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Stabilization of Poly(vinyl Chloride) by Eutectic Mixtures

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ABSTRACT

An eutectic mixture of sodium and potassium nitrites and nitrates which is liquid at the processing temperature is proposed as a new efficient stabilizer for PVC.

INTRODUCTION

Parallel to the wide industrial use of already established stabilizers the investigations directed to clarifying the nature of the degradation stabilization of PVC and creating new stabilizers are in process.

For several years, we have been studying the possibilities of PVC thermostabilization by alkaline nitrates, within the scope of a program of investigation of polymer nitration processes. The results to now [1-5] showed that this class of chemical compounds has stabilizing effects due to its well balanced accepting action, as well as by the nitric acid and nitric oxides, respectively, separated as a result of an exchange reaction. Such a combined action provides for a considerable stabilizing effect at comparatively low concentration of the stabilizer.

The alkaline nitrates remain solid at the temperatures used in PVC processing. Therefore, only the surface layer of the solid nitrate crystals is "active" in the stabilization process. For this reason, a very important problem is the maximal stabilizer dispersion. The solution of this problem is in all cases restricted on principle. The present work is an attempt to solve the problem of homogenization by use of an eutectic mixture of KNO_3, $NaNO_3$, and $NaNO_2$ which has a melting temperature of 142.5°C, which will liquefy under the temperature of PVC processing (150-230°C).

EXPERIMENTAL

The PVC used was a suspension-type, industrial grade S-PVC 64 with $K_V = 64$, a product of Devnia. The eutectic mixture was prepared by melting together 53 parts by weight of KNO_3, 7 parts of $NaNO_3$, and 40 parts of $NaNO_2$. The mixture was ground after cooling.

The samples for investigating the dehydrochlorination, for carrying out DTA and TGA, and for studying the color change, were prepared from films made by rolling PVC in the presence of the proper quantity of eutectic mixture for 3 min at 160°C.

The dehydrochlorination was studied using a procedure described previously [6].

The color stability was checked out by heating the samples in air-circulated oven at 175°C. The color change of the sample was rated on a 10-step scale where the following code was used: 0, no change, 1, visually detected change; (2) color change; (3) light yellow; (4) yellowish; (5) yellow-brownish; (6) yellow-brown; (7) dark yellow-brown; (8) brown, (9) dark-brown; and (10) brown-black.

DTA and TGA were performed on a Derivatograph, in air, at a heating rate of 6°C/min.

RESULTS AND DISCUSSION

The eutectic mixture we used is composed of two types of alkaline salts: nitric acid and nitrous acid. The alkaline nitrites have been shown [5-7] to accelerate dehydrochlorination. To study the concurrent action of the two types of salts in the ratios designated, we observed the release of free HCl under heating of PVC in the presence of the eutectic mixture (3.3×10^{-5} mole/g PVC), and the results obtained were compared to those of PVC without eutectic mixture (Table 1).

If the salts composing the mixture acted only as acceptors of HCl, or if predominant reaction were the acceleration of dehydrochlorination, on heating 25-30 min the salts would be converted entirely into chlorides,

TABLE 1. PVC Dehydrochlorination at 175°C in Air

	HCl evolved at various heating times (10^{-5} mole/g PVC)						
	15 min	20 min/	25 min	30 min	40 min	50 min	60 min
PVC	0.53	1.1	2.2	3.7	8.1	11.6	15.8
PVC plus 3.3 10^{-5} mole eutectic mixture/g	-	-	0.1	0.7	2.7	7.8	8.9

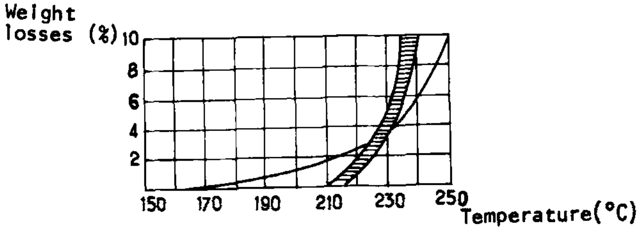

FIG. 1. TGA curves of PVC in the absence and presence (shaded band) of 0.1-2 wt % eutectic mixture.

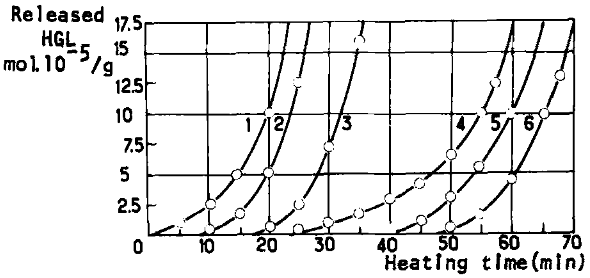

FIG. 2. Dehydrochlorination of PVC in air at 175°C: (1) PVC alone and with (2) 0.1 wt % (3) 0.3 wt %, (4) 0.5 wt %, and (5) 2 wt % eutectic mixture.

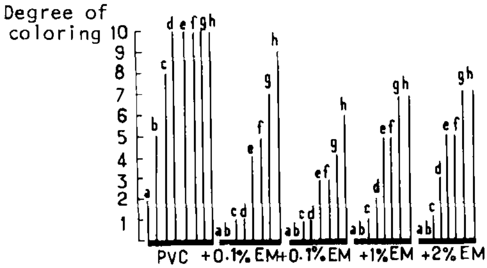

FIG. 3. Stability of the color of the PVC films in the presence of eutectic mixture with heating at 175°C for various periods: (a) 20 min; (b) 40 min; (c) 60 min; (d) 80 min; (e) 100 min; (f) 120 min; (g) 140 min; (h) 160 min. Color rated on 10-step scale as described in text.

and then the evolution of HCl from the two samples would be the same. The results in Table 1 show that the difference in the quantities of HCl evolved from the two samples is greater, the greater the HCl accepting facility of the added eutectic mixture. Therefore, irrespective of the presence of $NaNO_2$, the eutectic mixture has a stabilizing action towards the PVC.

No change was found on the DTA curves, neither in the temperatures at which intense decomposition begins (247°C), nor in the minimum temperature of dehydrochlorination (280°C). This fact agrees with the data of Gaylord and Takahashi [8] for the other PVC stabilizers, CdSt for instance. The TG curves show (Fig. 1) that the eutectic mixture delays the onset of dehydrochlorination. process. Another conclusion of the TGA is that the influence of the concentration of the eutectic mixture on the stabilizing effect is small. The small influence of the mass of the added eutectic mixture on its efficiency is stressed, especially on the concentration increase. This is confirmed by the dehydrochlorination curves (Fig. 2) which give more accurate data for the initial period of degradation. An explanation for this fact may be an increase in the quantity of $NaNO_2$ with the increase of the total quantity of eutectic mixture.

A very important aspect of the PVC stabilization is the delay of the polymer coloring on heating. The plots shown on Fig. 3 confirm the stabilizing action and the discussed concentration dependence. The best conditions for homogenization of eutectic mixture to compete with the acceleration of the dehydrochlorination action of $NaNO_2$ are important.

REFERENCES

[1] Bulg. Pat. 15940 (1970).

[2] I. Mladenov and G. Slavov, paper presented at International Symposium on Polymers, Varna, Oct. 7-10, 1971.
[3] I. Mladenov and G. Slavov, paper presented at International Conference, Bratislava, June 22-24, 1971.
[4] I. Mladenov and G. Slavov, paper presented at International Symposium on Polymers, Varna, Oct. 4-6, 1973.
[5] I. Mladenov and G. Slavov, paper presented at International Symposium on Degradation of Polymers, Brussels, Sept. 9-11, 1974.
[6] D. Braun and M. Thallmaier, Kunststoffe 2, 44 (1969).
[7] Z. Wimazalowa et al., Plast. Mod. Elast., 21, 157 (1969).
[8] N. Gaylord and A. Takahashi, Multicomponent Polymer Systems, Khimia, Moscow, 1974, p. 246.

DISCUSSION

Dr. Jungk (Metall Gesellschaften, Frankfurt, Germany): A comment on a completely different topic: Dr. Shakoor presented us a revolutionary new stabilizer system using the nitrates and nitrites. What is hindering us from using those nitrates and nitrites in pipe extrusion or calendering? What kind of gases will be evolved when those systems are used?

Dr. Shakoor: This program is not a new one. It was published after the last symposium on degradation and stabilization held in Brussels. We have a patent in this field. We can add this source of stabilization in the latex formation step because these stabilizers are water-soluble. Good results are obtained in this way for emulsion polymers of vinyl chloride. We have processed poly(vinyl chloride) polymerized by this method after drying from latex, and have good results in calendering and also in extruding processes.

To answer your second question, I have to give you some details about the influence of nitric acid and nitrous oxides on degradation of PVC. If PVC is processed with concentrated nitric acid, it will produce some colored water-heated PVC in an atmosphere of nitrous oxides; the process of dehydrochlorination will be accelerated at the same time discoloration is bleached. This can be explained by the possibility of adding the "nitro groups" to unsaturated bonds "polyene structures" which are formed through destruction of PVC. Anhydrous nitrates, such as sodium or other alkaline nitrates have a stabilizing effect, i. e., decrease the rate of dehydrochlorination. It is logical to assume the development of combination reactions:

$$HCl + NO_2 \longrightarrow HNO_2 + Cl^{\cdot}$$

$$HNO_2 + HCl \longrightarrow H_2O + NOCl$$

$$NOCl + {}^{\cdot}Cl \longrightarrow NO + Cl_2$$

in which allylic structures responsible for the chain propagation are destroyed. Both nitric oxides present in the system and chlorine obtained by the reaction can compete with the dehydrochlorination process and to a large degree improve the polymer thermal stability. Such stabilizers can work in both static and dynamic conditions. We have obtained good results by using the Brabender Plastograph at 190° C. PVC processed with these stabilizers show a longer stabilization period, then, for example, compounds containing lead, such as dibasic lead phthalate. From this point of view, we can decide that such stabilizers can be used successfully in industry, because they are cheap and do not lead toxic properties of the final products.

Dr. Jungk: Did you ever measure the evolution of nitric oxides from the PVC sheets?

Dr. Shakoor: In this system we have not seen any clear vapor. This means they might be formed for a very short time and then vanish, or that they form in very small amounts. There appears to be no deleterious effect to the surface of the metal of the processing machines.