ml of cyclohexane in a concentration of 0.01 ppm. To the second 1000 ml of solvent hexane 0.01 ppm 3,4 benzpyrene was added. Cetane was not used in either solvent. The full 1000 ml was evaporated in each test and the residues were dissolved in 10 ml of cyclohexane. UV analysis showed an absorbance of 0.128 at 385 mμ for the cyclohexane sample, and 0.120 for the solvent hexane sample. Assuming a straight line calibration curve, this would indicate 100% and 94% recovery, respectively.

These results prove the validity of the technique outlined in the procedure section. The techniques present an accurate and valid means of determining the amount of nonvolatile material in solvent hexane, and of analyzing the resulting residue. The addition of cetane is a precautionary measure to eliminate the critical nature of the evaporation step. The use of cetane is recommended as part of the procedure in cases where several samples are being analyzed simultaneously, or when the evaporation cannot be closely watched. However, as the results show, cetane addition is not essential.

It is also noted here that a blank determination should be made on the cyclohexane used for washing. The residue from the blank, after dilution, should be checked for UV absorption. A correction should be made in the final calculations for absorption noted here.

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Vernonia anthelmintica Willd. Seed Oil and Salts of Vernolic Acid as Stabilizers for Plasticized Poly (Vinyl Chloride)[1]

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Abstract

Vernonia anthelmintica seed oil, trivernolin, the main constituent of the oil, barium and cadmium salts of vernolic acid (epoxyoleic acid), and various combinations of the salts have been evaluated as heat and light stabilizers of plasticized poly(vinyl chloride). Evaluation was made at the 1 and 3% levels of the vernonia oil components. Transparent sheets whose color ranged from light amber to colorless were obtained after milling and molding. All compounds studied greatly improved both heat and light stability of the sheets; the 3% stabilizer level gave the better results. In general the stabilizing ability of the compounds studied increased as follows: vernonia oil < trivernolin < barium vernolate < cadmium vernolate and < barium-cadmium vernolate mixtures. Comparisons with 3 commercial stabilizers show that the vernonia oil and derivatives thereof are equal to or better than the comparative commercial controls.

Epoxidized oils are being used extensively to stabilize poly(vinyl chloride) containing plastics against heat and light degradation. When used in combination with metal salts of fatty acids the stabilizing action is improved through synergism (1,2). Therefore, a study was made of the heat and light stabilizing properties of the natural epoxy oil from the seed of *Vernonia anthelmintica*, trivernolin (the main constituent of the oil), the barium and cadmium salts of vernolic acid (epoxyoleic acid), and combinations of the salts.

Experimental

Materials. The materials used in this investigation are:

	% Oxirane		Iodine number	Hydroxyl %
	Experimental	Theory		
Vernonia oil	4.0	....	107.5	Neg.
Trivernolin	5.0	5.2	82.7	0.1
Barium vernolate	4.2	4.4	72.1	Neg.
Cadmium vernolate	4.4	4.5	73.9	Neg.
Epoxystearate ester (*commercial*)	3.4	....	1.4	....
Epoxidized soybean oil (commercial)	6.6	....	2.7	....

Preparation of Materials. Vernonia oil was obtained from *Vernonia anthelmintica* seed by the method previously described (3).

Trivernolin, the triglyceride of vernolic acid obtained by crystallization from vernonia oil (3), was a natural plant product, and the vernolic acid used in making metallic soaps was produced by enzymic hydrolysis (3) that occurred in the air-dry plant matter following grinding; therefore, the products were not exposed to artificial oxidation or saponification, which ordinarily are of concern as sources of hydroxylated contaminants of epoxides. Spectra of the materials at 3 μ indicated no significant contamination from hydroxyl. Hydroquinone, 0.03%, was added to prevent gel formation.

Barium and cadmium salts of vernolic acid were prepared as follows: vernolic acid (3) was dissolved in a moderate quantity of warm methanol, which was then mixed into a calculated equimolar proportion of NaOH in sufficient water to give an aqueous soap solution of considerable dilution, 5 g/100 ml or more dilute. This was slowly mixed into an equal volume of an aqueous solution of an equivalent proportion of a soluble salt of the appropriate metal, either the barium chloride or cadmium acetate hydrates. The resulting milky suspension was then frozen, thawed, filtered, washed with water and 80–90% acetone, air dried, ground, and finally vacuum desiccated over P_2O_5 until fresh replacements of it remained little changed.

The epoxystearate ester and epoxidized soybean oil were commercial materials.

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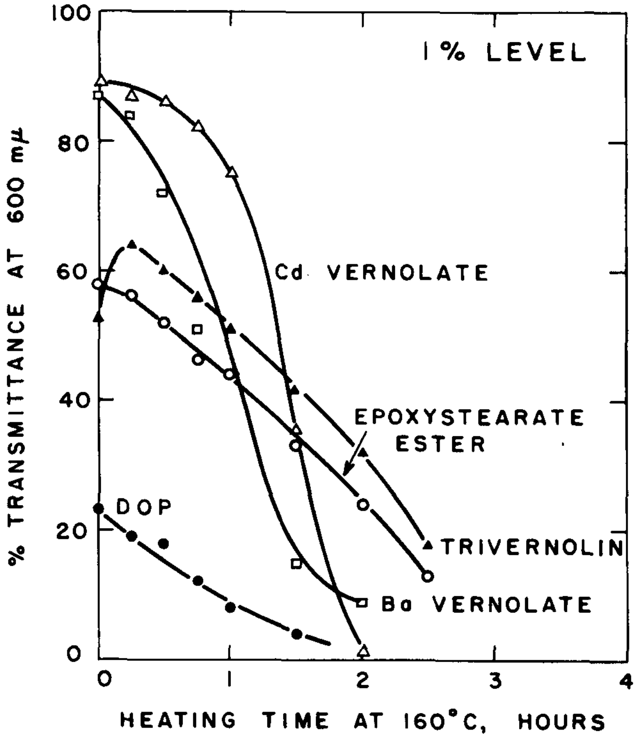

FIG. 1. Variation in transmittance with time of conditioning at 160C for plasticized poly(vinyl chloride) containing 1% stabilizer.

Stabilizer Evaluation. The resin used for this study was Geon 101, poly(vinyl chloride), plasticized with DOP (dioctyl phthalate), employing the following recipe: Geon 101, 65%; plasticizer-stabilizer combination, 35%. For simplicity, evaluation was made at both the 1 and 3% levels of the total mix listed above; evaluation could have been made based on oxirane or metal content. In addition, mixtures of barium and cadmium vernolate were evaluated at the 1 and 3% levels. The following weight ratios of barium to cadmium were studied: 1:3, 1:1, 3:1, 5:1, and 10:1. A commercial barium-cadmium complex (Mark M) liquid phenate stabilizer system was used as the control at the 1 and 3% levels for these mixtures. No attempt was made to prepare compositions of maxium attainable heat and light stability. All formulations were milled at 320F for approximately 7 min. The milled sheets were cut into 3-inch squares, stacked in the mold, preheated at about 320F for 10 min and then pressured to 1000 psi and held an additional 10 min at 320F. Heat stability tests were conducted on molded specimens in an air convection oven at 160C. Samples were removed periodically and examined with a visible range spectrophotometer. The % transmittance at a wavelength of 600 mμ was chosen as it provided the best quantitative measure of the development of color in the specimens. Light stability tests were conducted by exposing the molded specimens to the light emitted by twin carbon arcs. During exposure the samples were necessarily heated; the temperature averaged about 65C. Specimens were examined at 24-hr intervals for change in color or any other physical change. The time recorded for failure was that at which the samples showed a distinct overall color change or showed a decided spotting.

Results and Discussion

Physical Properties. The following physical properties (tensile strength, 100% modulus, % elongation, Clash-Berg T_g and T_4, migration, and volatility) were found to be essentially the same for all the specimens with no difference between the 1 and 3% levels and were also the same as those previously found for unstabilized poly(vinyl chloride) plasticized with DOP (4). All samples were transparent and color ranged from dark amber to colorless.

Heat Stability. The heat stabilizing effects at the 1 and 3% levels are shown in Figures 1 and 2, respectively, for the DOP control, commercial epoxystearate ester, trivernolin, barium vernolate, and cadmium vernolate. The ability of these materials to stabilize poly(vinyl chloride) against thermal degradation during processing is shown by the transmittance at 0 time. The DOP control (Fig. 1) which was a dark amber had a transmittance of 23% while the cadmium vernolate which was colorless had a transmittance of 89%. At 160C the stabilizing ability of the compounds investigated increased as follows: epoxystearate ester, trivernolin, barium vernolate, and cadmium vernolate. The whole vernonia oil and the epoxidized soybean oil (not shown) were intermediate to the trivernolin and the epoxystearate ester. The metal salts show the greatest improvement in the initial heat stability but exhibit a faster rate of degradation at increased time.

Increasing the stabilizer content to the 3% level (Fig. 2) results in an increased stabilizing effect. The transmittance after processing was in general lower at this level than at the 1% level. With the exception of the barium vernolate, all samples show increased transmittance during the first 30 min heating. The stability improves in the order epoxystearate ester, barium vernolate, trivernolin, cadmium vernolate. The whole oil and the epoxidized soybean oil (not shown) were intermediate between the barium vernolate and the trivernolin. The cadmium vernolate shows a pronounced increased heat stability with respect to the other compounds tested.

The effect of the mixtures of barium and cadmium salts on thermal stability is depicted at the 1% stabilizer level in Figure 3 for the 3:1, 5:1, and 10:1 Ba:Cd vernolate ratios. All the mixtures show good initial stability but differ in the rate of failure as noted by decrease in transmittance with respect to time. The mixed salts all show a slower rate of

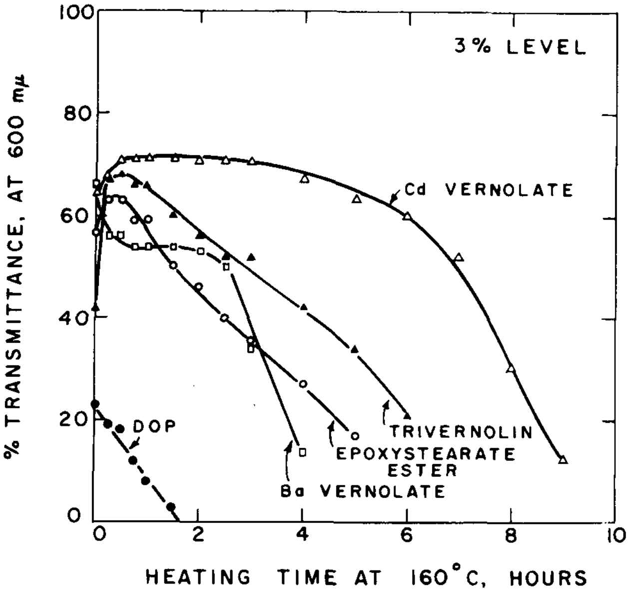

FIG. 2. Variation in transmittance with time of conditioning at 160C for plasticized poly(vinyl chloride) containing 3% stabilizer.

failure than the control. Essentially no difference in thermal stability was observed between the 1:1 (not shown) and the 3:1 ratios; however, by visual inspection initially the sample containing the 3:1 ratio had a slight yellowish color not exhibited by the 1:1 ratio sample. The 1:3 ratio (not shown) exhibited about the same transmittance during heat aging as the 10:1 ratio; however, initially the 10:1 ratio sample was pale amber and the 1:3 was colorless.

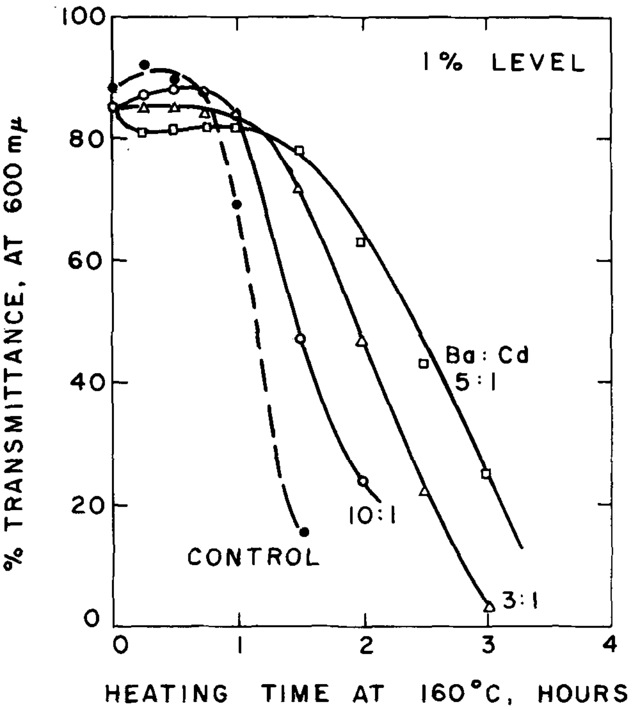

FIG. 3. Variation in transmittance with time of conditioning at 160C for plasticized poly(vinyl chloride) containing 1% (Ba/Cd) vernolic acid salt mixtures.

The effect of the metal salt mixtures at the 3% level is seen in Figure 4 for the Ba:Cd ratios of 1:1, 5:1, 10:1, and the barium-cadmium control. Unlike the control, the mixtures show an initial rapid loss of transmittance during the first 30 min which is followed by a period where the transmittance increases and then decreases with increased time. The control shows the highest transmittance up to about 4 hr, but then shows rapid failure. All the mixed salts show a more gradual rate of failure than the control with the 1:1 ratio still showing 66% of its original transmittance after 9 hr, while the control showed complete failure at 6 hr. The 1:3 ratio (not shown) had a high transmittance during the first 4 hr intermediate to the control and the 1:1 ratio. This was followed by a rate of failure intermediate to the control and the other mixtures. The 3:1 ratio (not shown) gave about the same transmittance as the 1:1 ratio up to about 5 hr followed by lower transmittance than the 1:1 ratio being intermediate to the 1:1 and 5:1 ratios.

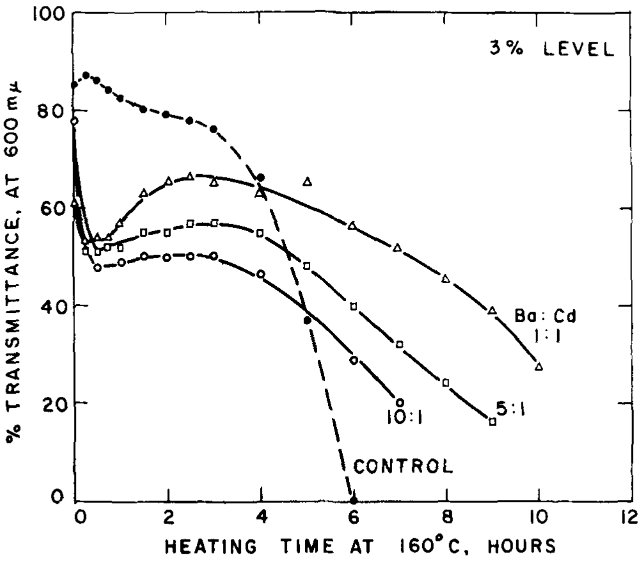

FIG. 4. Variation in transmittance with time of conditioning at 160C for plasticized poly(vinyl chloride) containing 3% (Ba/Cd) vernolic acid salt mixtures.

Comparison of the 1 and 3% levels show that the 1% level produces high initial transmittance with rapid failure after about 1 hr. The 3% level shows a lower initial transmittance than the 1% but continues to stabilize at much longer times, the 1:1 ratio at the 3% level exhibiting the greatest heat stability.

TABLE I

Light Stability

	Hr to failure, 1%	Hr to failure, 3%
Stabilizer		
Vernonia oil	72	144
Trivernolin	96	192
Barium vernolate	168	384
Cadmium vernolate	168	504
Control		
Epoxystearate ester	72	96
Epoxidized soybean oil	72	168
None	0 (decomposed)	....

TABLE II

Light Stability

	Hr to failure, 1%	Hr to failure, 3%
Stabilizer		
(Ba/Cd) vernolate		
Ratio		
1:3	192	528
1:1	192	504
3:1	240	336
5:1	240	408
10:1	240	456
Control		
Ba-Cd complex	120	576

Light Stability. The effect of light on the molded specimens is summarized in Tables I and II. Most of the samples developed varying degrees of color after milling and molding. The colors diminished or completely disappeared after exposure for about 24 hr. At the 1 and 3% levels the trivernolin shows a slight improvement over both of the commercial controls, and the barium and cadmium vernolates show a great improvement. All ratios of the mixed salts at the 1% level exhibit greater stability than the control. At the 3% level the 1:3 ratio produced the best stability but was not quite as good as the control. The mixtures show only slight improvement over those of the individual salts.

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