Studies on the Stabilization of Polyvinyl Chloride by Barium-, Cadmium-, and Zinc Stearates. I. Relationship between the Coloration and the Esterification[*1]

Toshio SHIMURA and Akihiko SAKAI
Industrial Research Institute of Kanagawa Prefecture, Kanazawa-ku, Yokohama
and Yoshikazu TSUJI[*2]
Department of Industrial Chemistry, Faculty of Engineering, Kanto Gakuin University, Kanazawa-ku, Yokohama

(Received June 6, 1966)

Although some kinds of metal carboxylate are used widely, the mechanism of their stabilization is not yet clear enough. Recently, studies on the dehydrochlorination and coloration of PVC charged with some metal stearates have been reported by Nagatomi *et al.*,[1] studies on the esterification of PVC by some metal 2-ethylhexanoates in which the carboxyl group is labeled by ^{14}C, by Frye *et al.*,[2,3] and studies on the stabilization of the co-polymer of vinyl chloride and vinyl acetate by some metal stearates, by Sakura *et al.*[4]

In this work, the behavior of the stearyl groups of barium-, cadmium-, and zinc stearates at the time of the heat-degradation of PVC has been studied by the use of a radioactive tracer technique; the degree of coloration of the polymer has also been determined. It has been found that the esterification by the metal stearates is closely related to the coloration of the polymer. The results obtained here are substantially the same as those reported by Frye and other workers.

This paper has been reported to give information which may be as to ascertain the mechanism of the stabilization of PVC by these salts.

Experimental

Radioactive Stearates. The radioactive barium-, cadmium-, and zinc stearates were prepared by a neutralization reaction between the corresponding metal hydroxide and the radioactive stearic acid which was labeled at the carboxyl group (0.2 mCi of the supplied acid[*3] was diluted by the addition of 18 g of the nonradioactive acid).

Preparation of the Sample for Heat Treatment. The PVC employed here was GEON 103-EP; it was used as it stands (in a state of powder) to avoid any influence in the course of processing from it or from plastisizers. The metal stearates (0.5 mmol) were charged into 40 g of PVC and the resulting mixture was well mixed by a ball mill for 24 hr.

Heat Treatment. The apparatus for heat treatment was set up with reference to the ASTM Standards[5] and to the paper reported by Nagatomi *et al.*[1] About 10 g of the sample was charged in a flask placed in an oil bath of constant temperature and heated at $150\pm0.5^\circ$C in a current of nitrogen.

Measurement of Reflectance. In the course of heat treatment, nearly 0.5-g portions of the ground powder were withdrawn at certain predetermined intervals, and their reflectances measured by a color-difference meter (model TK-101) manufactured by the Tokyo Kogyo Co., Ltd.

Preparation of the Sample for the Measurement of the Radioactivity. The sample of which the reflectance had been measured was dissolved in *ca.* 30 m*l* of tetrahydrofuran, and the resulting solution was filtered to remove the unchanged metal stearate as a residue. The filtrate was then treated by the slow addition of *ca.* 50 m*l* of methanol accompanied by vigorous stirring; by collecting the precipitated PVC by filtration and by washing it with small portions of methanol, the eliminated stearic acid was removed. The precipitate was then redissolved, reprecipitated, recounted through three successive cycles, and dried in air. Since, in the heat treatment, the polymer charged with the zinc salt becomes scarcely soluble in tetrahydrofuran after the induction period, in such a case the liberated acid was thoroughly extracted with diethyl ether.

Measurement of Radioactivity. In a measuring bottle, 0.1000 g of the dried sample was exactly weighed within a ±0.2 mg accuracy[*4]; then it was completely dissolved with 8 m*l* of tetrahydrofuran. Ten milliliters of toluene and 2 m*l* of a concentrated scintillator solution were then added with suitable syringes.

The radioactivity measurements were made using a liquid scintillation spectrometer (model TRICARB, series 314E) manufactured by the Packard Instrument Co., Inc. Each sample was counted for a period of 10 min and the count corrected for background radiation, which was counted every 2 hr.

[*1] Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

[*2] Present address: Nihon Riken Gomu Co., Zama, Koza-gun, Kanagawa.

1) R. Nagatomi and Y. Saeki, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 396 (1962).

2) A. H. Frye and R. W. Horst, *J. Polymer Sci.*, **40**, 419 (1959).

3) A. H. Frye and R. W. Horst, *ibid.*, **45**, 1 (1960).

4) T. Sakura and T. Koshiishi, The 13th Annual Meeting of the Chemical Society of Japan, Preprint, 5T54 (1960).

[*3] It is of the type of $C_{17}H_{35}{}^{14}COOH$ and was supplied as a benzene solution (0.25 mCi/m*l*) by the Daiichi Kagaku Yakuhin Co., Ltd. Its specific activity was 30 mCi/mmol and the purity, over 99%.

5) D 793-43.

[*4] The concentration of the sample solution must be kept constant in liquid scintillation counting.

Results and Discussion

At the time of the heat treatment of PVC charged with barium-, cadmium-, and zinc stearates, an inflection point was observed in the curves of the degree of coloration of the polymer where the introduction of radioactivity into the polymer reached a maximum. This point appears to be the end point of the so-called induction period.

In Figs. 1, 2, and 3 are plotted the measured extents of the coloration of the polymer and of the introduction of radioactivity into the polymer. The degree of coloration is represented in terms of a degree of the reflectance of the heat-treated polymer powder, and the introduced radioactivity is shown by the percentage of such introduced radioactivity to that of the sample before heat treatment.

When the barium salt was used, the inflection point was hardly observed at all because of its extreme obscurity. However, the existence of this point could be noticed where the curve of the introduced radioactivity reached a maximum (Fig. 1). In the case of the cadmium salt, the point was clearly observed not only where the lightness but also where the tone of color of the polymer changed, and where the curve of the introduced radioactivity reached a maximum (Fig. 2). In the case of the zinc salt, the polymer changed, in an instant, from white to dark blue *via* light purple at this point, and the curve of the introduced radioactivity reached a maximum (Fig. 3). Both the position and the height of the inflection point were determined, it is generally believed, by the particular metal ion composing the salt.

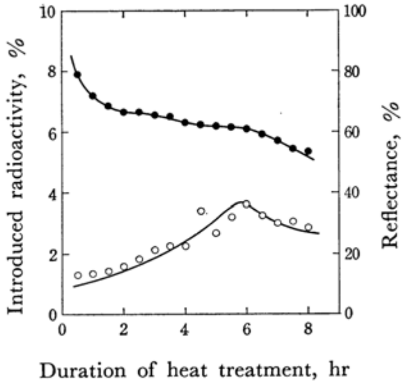

Fig. 1. Curves of the degree of coloration (●) and the introduced radioactivity (○) when barium stearate was used.

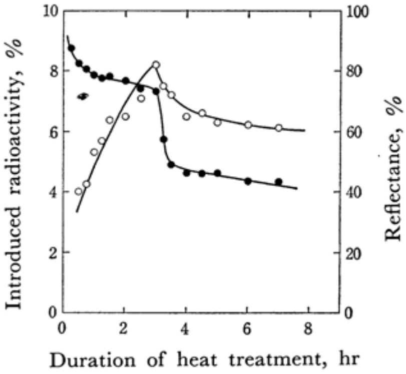

Fig. 2. Curves of the degree of coloration (●) and the introduced radioactivity (○) when cadmium stearate was used.

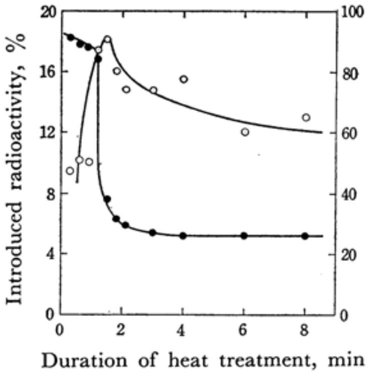

Fig. 3. Curves of the degree of coloration (●) and the introduced radioactivity (○) when zinc stearate was used.

Since the introduction of radioactivity appears to mean that an esterification reaction occurs between the polymer and these metal stearates, as has been stated by Frye *et al.*,[3] it may be said that the esterification ability of zinc stearate is greater than that of the cadmium or barium salt under the conditions studied. The ratio of the maxima of the degrees of esterification by these salts was:

barium stearate : cadmium stearate : zinc stearate=3.6 : 8.2 : 19.1.

The degree of esterification could not be determined quantitatively in the present investigation, because it is considered to be unreasonable, in a liquid scintillation counting, to regard the stearyl groups which are introduced by the esterification into the polymer chain in the same light as those of the metal stearate; the count number of the former can not be compared with that of the latter. Therefore, another, more proper method must be devised to determine it quantitatively.

The authors wish to thank Mr. Akira Ohno and Mr. Isamu Ono, engineers of the Radioisotope Laboratory of their Institute, for the suggestions and directions during their work of radioactive assay.