

Mechanism of Action of PVC Thermal Stabilizers

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Synopsis

Based on experimental data, changes of properties of plasticized PVC containing stearates of Ca, Zn, Cd, and Pb stabilizers during thermal degradation are discussed. The mechanism of action of these stabilizers is described in kinetic form.

INTRODUCTION

Investigations of the mechanism of stabilization have been frequent, resulting in a number of confirmed observations. It was found uncontrovertibly that reaction products of stabilizers containing zinc and cadmium accelerate the thermodestruction of PVC, whereas barium and calcium stabilizers have no effect on the rate of thermal degradation of PVC. On the other hand, zinc and cadmium carboxylates moderate the change of color, while stabilizers of barium and calcium have no effect, in this respect.¹⁻³

PVC compositions observed after removal of the product of reaction with HCl and cadmium chloride had an unchangable rate of decomposition.⁴ The polymerization degree of PVC did not change when the stabilizer was in active form.³

By IR spectroscopy, absorption in the region characteristic for C=O bond was found,⁵ which confirmed the possibility of substitution of acid radicals into the polymer chain.

During thermodestruction, crosslinking caused by metal chlorides of cadmium and zinc took place.^{6,7} These same metal chlorides created also a formation of cyclic compounds between neighboring sections of two chains.^{8,9}

Until now, a universal kinetic mechanism of stabilizer action, including the above-mentioned experimental data, has not yet been proposed. This was caused by lack of experimental data on kinetic changes during thermal decomposition of PVC before the beginning of HCl emission.

In previous parts of this work,^{10,11} results of investigations connected with the character of the stabilization process and its kinetic parameters have been described. Based on those data and the above-mentioned works, the subject of this paper is an attempt to explain the mechanism of action of some stabilizers.

EXPERIMENTAL

Materials

Poly(vinyl chloride): industrial types of PVC (Hostalit PVP 5470 and Vestolit B 7021).

Plasticizer: di(2-ethylhexyl) phthalate, purified technical product.

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

Methods

The methods of measuring PVC thermal degradation are the same as those given earlier.¹⁰

Determination of Color of Foil. Tristimulus values of color of thermally aged samples at 180°C in N₂ atmosphere were determined by the automatic reflection spectrophotometer Spectromat in the range of 400–700 nm for a standard light source C.

A test sample was placed on a plate of baryta white.

Determination of Color of Solution. An aliquot of foil 0.1000 ± 0.0001 g in quantity after thermal degradation (180°C under N₂) was dissolved in 25 cc tetrahydrofuran. Absorption of solution was determined at 400 nm.

Determination of Viscosity Number. An aliquot of foil weighed with accuracy ± 0.0001 g after thermal degradation under the above-mentioned conditions was dissolved in a quantity of cyclohexanone to obtain 0.5% solution of PVC. Viscosity was determined by Ubbelohde's viscosimeter.

Paper Chromatography. A weighed sample of foil 0.1000 ± 0.0001 g in quantity was heated as above. Next, the foil was extracted with 5 cc CH₃OH for 24 hr at room temperature. The extract was put in a separate vessel and the sample was extracted again for 5 hr. The joined extracts were evaporated, and then stearic acid (present in sample) dissolved in 0.4 cc CH₃OH was carried on chromatography paper Schleicher-Schuell No. 2045b/21ac in a quantity of 10 μ l. The separation solvents mixture consisted of tetrahydrofurane:ethyl alcohol:water 30:55:15. The chromatogram was developed by 0.04% ethanolic solution of basic red neutralized to pH 7 by NaOH solution. Because of the low stability of the colored spots, their outlines were marked at once after developing.

DISCUSSION

Rate of Thermal Degradation

The character of the process of thermal degradation of the stabilized composition is closely connected with the kind of stabilizer used. Fig. 1 shows curves of rate of degradation of compositions including different thermal stabilizers. Characteristic of decomposition is the increase in the rate of HCl emission immediately after the beginning of the degradation.

In the case of stabilizers whose reaction products do not influence degradation kinetics (tribasic lead sulfate, calcium stearate), the increase in the rate of HCl

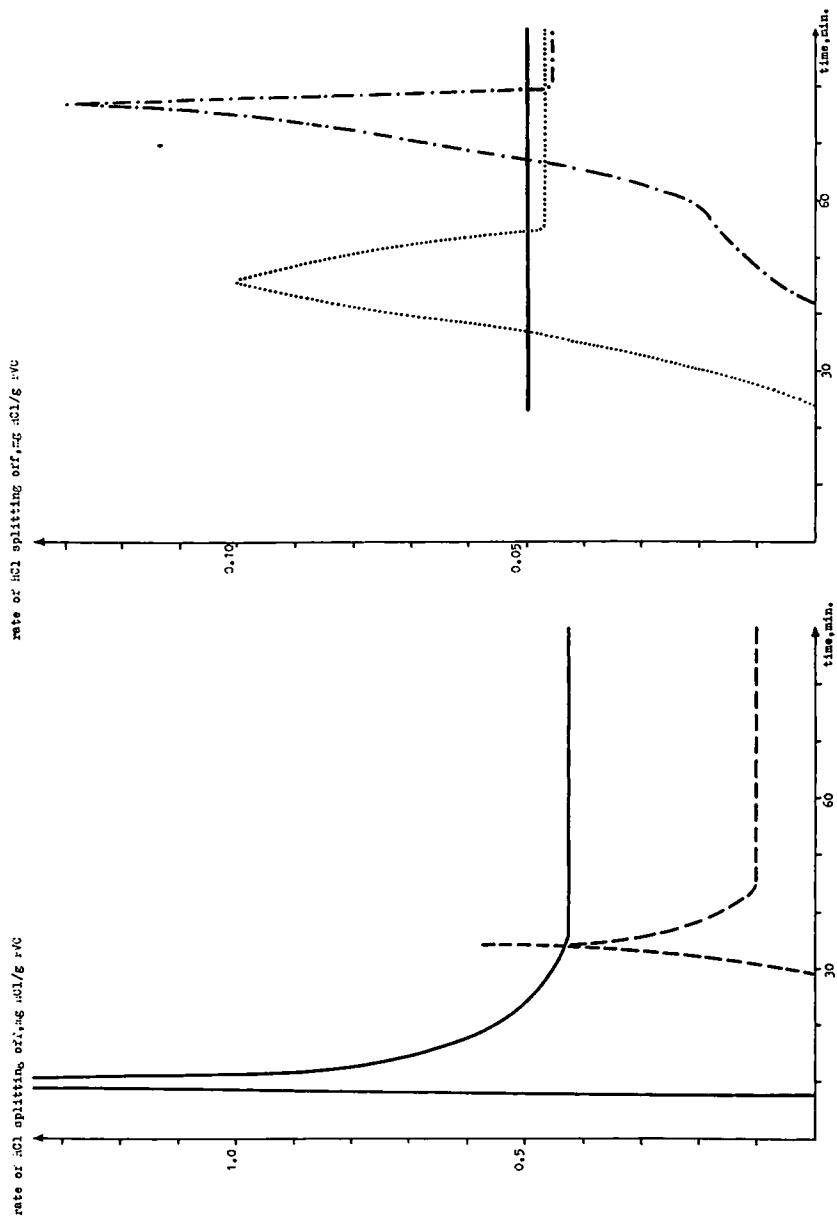


Fig. 1. Rate of HCl emission from PVC composition including different stabilizers (PVC-100, DOP-60, stabilizer-2): (—) zinc stearate; (- - -) cadmium stearate; (· · ·) tribasic lead sulfate; (- · -) calcium stearate; (—) without stabilizer.

emission near time t_0 proceeds slowly, which is connected with the time required for obtaining the corresponding pressure of hydrogen chloride in the sample. Starting from the point at which the foil has a porous structure, the rate of decomposition is stabilized in a short time, but degradation rates were lower than v_0 because of incompletely reacted stabilizer.

Reaction products of Cd stearate-HCl have less influence on the rate of PVC degradation than reaction products of Zn stearate, and therefore the maximum rate of HCl emission is less for composition stabilized with cadmium stearate. Simultaneously, it should be noted that the rate of PVC thermal degradation was stabilized the longest in the case of composition including zinc stearate. So the conclusion could be drawn that at time t_0 zinc stearate is not reacted fully and the products catalyzing the decomposition are present in the composition. Concentration of these products decreases during thermal degradation.

Figure 2 shows the data concerning the quantity of active stabilizer during PVC thermal degradation calculated using program CON 1 written in the earlier part of this work.¹¹ It can be seen that calcium stearate and tribasic lead sulfate do not accelerate the decomposition rate and react only partially up to time t_0 . Cadmium stearate, in the first step of PVC degradation, acts similarly as mentioned above. Not until after about half the added quantity of stabilizer has been reacted does the rapid increase in the rate of HCl emission occur.

The above-mentioned data are confirmed by results shown in Figure 3. Length of induction period increases more than the weight addition of cadmium stearate. The character of the curve of quantity of active stabilizer (Fig. 2), because the period of reaction time of 50% of quantity of active stabilizer is considerably longer than the period of time from 50% of quantity of active stabilizer to time t_0 , so increasing the quantity of added stabilizer leads to prolongation of duration time of the noncatalyzed decomposition process, which in a primary step influences the length of induction period.

The curves of zinc stearate shown in Figures 2 and 3 have another course. Quantities of active stabilizer, except in the initial stage, are nearly proportional to the time, but the catalytic effect could be observed from the beginning of the decomposition. Consequently, a different mechanism of action of this stabilizer should be taken into account.

In the previous part of this paper¹¹ it has been found that reaction products of stabilizer type $RZnCl$ catalyzed the decomposition process of PVC, and a value of the constant k_3 of the kinetic equation of this process was given. So, as at first understood, zinc stearate influences PVC thermal degradation in a different way than cadmium stearate and the two remaining stabilizers that were discussed.

Change in Color

From Figure 2, it can be seen that half the quantity of zinc stearate has reacted after about 5 min of time of degradation. About this time, a change in color of the sample began (Fig. 4). This change occurred after initiation very rapidly. These same results gave measurements of the absorption of solution of destroyed PVC, but the final changes were less, resulting from poor solubility of degraded polymer (Fig. 5). At the same time it could be noted that the colored polymer, in the course of degradation, was less soluble.

Changes in color of plasticized PVC including calcium stearate occurred after the start of heating, but after some time, the color of the sample became stable.

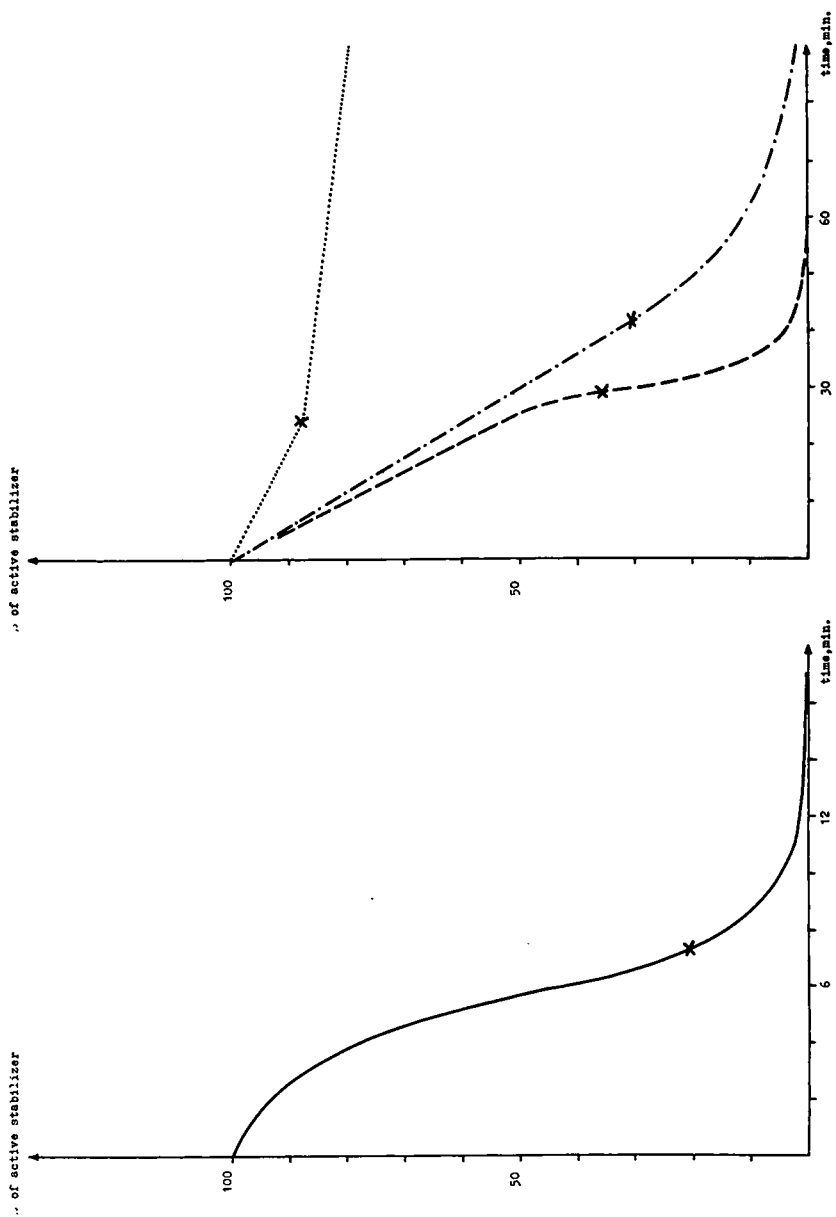


Fig. 2. Consumption of stabilizers (PVC-100, DOP-60 stabilizer-2): (—) zinc stearate; (---) cadmium stearate; (-.-.-) calcium stearate.

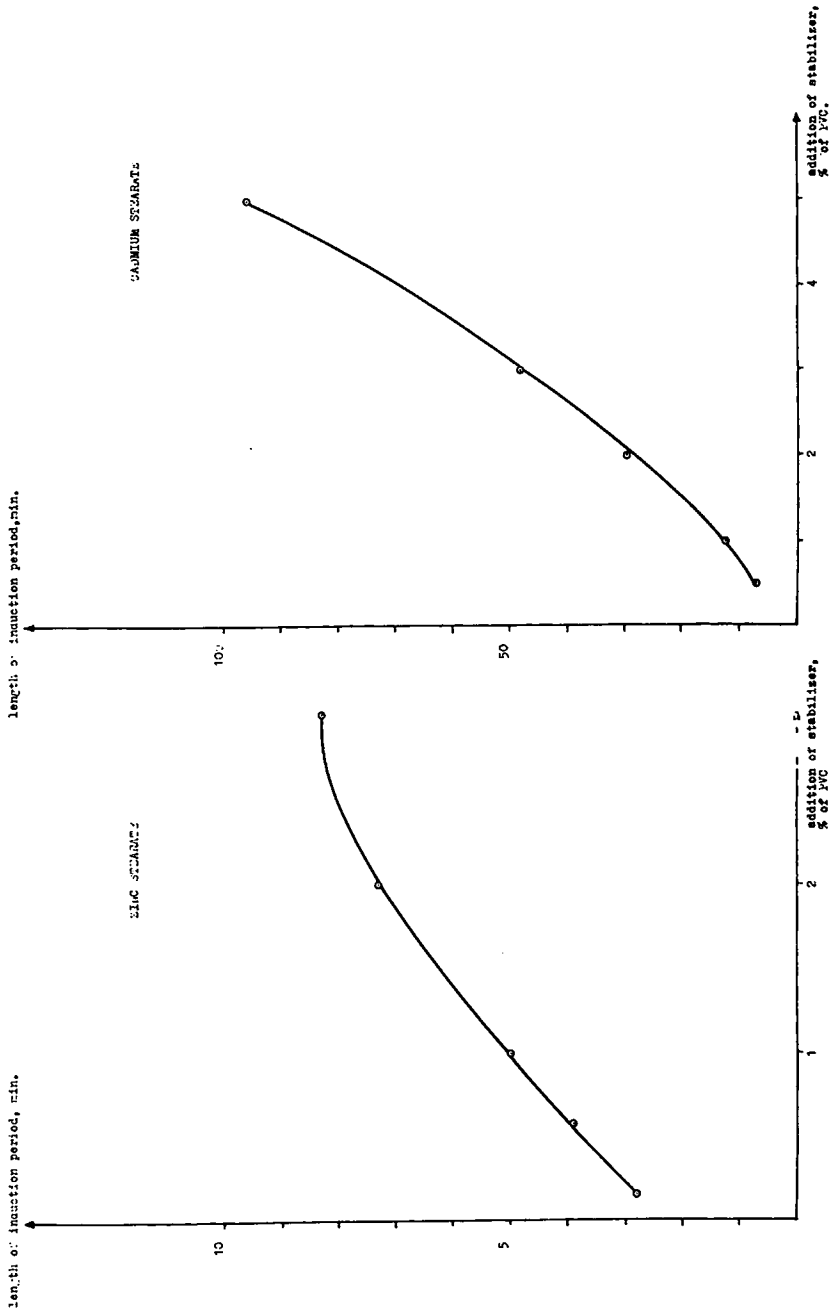


Fig. 3. Relation between the length of induction period and quantity of stabilizer.

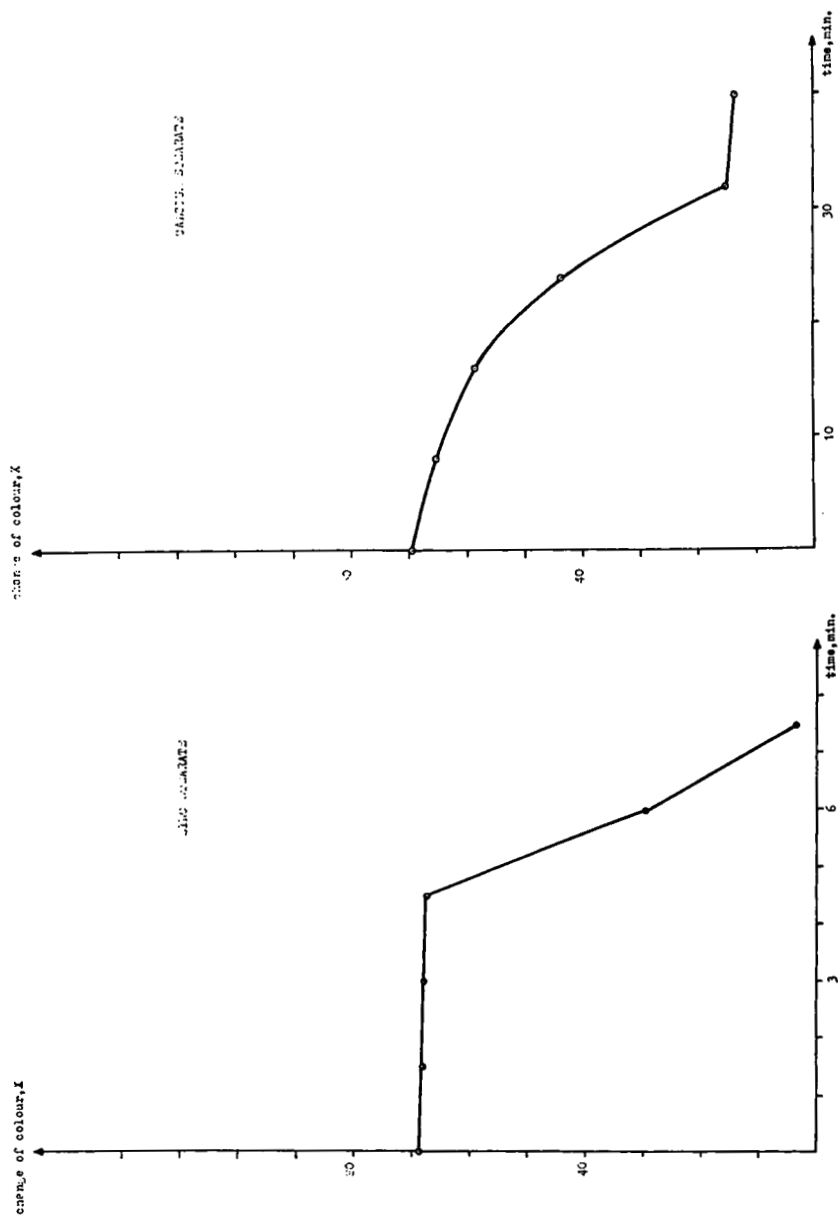


Fig. 4. Change in color during thermal degradation.

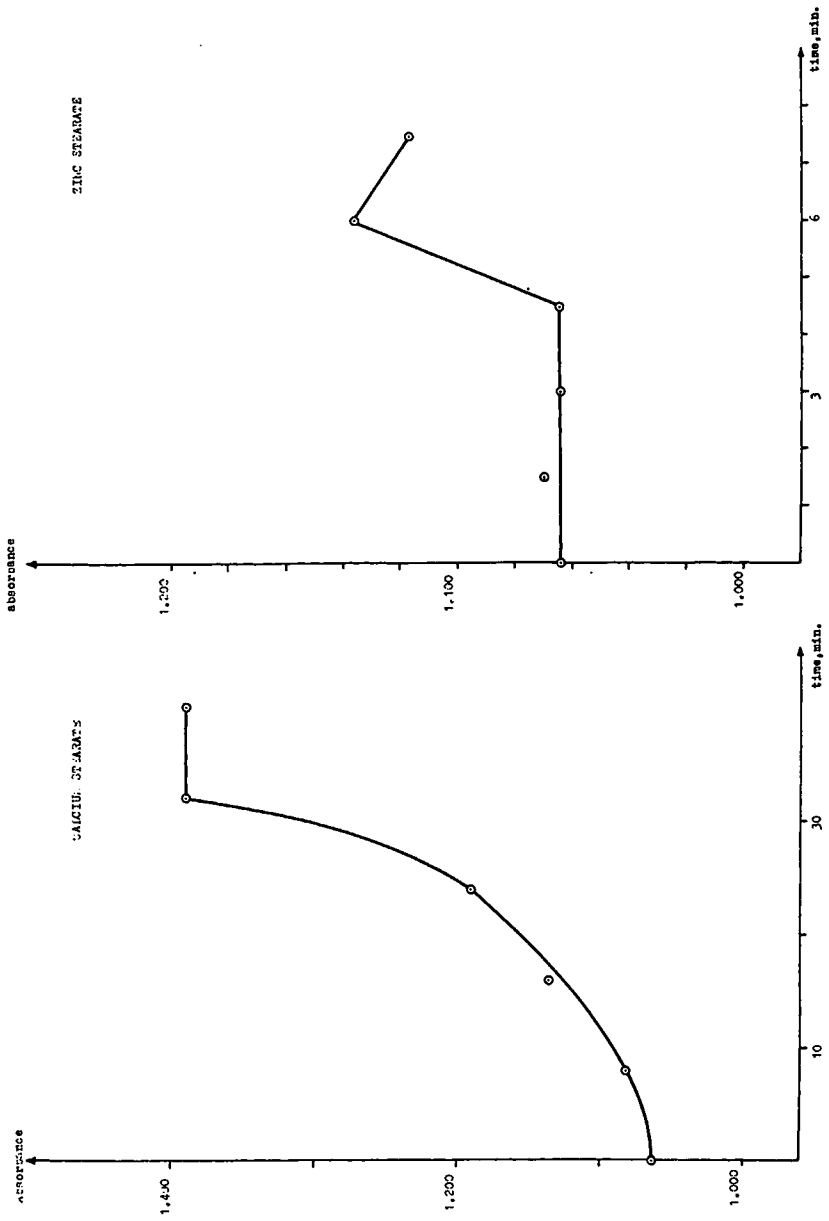


Fig. 5. Change in absorbance of solutions of thermally degraded PVC.

In this case, difficulties in the solution of the sample did not take place and because of that the character of both curves was identical.

Recapitulating, one reaches the conclusion that calcium stearate, although it absorbs hydrogen chloride, does not influence the color of the sample, which changes in the same way as an unstabilized composition. So acceptance of HCl alone is not sufficient for full polymer stabilization. The color of PVC was stabilized by zinc stearate more or less up to the moment of consumption of half of active stabilizer.

Change in Molecular Weight of Polymer

Changes in viscosity number during thermal degradation of PVC composition without stabilizer and the composition including calcium stearate were not found (Fig. 6). Therefore, calcium stearate is only an HCl acceptor; moreover, it is an almost neutral addition when it appears alone in the PVC composition.

A rapid crosslinking process takes place in the presence of zinc stearate at the same time as it stops the color stabilization, e.g., after consumption of 50% of active stabilizer. Therefore, only the crosslinking process connected with the action of zinc chloride should be taken into consideration.

The same results were also obtained with cadmium stearate, which in the first stage of the process of degradation did not cause a change in viscosity. This change appears between 18 and 24 min of decomposition time, which equals the reaction of about 50% of the active stabilizer shown in Figure 2.

The crosslinking process is also caused by dibasic lead stearate.

Taking into account the above mentioned data, the problem of the concentration of active stabilizer should be considered fully. Program CON 1, used in the calculation of the data shown in Figure 2, does not give separate quantities of stabilizer in initial form (stearate of corresponding metal) nor the partially reacted stabilizer with one molecule of HCl. Thus, concentration of active stabilizer refers to the HCl acceptance possibility.

At first, it seems to be impossible that all the stabilizer first reacts with one molecule of HCl and then with the next one. However, this can be easily understood if we take into consideration the rate of reaction of the stearate of the corresponding metal and the rate of reaction of the partially reacted stabilizer.

The values found in alcoholic dispersion¹² are as follows:

	Rate of reaction of R ₂ Me/ rate of reaction of RMeCl
Zinc stearate	18.92
Cadmium stearate	5.58
Calcium stearate	9.94

The considerably greater reactivity of metal stearate causes its reaction with HCl before the reaction of its monoadduct. In that case, it can be said that up to the moment of formation of metal chloride, crosslinking reaction of the polymer does not take place; thus, the cited opinions^{6,7} are confirmed. However, the dissimilarity of the action of zinc stearate still requires explanation.

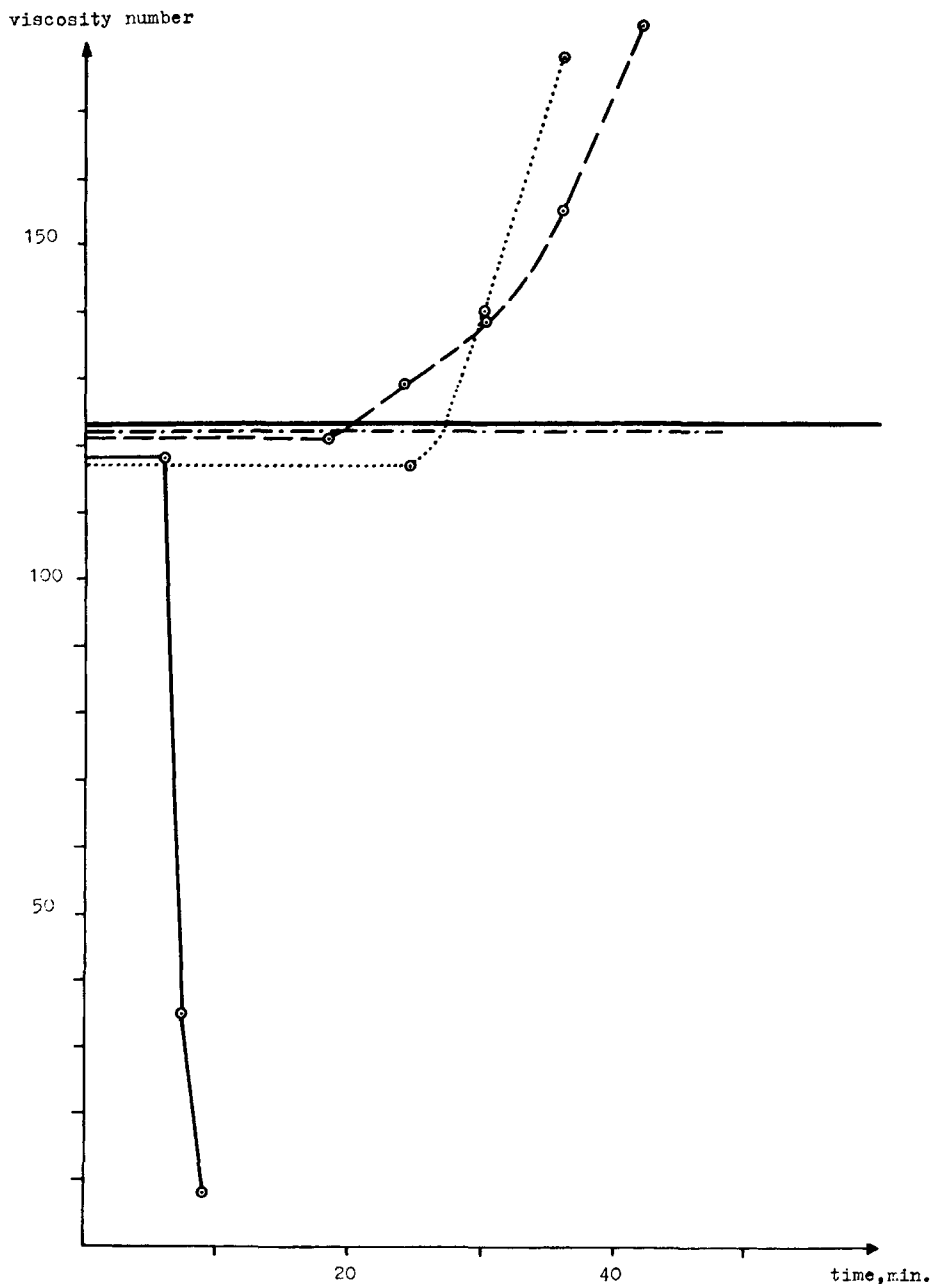


Fig. 6. Change in viscosity number of solutions of thermal degraded PVC.

Influence of Epoxy Stabilizers on Thermal Stability of PVC Composition

It was found that epoxy stabilizers participate in reversible reaction of HCl transference from degrading polymer to thermal stabilizer.¹³ This being so, epoxy stabilizers, in a way, isolate the thermal stabilizer from polymer. Based on data shown in Figure 7, it can be stated that the presence of epoxy stabilizers causes better consumption of thermal stabilizers.

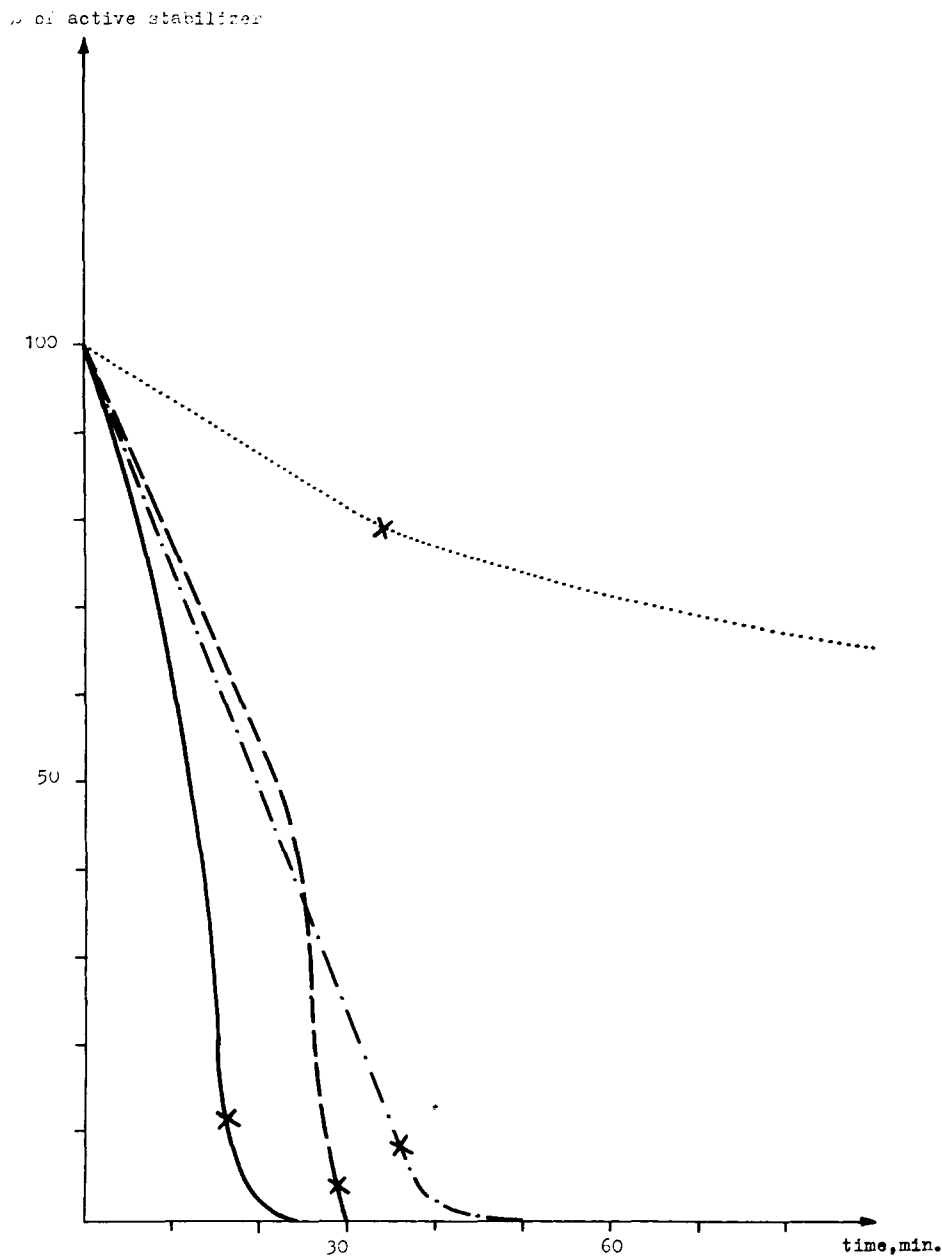


Fig. 7. Influence of epoxy stabilizer on consumption of thermal stabilizers of PVC.

Zinc stearate should be discussed separately. The addition of an epoxy stabilizer more than doubles the length of induction period. This fact cannot be explained by better utilization of the stabilizer, because this difference is too small for a considerable delay in the beginning of HCl emission. Explanation of this fact should be looked for in the mechanism of action of this stabilizer.

In the first stage of decomposition (up to the use of 50% zinc stearate acceptance ability), utilization of the stabilizer was nearly proportional to duration

time of degradation. Hence, reaction products of the zinc stearate accelerating PVC decomposition when zinc stearate alone was used, after introducing the epoxy stabilizer, did not have the same effect.

As was stated above, the epoxy stabilizer transfers HCl to the thermal stabilizer, and zinc stearate reacts with HCl bonded by epoxy stabilizer, producing free stearic acid. Hence, in the absence of an epoxy stabilizer other reaction should take place. The existence of two possibilities connected with the action of zinc stearate alone can be taken into account: (1) substitution of stearic acid into polymer chain, (2) acceleration of dissociation of C-Cl bonds connected with chemical affinity of zinc to chlorine.

Mechanism of Stabilizer Action

Zinc chloride is well-known in organic chemistry as a catalyzing agent in the substitution of acids and alcohols to double bonds. Based on this, free stearic acid was introduced to PVC composition including zinc chloride, but the anticipated decrease in the change in color and prolongation of induction period did not follow; contrariwise, the degradation of polymer was more rapid. From this fact the conclusion could be drawn concerning the ionic mechanism of PVC degradation. On the other hand, the possibility of substitution of stearic acid into the polymer chain is not fully excluded, but this process cannot have a catalytic character.

The possibility of substitution of stearic acid into a polymer chain can be confirmed only by determination of its concentration in the reaction mixture during thermal degradation, e.g., by paper chromatography. The chromatograms (Fig. 8) show that, in the case of calcium stearate, quantities of stearic acid proportional to time, were formed during degradation. PVC compositions including zinc stearate contained only trace quantities of stearic acid in the first step of degradation; but after 50% of this stabilizer had been reacted in the mixture, large concentrations of stearic acid were found. It may therefore be supposed that the substitution reaction of the second molecule of stearic acid proceeds at a poor rate, and the possibility of hydrolysis of stearic acid bonded with a polymer chain can be taken into account.

It may be assumed from evidence of kinetic data that the high chemical affinity of zinc to chlorine could cause the rate increase in HCl emission, but then in the case of compositions including calcium stearate the same process should be observed in connection with calcium position in the electromotive sequence. The accelerating effect of calcium stearate is not found, and consequently it can be said that the acceleration of the process of PVC thermal degradation is connected only with the presence in the polymer chain of stearic acid residue.

Taking into consideration the experimental data mentioned above, the mechanism of action of the investigated stabilizers can be explained.

Calcium Stearate. This stabilizer takes part in the reaction of acceptance of hydrogen chloride without additional influence on the composition color and the kinetic rate of its degradation (except the elimination of HCl catalytic influence). On the ground of its poor solubility in plasticizer at 180°C it is dissolved only partially, it has less reactivity than the place of calcium in the electromotive sequence of metals would lead one to expect. During thermal degradation two processes run simultaneously: (1) hydrogen chloride acceptance, (2) solution of the following portions of calcium stearate in place of reacted portions.

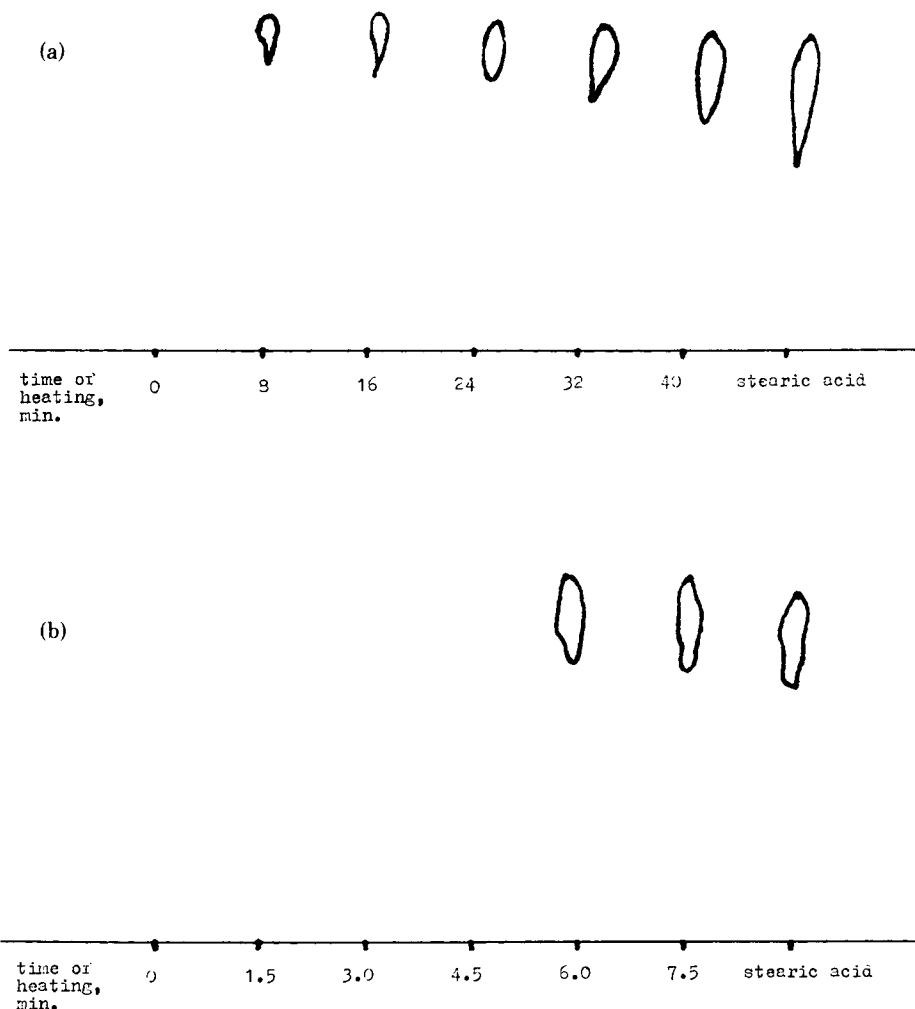


Fig. 8. Paper chromatography of stearic acid (PVC-100, DOP-60, stabilizers-2): (a) calcium stearate; (b) zinc stearate.

The beginning of HCl emission is connected with a decrease in the concentration of active stabilizer with the following relation:

$$v_2 = k_2[\text{RCaCl}]a_i$$

in $t_i = t_0, a_{t_0} = v_{2t_0}$. Hence

$$v_{2t_0} = k_2[\text{RCaCl}]a_{t_0}$$

and

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

where t_0 = beginning of HCl emission, k_2 = constant of reaction rate of partially reacted stabilizer with HCl, v_2 = rate of bonding HCl by partially reacted stabilizer, and a_i = quantity of HCl split-off in time $t_{i-1} \div t_i$.

Zinc Stearate. Beginning from the first stage of heating, zinc stearate reacts with great activity with hydrogen chloride according to the following

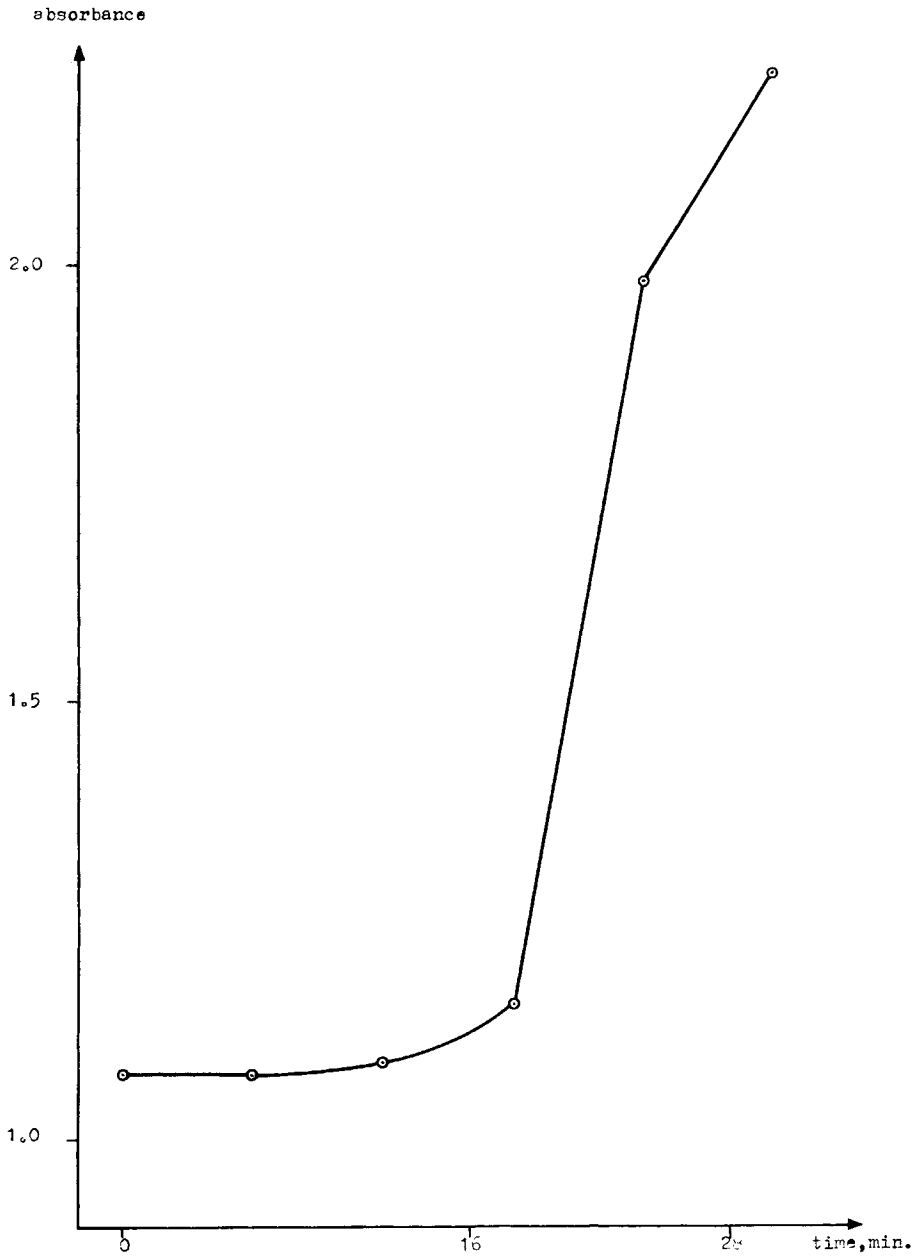
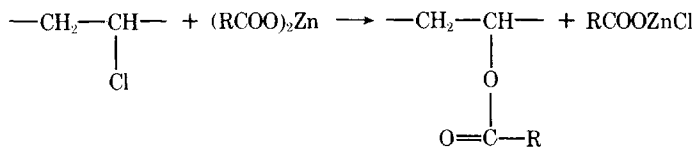


Fig. 9. Change in absorbance of thermal degraded PVC.

equation:



The reaction of substitution of stearic acid into the polymer chain takes place

only through the medium of zinc stearate. This reaction does not occur as a catalyzing process by using zinc chloride as the catalyst promoting addition of stearic acid to double bonds.

Because of the great difference between the reactivity of R_2Zn and $RZnCl$, zinc stearate reacts first. As a result, the polymer has an unchanging color because of the absence of correspondingly long polyene structures, but the presence in the chain of stearic acid residue causes changes in the distribution of charges, and at the same time the weaker C-Cl and C-H bonds undergo destruction more easily.

After nearly 95% of zinc stearate has been reacted (a result of the proportion of reactivity of the components), $RZnCl$ begins to react with corresponding efficiency, so zinc chloride forms as a product of this reaction. Zinc chloride intensively catalyzes the degradation process and causes crosslinking. This process is very rapid and leads to speedy and complete destruction of initial polymer properties.

During the degradation process, after the beginning of HCl emission, the rest of the stabilizer reacts, in connection with the reaction of degradation catalyzed by two products— $RZnCl$ and $ZnCl_2$ —and the presence in the chain of stearic acid residue, decomposition taking place increasingly slowly.

A considerable decrease in the rate of HCl emission suggests that hydrogen chloride in larger quantity causes the splitting off of the stearic acid residue from the polymer chain. The value of the rate constant of PVC thermal degradation is connected with the quantity of the residue of stearic acid remaining in the chain, the stage of crosslinking of the polymer, and the quantity of zinc chloride present in the composition.

The addition to the composition of the epoxy stabilizer causes a partial change in the mechanism of action of zinc stearate because of the greater reactivity of the epoxy stabilization. In that case, less of the stearic acid residue is substituted into the polymer chain, therefore the rate of PVC thermal degradation is decreased.

The participation of the reaction through mediation of the epoxy stabilizer and without it is proportional to the products of constant rates of reaction and concentrations of the epoxy stabilizers and zinc stearate.

Cadmium Stearate. The mechanism of action of cadmium stearate is similar to the mechanism of zinc stearate, with the dissimilarity that the rate of substitution of stearic acid residue is less than in the case of zinc stearate, so the catalytic effect is inconsiderable. In investigations of thermal stability, the effect of this process on the kinetics of degradation was not discovered (Fig. 2), but change in color occurs more slowly than in the case of a composition stabilized by addition of calcium stearate (Fig. 9). This leads to the conclusion that the process of stearic acid addition to the polymer chain is probable.

Lead Stabilizers. Their functions are similar to those of calcium stearate, excluding participation in crosslinking reactions. This reaction probably causes the stabilization of color for the isolation of sequences of double bonds. These stabilizers have the greatest acceptance possibility of HCl, which however, owing to poor reactivity of PbO , is used only partially. The chemical structure of lead stabilizers containing PbO favors the reaction of HCl acceptance, as can be seen from the reactivity of their components.¹²

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