewicz and J. Wypych, *Tenside*, **13**, 74 (1976).
14. J. Wypych, *J. Coated Text.*, to appear.
15. J. Wypych, unpublished.