

NOTES

Reactivity of PVC Thermal Stabilizers with Hydrogen Chloride in Alcoholic Solutions

Some works on the PVC destruction kinetics yielded doubtful mechanisms of stabilization of that polymer. The catalytic influence of HCl on the destruction^{1,2} has been called in question. Therefore, in the light of these investigations, some stabilizers, which are only acceptors of hydrogen chloride, should not react. The positive influence of these stabilizers pointed out in practice, on the other hand, cannot be contested.

Partial knowledge of the mechanism of destruction of PVC or of the mechanism of stabilization should not be so important if one can know the criteria of testing, choice, and dosage of thermal stabilizers.

Presently used laws of testing of full or even partial composition of stabilized polymer estimate only the stability of investigated composition. Except for knowing both above-mentioned mechanisms, the only way to know and to rationally apply the stabilizers is settlement of testing method on the basis of their own physical and chemical nature.

The one undoubtedly important behavior of stabilizers is their reactivity with HCl, because the reaction with hydrogen chloride is always the most important step in the stabilization process. Irrespective of the true mechanism of stabilizer action, this reaction is the first step of the stabilization process.

EXPERIMENTAL

As generally applied substances calcium, cadmium, and zinc stearates as well as plumbous stabilizers such as dibasic lead stearate and phthalate and tribasic lead sulfate were used. Lead oxide was applied for comparison.

Except for the above-mentioned, investigations of the reaction kinetics with HCl were done for the following industrial liquid stabilizers: Ba, Cd, Irgastab BC-30; Sn, Ergoterm BMB.

As one can see, the investigations were intended of the influence of kind of metal, organic radical, and state of stabilizer on the rate of reaction between stabilizer and hydrogen chloride.

The measurement of the kinetics of the reaction were carried out by the conductometric method in alcoholic solutions. The method of measurement of solution conductivity is very useful, because the rate of reaction can be recorded continually and, on the other hand, accurate determination of reacted stabilizer as a function of time is possible.

If the conductivity of 0.04N HCl may be compared to 100%, the conductivities of equal quantities of stabilizers and their reaction products with HCl will be as follows: stabilizers, 0.6-1%; PbCl₂, 0.7%; CdCl₂, 0.8%; ZnCl₂, 4.9%; CaCl₂, 10.2%; stearic acid, 0.4%.

While residual conductivity of solution, after the reaction of all components is finished, may be compensated, the error of the immediately measured value in the investigated range of concentration is very low, even if linear distribution of reaction products conductivity will be taken into account.

For greater accuracy, the results were read on the standard curves and the real quantity of reacted component was obtained. One method of measurement was applied for the elimination of casual errors.

An equimolar quantity of stabilizer was added to 130 cc of 0.04N HCl in *n*-propyl alcohol. Standard stirring and one-portion addition of stabilizer aliquot on the polyethylene plate were applied.

Changes in conductivity were recorded during the whole time of measuring. Obtained results were used to plot the per cent unreacted stabilizers versus time on Figures 1-3.

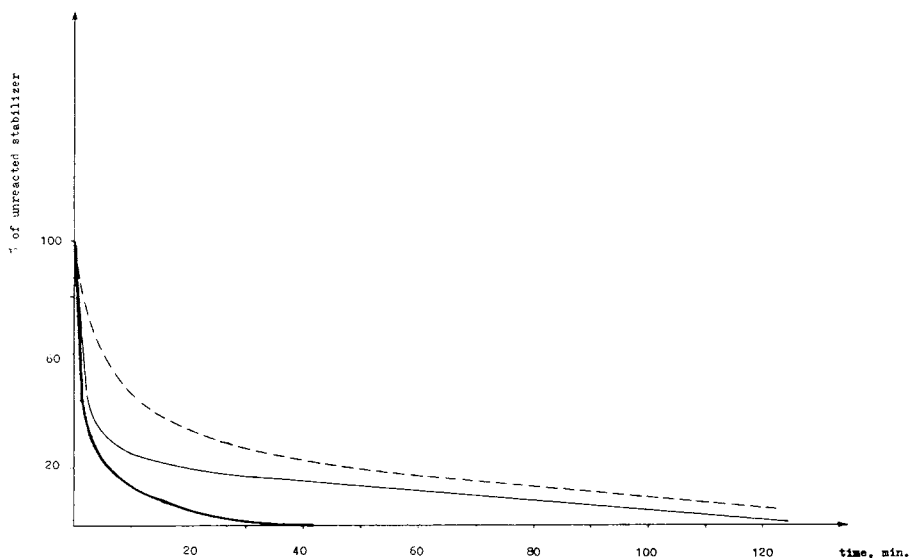


Fig. 1. Kinetics of reaction of PVC thermal stabilizers with HCl in *n*-propanolic medium: (---) Cd stearate; (—) Zn stearate; (-·-) Ca stearate.

The described method gave reproducible and quantitative data for all stabilizers, except for tribasic lead sulfate. The last one cannot be accurately measured by the described method while the conductivities of HCl and H₂SO₄ solutions are similar. Therefore, the curve of Figure 2 must be seen only as an illustration of probable changes.

DISCUSSION

Figure 1 illustrates the rate of reaction of stabilizers of metallic soap type. Salts of stearic acid with different metals were used. Reactivity of these stabilizers increased, as follows: Cd < Zn < Ca. It should be underlined that metals have the following normal potentials: Ca/Ca, 2.84 V; Zn/Zn, 0.76; Cd/Cd, 0.40 V.

On the basis of the obtained data, it can be confirmed that reactivity of PVC thermal stabilizers of metallic soap type depends on the place of the metal in electromotive series. Reactivity of these stabilizers increases with increase in electronegativity of the metal.

The above-mentioned observation leads to the partial explanation of the basis of the synergistic action of calcium and zinc stearates, mixtures of which are generally used with composition confirmed experimentally.³

The products of reaction of zinc stearate with HCl catalyze strongly the destruction of PVC. That is the reason why pure zinc stearate or another zinc derivative is not used for stabilization. Products of reaction of calcium stearate with HCl do not influence unfavorably the kinetic of PVC degradation. Synergistic mixtures of stabilizers of Ca-Zn, on the other hand, always contain low percentages of Zn derivatives.

With the help of the above-cited data, one can explain the role of Ca derivatives in those mixtures. This role probably consist in displacement of zinc from products of its reaction with HCl, which catalyze the destruction.

It does not explain, however, completely the problem of synergistic action because the role of organic Zn derivatives in synergistic mixtures is unknown in theoretical aspect. The explanation is a result of the method used and of the report.

The influence of the kind of acid on reactivity of stabilizer obtained from this acid is illustrated in Figure 2. It can be seen that dibasic lead phthalate is less reactive than dibasic lead stearate.

On the basis of these data, one can come to the conclusion that reactivity of stabilizers decreases when the power of the acid from which the stabilizer is obtained increases.

The illustrated curves lead to the conclusion as well that in the case of plumbous stabilizers

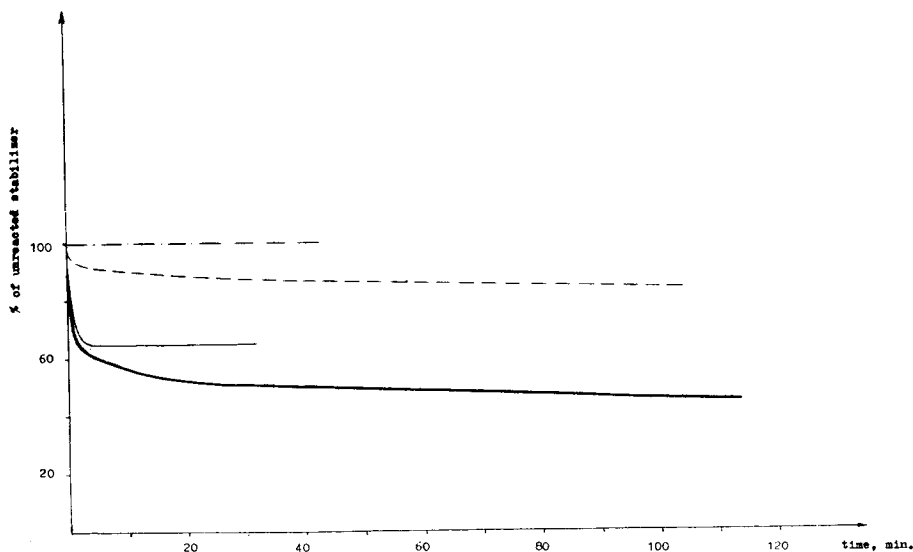


Fig. 2. Kinetics of reaction of PVC thermal stabilizers with HCl in *n*-propanolic medium: (---) PbO; (- · - · -) tribasic lead sulfate; (—) dibasic lead phthalate; (—) dibasic lead stearate.

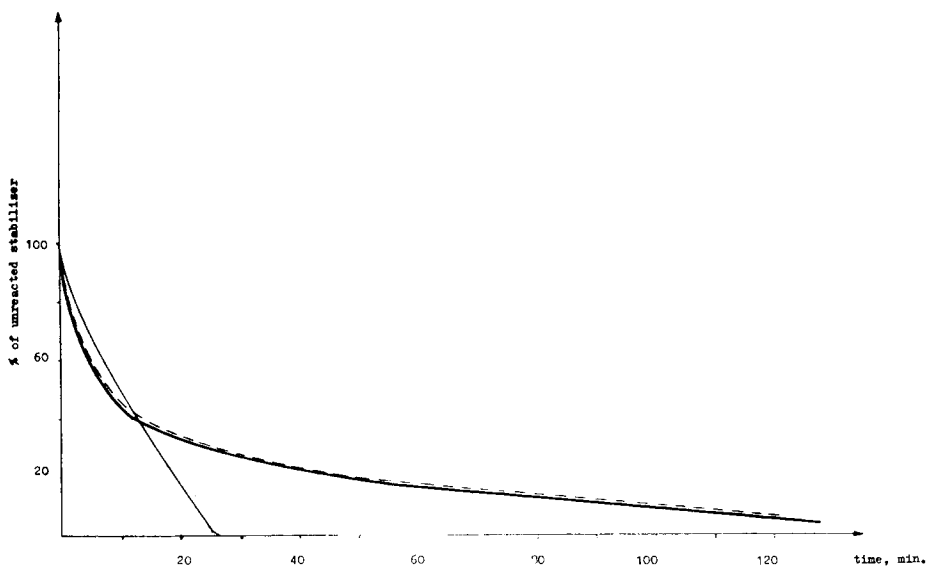


Fig. 3. Kinetics of reaction of PVC thermal stabilizers with HCl in *n*-propanolic medium: (---) Cd stearate; Ergoterm BMB (—); (—) Irgastab BC-30.

the lead salt first reacts with a big rate and then lead oxide reacts at low velocity. Rates of reaction of PbO in dibasic lead stearate and tribasic lead sulfate are the same. It is not confirmed that reaction between HCl and PbO from dibasic plumbous phthalate takes place.

The influence of lead sulfate and lead stearate on the reactivity of bonded PbO is another interesting fact. Without any presence of these salts, PbO does not practically react with hydrogen chloride. The last reaction is influenced by chemical structure of tribasic lead sulfate or dibasic lead stearate, while the mechanical mixing of PbO with PbSO₄ does not lead to mixtures with reactive properties.

The question of stabilizer state is the last one to be discussed. According to general meaning, solid stabilizer is less reactive than liquid one. This does not agree, however, with the obtained results. The rate of reaction of Cd stearate is the same as the rate of reaction of Irgastab BC-30 (Fig. 3) because of similar structure. Therefore, observed differentiations between the effectiveness of action of liquid and solid stabilizers cannot be explained by the higher reactivity of the former.

On the basis of the curve illustrating the rate of reaction of Ergoterm BMB, one can explain the high effectiveness of action of organotin stabilizers, which are very reactive and their rate of reaction is approximately constant until all components are used.

References

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