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THE IDENTIFICATION OF EPOXY PLASTICIZERS USING THIN-LAYER CHROMATOGRAPHY

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SUMMARY

The multicomponent epoxy plasticizers and stabilizers commonly used in poly(vinyl chloride) formulations are readily identified by thin-layer chromatography when a balanced solvent system and a chromogenic indicator are employed. A representative selection of commercially available epoxy materials, three commonly used ester plasticizers and extracts from known poly(vinyl chloride) compounds have been examined by the above method.

INTRODUCTION

Only a few of the many thin-layer chromatographic (TLC) studies reported on the analysis of plasticizers used in vinyl compounds have included epoxy plasticizers¹⁻⁴. The results obtained in these studies were usually not adequate for identification of epoxy compounds since these studies were primarily aimed at determining other types of plasticizers. Recently, two publications have appeared in which epoxy plasticizers have been studied in greater detail. In the first, VERES⁵ examined alkyl epoxy stearates and the epoxidized triglycerides of soybean and linseed oils. The triglycerides were chromatographed on specially prepared layers composed of air-dried Silica Gel G equilibrated for at least three days in an atmosphere of 92% relative humidity before use. The developing solvent was dichloromethane saturated with water. The epoxidized alkyl fatty esters were eluted with benzene-dichloromethane (2:1) on Silica Gel G activated at 100°. This system failed to fractionate the epoxidized triglycerides. In the second report, RONEN⁶ used thick layers (500 μ) of Silica Gel G and a solvent mixture of hexane-ether-glacial acetic acid (70:40:3) to chromatograph a number of epoxidized triglycerides and alkyl fatty esters. Difficulties may be encountered with this system if phthalate, adipate or phosphate plasticizers are present since some of these overlap some of the epoxy fractions.

Epoxy stabilizers which are usually low-molecular-weight bisphenol A-epichlorohydrin polymers have not been included in any of the above cited reports.

TABLE I

APPROXIMATE $R_F \times 100$ VALUES AND COLORS OBTAINED FOR EPOXY PLASTICIZERS AND STABILIZERS

Development on Silica Gel G with (A) 1,1,1-trichloroethane-dichloromethane (3:1) and (B) 1,1,1-trichloroethane-dichloromethane-methyl ethyl ketone (75:25:2) as solvent; indicator: sulfuric acid-anisaldehyde.

No.	Sample	Trade name	Manufacturer	$R_F \times 100$		Color
				A	B	
1	Epoxydized soybean oil	Paraplex G-62	Rohm and Haas	0, 3, 5, 9, 11, 15, 19, 21, 25, 27, 31	0, 3, 5, 7, 9, 13, 19, 22, 27, 29, 32, 36	Rose, brown, yellow
2	Epoxydized linseed oil	Drapex 10.4	Argus	0, 3, 5, 8, 10, 15, 18, 20, 25, 26, 30	0, 3, 4, 7, 9, 15, 20, 22, 26, 28, 36	Rose, brown, yellow
3	Isocetyl epoxy stearate	Estynox 408	Baker Castor Oil	25, 39	30, 34, 55	Rose, brown, yellow
4	2-Ethylhexyl epoxy tallate	Flexol EP8	Union Carbide	25, 40	30, 34, 56	Rose, brown, yellow
5	Butyl epoxy tallate	Truflex E-64	Teknor Apex	22, 32	28, 50	Rose, brown, yellow-green
6	Butyl ester of epoxydized linseed fatty acid	Epoxol 8-2B	Swift Chemical	0, 11, 23, 30	0, 16, 29, 50	Rose, brown, yellow
7	Di(isodecyl)-4,5-epoxy tetrahydrophthalate 3,4	Flexol PEP	Union Carbide	25, 28	33, 39	Brown
8	-epoxy-6-methylcyclohexylmethyl 3,4-Epoxy-6-methylcyclohexane-carboxylate	Unox 201	Union Carbide	16	20	Brown
9	Epoxy resin	Ferro 909	Ferro Corp.	0, 5, 9, 11, 15, 24	0, 2, 3, 5, 8, 13, 21, 30	Violet
10	Epoxy resin	Synpron 473	Synthetic Products	0, 2, 5, 9, 11, 15, 23	0, 2, 5, 8, 14, 21, 30	Violet, blue
11	Epoxy resin	Mark 224	Argus	0, 3, 5, 7, 9, 11, 15, 23	0, 2, 4, 5, 8, 10, 13, 16, 20, 24, 30	Violet, yellow, brown, rose
12	Di(2-ethylhexyl)phthalate	Kodaflex DOP	Eastman	56	60	Rose
13	Di(2-ethylhexyl)azelate	Plastolein 9058	Emery	43	60	Rose
14	Tri(2-ethylhexyl)trimellitate	Morflex 510	Pfizer	53	71	Rose

WEATHERHEAD⁷ has fractionated a number of epoxy resins, some of which were low-molecular-weight materials similar to those used as vinyl stabilizers and found that a double chloroform development on Silica Gel G layers gave good separation of the contained components.

For many years, our laboratory has characterized vinyl extracts by TLC using standard thickness, activated Silica Gel G layers and a solvent system obtained by modification of the dichloromethane eluent suggested for plasticizers by BRAUN⁸. The addition of increasing amounts of 1,1,1-trichloroethane was found to give greater movement to and fractionation of the epoxy additives. These separations were mainly due to the inhibitor, 1,4-dioxane, which is normally present at the 3% level in most commercial 1,1,1-trichloroethanes. A 3:1 ratio of inhibited 1,1,1-trichloroethane to dichloromethane produced the best epoxy movement with the least interference from other plasticizers that might be present. A minor failing of this system was a frequently observed, weak solvent front attributable to the dioxane. Although the front did not hinder the identification of any of the materials studied, the system was modified by addition of a small amount of methyl ethyl ketone to smooth the dioxane front. This yielded moderately increased R_F values without disturbing the quality of the fractionations. The increase in R_F values was, in fact, helpful since more fractions were now visible in several of the samples.

EXPERIMENTAL

A slurry containing a 2:1 weight ratio of water to Silica Gel G (E. Merck AG, Darmstadt) was used to prepare layers 250 to 300 μ thick which were dried 1 h at 110° in a forced air oven and cooled in a desiccator where stored until used. All samples were applied to the layers as 1% solutions in acetone with 2- and 5- μ l disposable capillary pipets. A 20- μ g (2- μ l) sample size was used for all analyses except the triglycerides, in which case a 50- μ g (5- μ l) sample was used. All samples were used as obtained from the suppliers and are listed in Table I.

Three vinyl compounds of known formulations were prepared for TLC analysis (Table II). Approximately 1 g of finely cut vinyl was extracted overnight with methanol in a Soxhlet apparatus. The extract was concentrated to yield a solution

TABLE II

POLY(VINYL CHLORIDE) COMPOUND FORMULATIONS

All ingredients were used as received from suppliers and are given in parts by weight.

<i>Ingredient</i>	<i>A</i>	<i>B</i>	<i>C</i>
Poly(vinyl chloride) resin	100	100	100
Kodaflex DOP	40	—	60
Plastolein 9058	20	—	—
Morflex 510	—	60	—
Paraplex G-62	—	5	—
Flexol EP8	5	—	—
Ferro 909	—	—	1
Liquid barium-cadmium-zinc stabilizer	2.5	2.5	2.5
Stearic acid	0.3	0.3	0.3
Calcium carbonate	10	10	10
Titanium dioxide	2	2	2

suitable for TLC analysis of the epoxy constituents, which, when a 5- μ l sample was used, gave spot sizes comparable to those produced by control solutions containing the plasticizers in the ratios of the compound formulations.

A solvent of either 1,1,1-trichloroethane - dichloromethane (3:1), or 1,1,1-trichloroethane-dichloromethane-methyl ethyl ketone (75:25:2), was used to develop the chromatograms. Only 1,1,1-trichloroethane inhibited with 3% 1,4-dioxane was used since the presence of 1,4-dioxane was necessary for good separations. Several major chemical suppliers in the U.S.A. offer 1,4-dioxane inhibited 1,1,1-trichloroethane (Table III). Two suppliers, Aldrich and Eastman, have the type and amount

TABLE III

INHIBITED 1,1,1-TRICHLOROETHANE USED FOR TLC

Supplier	Catalog No.	1,4-Dioxane (%)
Aldrich	T5470-4	3.0 ^a
Eastman	T3013	3.0 (also contains 0.25% <i>sec.</i> -butanol) ^a
Baker	W509	3.0 ^b
Fisher	T-391	3.0 ^b
Matheson, Coleman and Bell	TX1074	3.0 ^b

^a Stated on label.

^b Presence determined by gas-liquid chromatography and infrared spectroscopy. Quantitative estimation by infrared spectroscopy.

inhibitor printed on the container labels. Other suppliers merely state the solvent is inhibited or stabilized. The presence of 1,4-dioxane in these products was confirmed by gas-liquid chromatographic and infrared spectroscopic examinations. The quantitative estimations were made by infrared spectroscopy. The 1,1,1-trichloroethane from each of the five sources was found to be satisfactory for TLC; however, unless one wishes to analyze each new lot of solvent, it is probably best to use one of the solvents with the inhibitor type and amount stated on the label.

The chromatograms were developed a distance of 15 cm in a tank lined with solvent saturated filter-paper. After development, the chromatogram was removed from the tank, air-dried, and sprayed with 2 *N* sulfuric acid until just damp. This was followed by a light spray of 2.5% anisaldehyde in methanol. Colored spots were observed after heating the plate 10 to 20 min at 120° in a forced air oven.

RESULTS AND DISCUSSION

The TLC separations obtained for a representative number of commercially available (U.S.A.) epoxy plasticizers and stabilizers are shown in Fig. 1. The materials shown in the chromatogram are listed in Table I with the chromatographic data. All R_f values are the average of ten determinations. The description of colors must be considered approximate since most of the colors will vary depending upon the amount of heating the sample receives after spraying.

Many of the samples were readily identified by the fractionation patterns and colors they yielded. In some cases, no readily apparent variations in pattern or color were discerned. For instance, no differences could be detected between samples of epoxidized soybean oils obtained from several different manufacturers. Therefore,

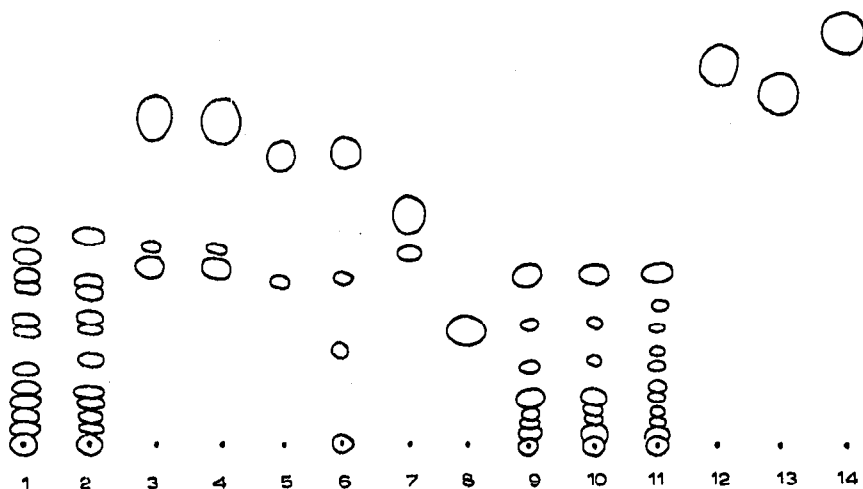


Fig. 1. Separation of epoxy plasticizers and stabilizers by TLC. Solvent: 1,1,1-trichloroethane-dichloromethane-methyl ethyl ketone (75:25:2); development distance: 15 cm; indicators: (a) sulfuric acid, followed by (b) anisaldehyde. The numbers refer to the compounds listed in Table I.

only one sample was included as an example. Also, since linseed and soybean oils contain the same unsaturated fatty acids; oleic, linoleic and linolenic, but in different ratios, the TLC fractionations of the epoxidized triglycerides were quite similar. Only the relative abundances of some of the fractions were different. It was not possible to distinguish between the epoxy stearate and epoxy tallate of a given alcohol. This was expected since tall oil fatty acids are mainly composed of oleic acid

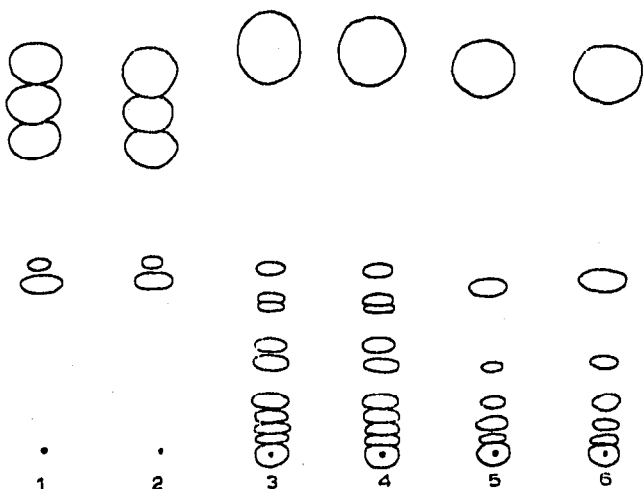


Fig. 2. Separation of extracts from known poly(vinyl chloride) formulations by TLC. Solvent: 1,1,1-trichloroethane-dichloromethane-methyl ethyl ketone (75:25:2); development distance: 15 cm; indicators: (a) sulfuric acid, followed by (b) anisaldehyde. 1 = Control mixture of di(2-ethylhexyl)phthalate, di(2-ethylhexyl)azelate and 2-ethylhexyl epoxy tallate; 2 = extract from formulation A; 3 = control mixture of tri(2-ethylhexyl)trimellitate and epoxidized soybean oil; 4 = extract from formulation B; 5 = control mixture of di(2-ethylhexyl) phthalate and epoxy resin; 6 = extract from formulation C. The formulations A, B, and C correspond to those in Table II.

and the product upon epoxidation is an epoxy stearate. The butyl epoxy tallate was easily differentiated from the octyl esters by the lower R_F values of the butyl fractions. The butyl ester of epoxidized linseed fatty acid exhibited fractions similar to those of the butyl epoxy tallate but contained an additional component that permitted identification.

Several epoxy stabilizers were examined. Most are viscous, low-molecular-weight polymers of bisphenol A-epichlorohydrin and contain a large quantity of the diglycidyl ether of bisphenol A. Three samples representing the different fractionation patterns found were included in the sample group. One of these samples, Mark 224, contained several uncharacteristic components indicating it might be a blend of stabilizers.

Three commonly encountered ester plasticizers; di(2-ethylhexyl)phthalate, di(2-ethylhexyl)azelate and tri(2-ethylhexyl)trimellitate were used to provide a measure of the R_F relationships to be obtained for ester types when using these solvent systems. The esters were found to be well separated from the epoxy fractions. This was demonstrated by the TLC results for extracts from the known vinyl formulations shown in Fig. 2. The extracts were chromatographed beside control mixtures of the plasticizers in the same ratios as mixed into the vinyl compounds. Agreement between the extracts and control mixtures was good. These systems, and hence most solvent systems capable of fractionating epoxides, will also fractionate portions of some polyester plasticizers. For this reason, one may experience difficulties when characterizing the epoxy portion of certain epoxy-polyester mixtures.

The sulfuric acid-anisaldehyde indicator functions very well with the compounds examined. It is not a good indicator for phosphates. An indicator such as phosphomolybdic acid, a diazonium reagent, or antimony pentachloride is required when phosphates are encountered.

CONCLUSIONS

A TLC method capable of identifying the epoxy plasticizers and stabilizers used in poly(vinyl chloride) formulations has been described. This method functioned well when applied to extracts from known vinyl compounds.

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