

## Radiation Yield of Hydrogen Chloride in Gamma-Irradiated Poly(vinyl Chloride) Stabilized by Epoxy Compounds

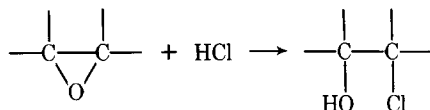
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### Synopsis

The  $G_{\text{HCl}}$  values of  $\gamma$ -irradiated PVC mixtures were studied after addition of various amounts of three epoxy stabilizers: diglycidyl ether of 2,2-bis(4-hydroxy-3-methylphenyl)propane (I); diglycidyl ether of 1,1-bis(4-hydroxyphenyl)cyclohexane (II), and butyl-*cis*-9,10-epoxystearate (III). The results indicated that two processes are essential for the stabilization: HCl capture by the epoxy groups, and an external protective effect, due to the remaining part of the stabilizer molecule. The role of the benzene rings in stabilizers I and II, as compared with the protective effect due to the long chains of stabilizer III, is not as dominant as one would expect.

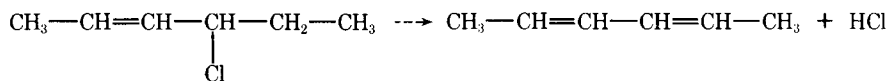
### INTRODUCTION

Epoxy compounds have been used as heat stabilizers of PVC for a long time.<sup>1-3</sup> In thermal degradation of PVC, it is usually assumed that the mechanism of the stabilizing action of the oxirane group is due either to a linkage of the group to double bonds in the PVC<sup>4</sup> or to a reaction with HCl according to the scheme

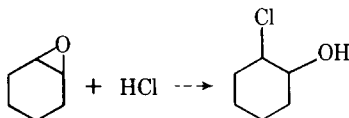


The synergistic effect in the presence of metal soaps as stabilizers<sup>5</sup> was believed to have its origin in the creation of a corresponding chlorohydrin and subsequent regeneration of the oxirane groups which, in turn, react with the HCl, a catalyst for the dehydrochlorination process.

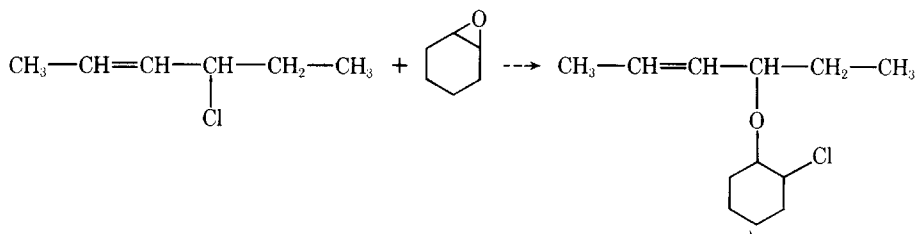
However, as a consequence of an investigation of the cyclohexene oxide used as an epoxy stabilizer model, in a reaction with the 4-chlorohexene-2 as a PVC model, a different mechanism of stabilization was suggested.<sup>6</sup> Instead of the conventional explanation



and



the creation of an ether linkage was assumed:



This assumption seems to be well founded in view of the results of IR analysis, mass-spectral analysis, NMR spectrometry, and thermal studies discussed extensively in reference 6. However, there still remains an open question of whether or not the mechanism of forming an ether linkage can be used also for the interpretation of other cases of stabilization with epoxy compounds which are different from the cyclohexene oxide model system.

Presently, there are practically no results concerning the stabilization with epoxy compounds of PVC irradiated with ionizing radiation. The few papers published on the subject of irradiated epoxy compounds concern only practical methods of producing improved plastics.<sup>7</sup>

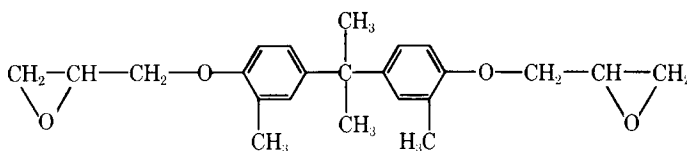
In this connection, it is our aim to study the mechanism of the epoxy stabilizer action in PVC systems, exposed to ionizing radiation. In this paper, we present some results of an investigation of different stabilizer behavior depending on its structure.

## EXPERIMENTAL

### Stabilizers

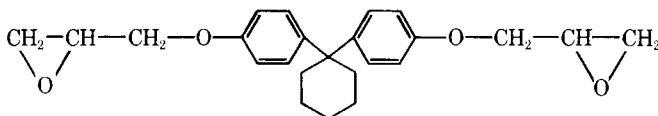
Three stabilizers were used:

I. Diglycidyl ether of 2,2-bis(4-hydroxy-3-methylphenyl)propane



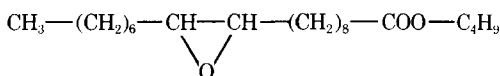
oxirane group content: calculated, 8.68%; determined, 6.63%.

II. Diglycidyl ether of 1,1-bis(4-hydroxyphenyl)cyclohexane



oxirane group content: calculated, 8.41%; determined, 7.54%.

III. Butyl-*cis*-9,10-epoxystearate



oxirane group content: calculated, 4.52%; determined, 3.02%.

### Preparation of Samples

Poly(vinyl chloride) S-68 P was used in all experiments.<sup>8</sup> A homogeneous mixture of PVC and stabilizer was obtained by settling the stabilizer from 1:1 methanol-acetone solution in a rotary vacuum evaporator at a temperature of 45°C. The samples were then dried at the same temperature in a vacuum drier until the solvent was completely removed. It was found that the  $G_{\text{HCl}}$  value for PVC treated with solvents did not differ from that of pure commercial PVC.

The samples were irradiated with  $\gamma$  rays from a  $^{60}\text{Co}$  source in a RHM- $\gamma$ -20 irradiation unit in a nitrogen flux of 50 ml/min. The dose rate, determined by a Fricke dosimeter, was  $0.97 \times 10^{18} \text{ eV cm}^{-3} \text{ min}^{-1}$  in the experiments with stabilizers I and II and  $0.88 \times 10^{18} \text{ eV cm}^{-3} \text{ min}^{-1}$  when stabilizer III was used.

### Measurements

The amount of hydrogen chloride which evolved during the irradiation of samples was determined continuously by the pH-metric method with the use of a measuring assembly as described in reference 9. The method consists in measuring the time required for neutralization of successively introduced, small amounts of a carbonate-free KOH solution with a concentration of 0.0134*M*.

It was found that the time needed for neutralization of the first 0.01-ml. portion of KOH was the initial time that characterizes the changes, depending on the stabilizer used, during the induction period. The initial yield,  $G_{\text{HCl}}^i$ , corresponds to the initial time.

The total radiation yield  $G_{\text{HCl}}$  for a given dose is characteristic of the entire process from the beginning of the irradiation to the moment at which the total dose is absorbed. Therefore, in order to visualize the changes caused by the irradiation in the system in short time intervals, we expressed the results in terms of the momentary radiation yield  $G_{\text{HCl}}^{\Delta t}$ . The  $G_{\text{HCl}}^{\Delta t}$  values were computed at time intervals of 5 min for the first 100 min and at intervals of 10 min for irradiation times exceeding 100 min.

## RESULTS AND DISCUSSION

Figures 1, 2, and 3 present the  $G_{\text{HCl}}$ -versus-dose dependence for PVC mixtures containing various amounts of stabilizers I, II, and III, respectively.

The similarity of the three curves is striking. The radiation yield  $G_{\text{HCl}}$  increases sharply in the initial period of irradiation. Starting with a dose of 1–1.5 Mrad, however, the rate of increase diminishes considerably, as in the case of pure PVC. The samples containing more than 2% stabilizer I, more than 1.5% stabilizer II, or above 4% stabilizer III show a much slower increase in  $G_{\text{HCl}}$  with increasing dose. The introductory time interval, corresponding to the fast increase in  $G_{\text{HCl}}$ , is especially short for stabilizer III.

To give a better idea of the time dependence of the studied processes, we plotted in Figures 4, 5, and 6 the momentary yield  $G_{\text{HCl}}^{\Delta t}$  versus the irradiation time for stabilizers I, II, and III, respectively.

In the case of mixtures containing only a small percentage of stabilizer, there are intervals where the  $G_{\text{HCl}}^{\Delta t}$  curve is parallel to the  $x$  axis, i.e., where  $G_{\text{HCl}}^{\Delta t}$  is dose independent. When the relative content of stabilizers I or II increases, some

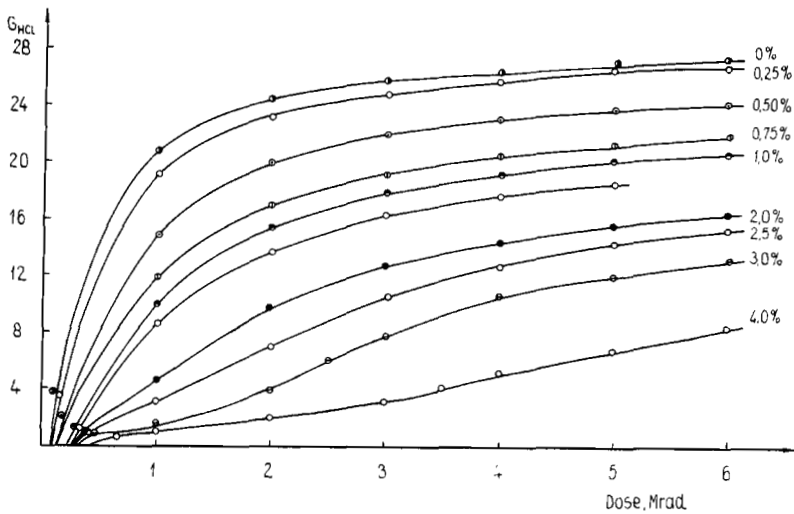


Fig. 1.  $G_{HCl}$  vs  $\gamma$ -irradiation dose for PVC with an admixture of stabilizer I (%).

inflection points turn up and the abscissas of these points increase with the amount of stabilizer.

In the case of stabilizer III, three different parts of the curves can be distinguished: The first portion of the curve is that where  $G_{HCl}^{\Delta}$  increases rapidly. In the second part of the curve, the  $G_{HCl}^{\Delta}$  is an almost linear, slowly varying function of the dose with a slope increasing with stabilizer content. In the last portion of the curve,  $G_{HCl}^{\Delta}$  is practically dose independent. For higher stabilizer contents, the differences become more apparent, and the second and third segments of the curves are shifted in the direction of higher doses.

One can infer from the curves in Figures 1-6 that two processes are essential for stabilization. The first process consists of HCl capture by the epoxy groups

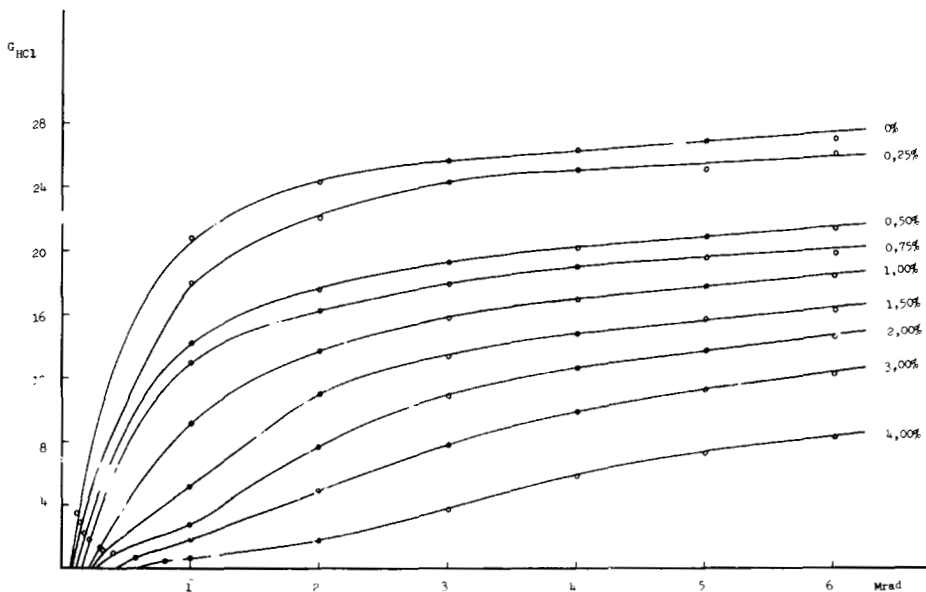


Fig. 2.  $G_{HCl}$  vs  $\gamma$ -irradiation dose for PVC with an admixture of stabilizer II (%).

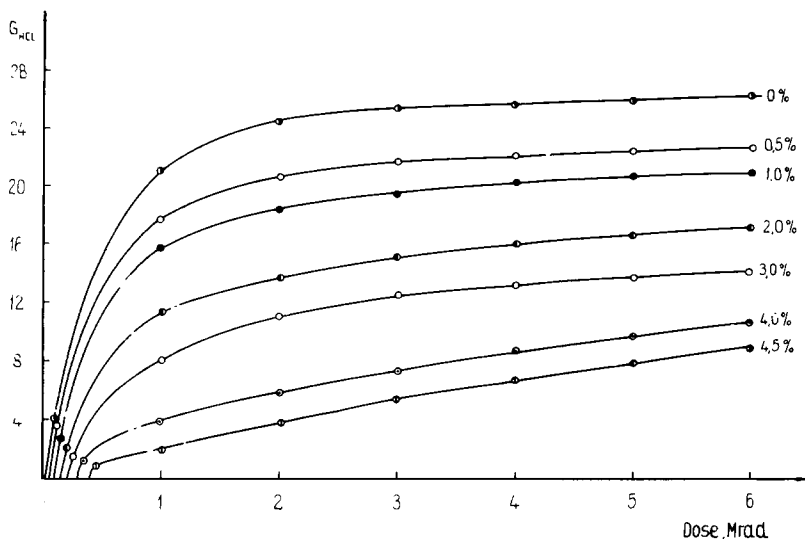


Fig. 3.  $G_{HCl}$  vs  $\gamma$ -irradiation dose for PVC with an admixture of stabilizer III (%).

in the early stages of the stabilization. This is illustrated by the inflection points, which are connected with the disappearance of the epoxy groups and, thus, are more apparent if the sample contains a higher percentage of the stabilizer. The second process, which is due to the influence of the remaining part of the stabilizer molecule, is the external protective effect. This effect becomes apparent where the curves run parallel to the  $x$  axis; it is dominant in the higher-dose region, and the higher the stabilizer concentration, the higher the dose required to reach this region.

Figure 7 shows the  $G_{HCl}^i$  as a function of stabilizer content (in per cent) during the induction period. The similarity of the results for both stabilizers I and II

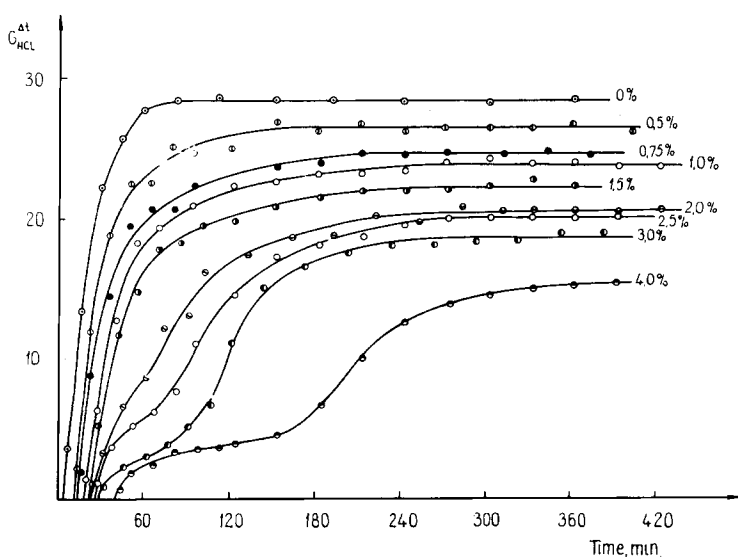


Fig. 4.  $G_{HCl}^i$  vs  $\gamma$ -irradiation time for PVC with an admixture of stabilizer I (%).

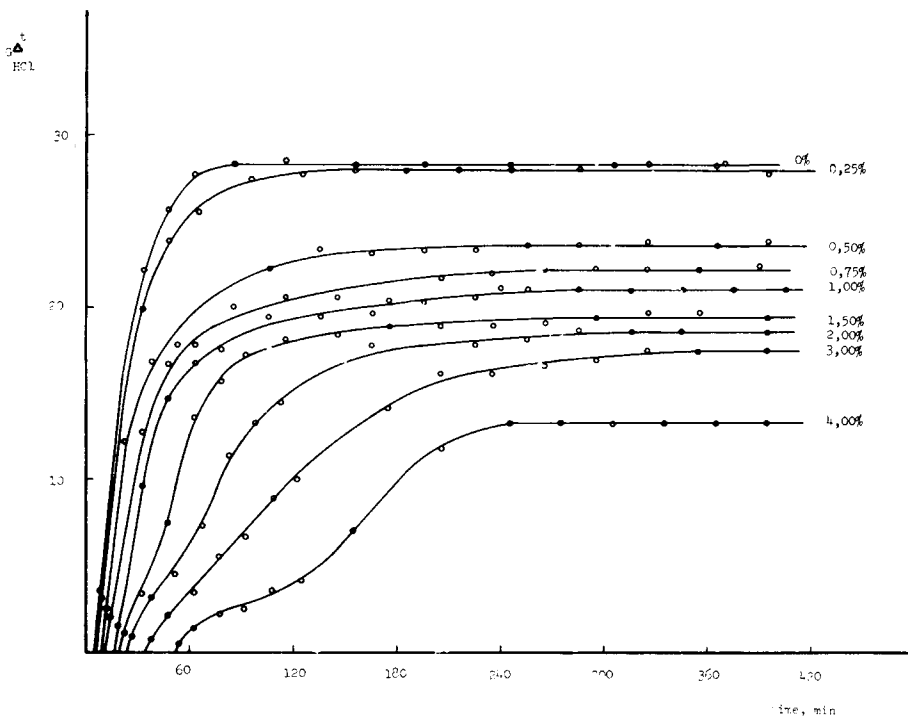


Fig. 5.  $G_{\text{HCl}}^i$  vs  $\gamma$ -irradiation time for PVC with an admixture of stabilizer II (%).

can be explained by the fact that the number of epoxy groups is similar in both cases: 6.63% and 7.54% oxirane groups, respectively. Since stabilizer III contains only 3.02% oxirane groups, the above arguments can also be used to explain the higher initial  $G_{\text{HCl}}$  value,  $G_{\text{HCl}}^i = 1.2$ , for stabilizer III (4% stabilizer) as compared with 0.65 and 0.51 for stabilizers I and II, respectively.

Taking into account the characteristic features of the stabilizer structures, one should expect more pronounced differences in stabilization with stabilizer III than with stabilizers I and II. The differences should become visible in consequence of the protective effect by the benzene rings, since the cyclohexane ring in stabilizer II has apparently little influence on the results.

The above supposition is supported, to some extent, by a comparison of the  $G_{\text{HCl}}$  values for mixtures containing the same amounts of the three stabilizers, and exposed to arbitrarily chosen doses of gamma radiation. Some of the results are presented in Table I.

The markedly weaker stabilizing effect of stabilizer III, however, does not justify the usually accepted opinion that the role of benzene rings is dominant in the stabilization. In view of the present results, we must conclude that, despite the fact that the protective effect of the benzene ring is quite significant, it is not dominant because the protective effect due to the long chains of the butyl epoxystearate is unexpectedly large.

Compounds similar to those in our work, but without oxirane groups, were reported by Popova and Janovski<sup>10</sup> as heat stabilizers. As a measure of the stabilizing effect, these authors used the rate of the dehydrochlorination process ( $\text{HCl}\uparrow$ )  $d(\text{HCl})/dt$ , which was assumed to be 100% for nonstabilized PVC.

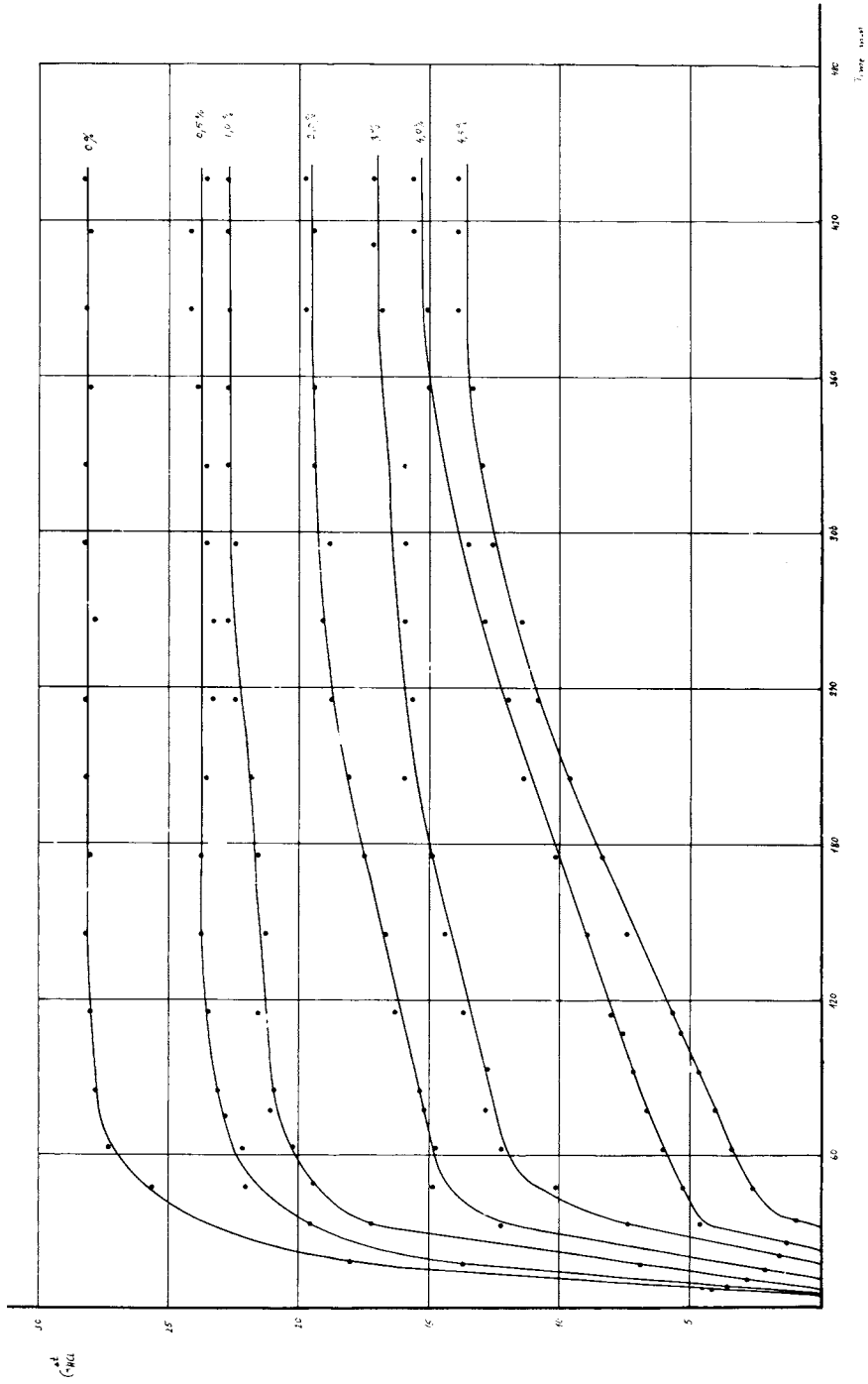


Fig. 6.  $G_{HCl}$  vs  $\gamma$ -irradiation time for PVC with an admixture of stabilizer III (%).

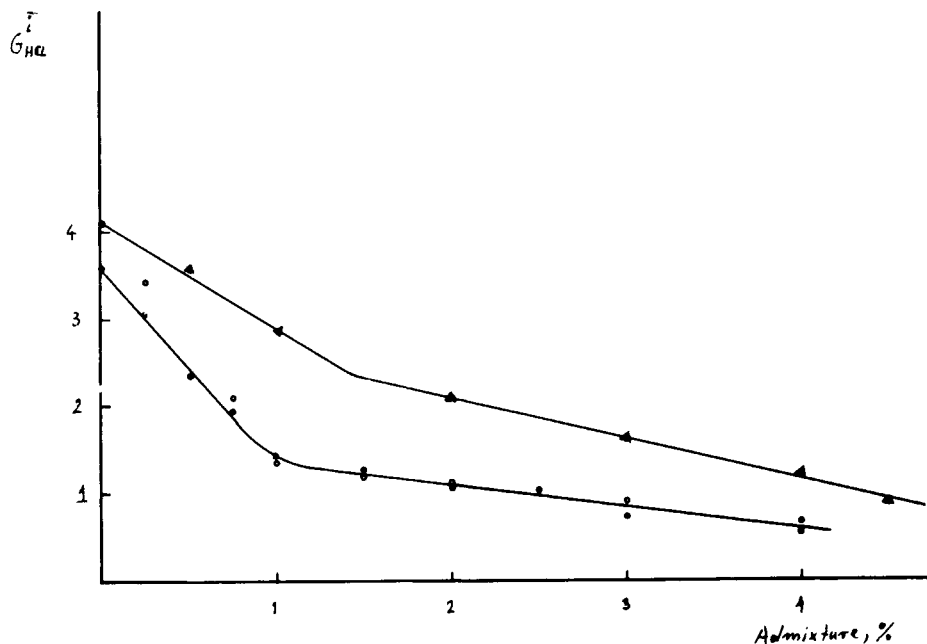


Fig. 7.  $G_{\text{HCl}}^i$  vs the stabilizer admixture (%): (O) stabilizer I; (●) stabilizer II; (▲) stabilizer III.

For several hydroxyphenone stabilizers, with four OH and two CO groups, the  $\text{HCl}\uparrow$  rate was 122%, 112%, and 123% when the number of the  $\text{CH}_2$  groups was 5, 7, and 8, respectively. In the case of 1,1-bis(4-hydroxyphenyl)cyclohexane with two OH groups and no  $\text{CH}_2$  and CO groups, the  $\text{HCl}\uparrow$  rate was 90%, while for hydroxydiphenyldecane with no CO, four OH, and ten  $\text{CH}_2$  groups, the  $\text{HCl}\uparrow$  rate amounted to 55%.

Consequently, it was natural to expect a protective effect of the benzene rings, especially in view of the fact that in our case the benzene was exceptionally resistant to radiation.

On the other hand, as is seen from the data above, the effect of chain length was not so apparent.

Therefore, the effect that occurs when stabilizer III is used is worth noting. This stabilizer was previously used by Berlin and co-workers<sup>11</sup> as a thermal stabilizer; epoxystearates behaved in a similar fashion.<sup>12</sup> According to the lit-

TABLE I  
Decrease in Yield of Hydrogen Chloride ( $G_{\text{HCl}}$ ) for PVC Mixtures at a 4% Admixture of Stabilizer

Stabilizer	Decrease in $G_{\text{HCl}}$ , %		
	1 Mrad <sup>a</sup>	3 Mrad	6 Mrad
I	94.7	87.8	69.6
II	96.9	85.0	69.1
III	80.1	71.4	59.2

<sup>a</sup> Irradiation dose.



erature, in the case of thermal stabilization, this stabilizer has both stabilizing and plasticizing properties. In our case, in view of the  $G_{\text{HCl}}$  values, it appears that protection against radiation takes place.

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