FRANK P. GREENSPAN
FMC Organic Chemical Division, Food Machinery & Chemical Corp., New York, N. Y.

RALPH J. GALL
Becco Chemical Division, Food Machinery & Chemical Corp., Buffalo 7, N. Y.

Vinyl Epoxy Plasticizers

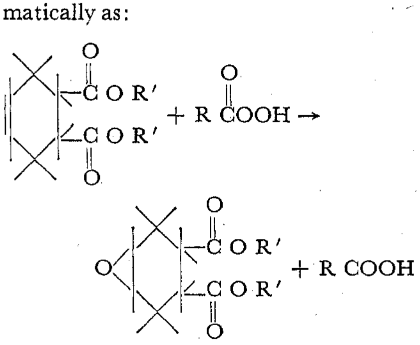
The Epoxyhexahydrophthalates

The alkyl epoxyhexahydrophthalates represent a new class of improved epoxy plasticizers with built-in stabilizing properties, protecting poly(vinyl chloride) resins against degradation caused by heat and light. They are primary plasticizers and show excellent compatibility at high concentration use levels with no evidence of bleed after prolonged exposure to light. As combination stabilizer-plasticizers they are applicable to a wide range of vinyl resin formulations and products—e. g., hose, toys, flooring, packaging, film, and foam

THE epoxy plasticizers, widely used in vinyl resin processing, are epoxy fatty acid esters (*5*, *6*, *12*, *13*), prepared by epoxidation of unsaturated fatty acid esters of mono- and polyhydric alcohols. A new series, alkyl epoxyhexahydrophthalates, has been developed in these laboratories in a broad program of research on epoxy plasticizers. The epoxyhexahydrophthalates combine the excellent stabilizing properties of the epoxy fatty acid esters with the good over-all plasticizing properties of the phthalates. They are compatible with poly(vinyl chloride) at primary use levels and show no evidence of bleed, sometimes observed with specific epoxy fatty acid ester plasticizers at high use levels, after prolonged exposure to ultraviolet or diffused light.

Experimental

The epoxyhexahydrophthalate esters (*4*, *10*) can be prepared by epoxidation of the corresponding unsaturated tetrahydrophthalic acid esters with preformed peracetic acid or by in situ techniques (*2*, *3*, *7*, *9*) employing hydrogen peroxide. The reaction can be represented schematically as:



The tetrahydrophthalate esters were made by esterifying *n*-butyl, *n*-hexyl, isooctyl, and *n*-decyl alcohols (Enjay Co., Inc.) with tetrahydrophthalic anhydride (National Aniline Division) in the presence of an acid catalyst, water-washed, and vacuum-distilled.

The in situ epoxidation process (*8*) is illustrated below for the preparation of di-2-ethylhexylepoxyhexahydrophthalate.

One hundred grams of di-2-ethylhexyltetrahydrophthalate (Union Carbide Chemicals) and 20 grams of benzene were weighed into a three-necked flask equipped with a reflux condenser, thermometer, and a mechanical stirrer; 7.7 grams of glacial acetic acid and 1.1 grams of 50% sulfuric acid were added and the mixture was warmed to 50° C. Then 19.0 grams of 50% hydrogen peroxide (Becco Chemical Division) were slowly added over a 2-hour period. The temperature was allowed to rise to 60° C. and controlled between 60° and 65° C. until the reaction was complete as determined by periodic titrations of the reaction mixture for unreacted hydrogen peroxide (8 to 10 hours). The reaction mixture was poured into a separatory funnel and the aqueous layer drawn off. The oil layer was washed with successive portions of warm water (40° to 50° C.) until free of acetic acid. The benzene and last traces of water were removed under vacuum at 60° to 70° C. and 5- to 10-mm. pressure. The resultant product contained 3.5% of oxirane oxygen. Oxirane oxygen was determined by the modified method of Swern and others (*11*).

Analytical data for the epoxyhexahydrophthalates, with changes in alkyl group, were compared (Table I). In general, the boiling points of the epoxy compounds were 10° to 20° C. higher than that of the unsaturated analog.

Compatibility ratings of epoxyhexahydrophthalates with various polymers (Table II) were based upon the characteristics of films cast from solvents in the

Table I. Analytical Data for Epoxyhexahydrophthalate Esters

	Per Cent		Sp. Gr.,	Boiling Point	
	Oxirane O_2	Epoxy ester	25°/25°	° C.	Press., mm. Hg
Di-2-ethylhexylphthalate			0.986	222–30	4
Epoxyhexahydrophthalates					
Di-*n*-butyl	4.1	76	1.06	183–202	4
Di-*n*-hexyl	3.9	87	1.03	>200–4	6
Di-2-ethylhexyl	3.5	90	1.0	230–6	4
Diiso-octyl	3.5	90	1.0	>180[a]	0.1
Di-*n*-decyl	3.2	94	0.98	>219[a]	2
***n*-Butyl decyl**	3.2	76	1.05	>160–70[a]	0.3

[a] Unepoxidized unsaturated raw material.

Table II. Compatibility of Di-2-ethylhexylepoxyhexahydrophthalate

Resin	Resin Plasticizer	Compatibility
Poly(vinyl chloride)	**2:1**	**Very good**
Nitrocellulose	**2:1**	**Fair**
Cellulose acetate	**3:1**	**Poor**
Ethylcellulose	**2:1**	**Very good**
Polystyrene	**3:1**	**Good**
Methyl methacrylate	**4:1**	**Good**

ratio of resin to plasticizer noted. Cast films were air-dried at room temperature, and oven-dried overnight at 70° C. in an air circulating oven. Clarity, gloss, surface smoothness, hardness, flexibility, strength, brittleness, adhesion, and bleedings of the films were checked, and ratings assigned.

Milled sheets of poly(vinyl chloride) were prepared on a laboratory roll mill from the following formulation:

Ingredient	Parts
PVC resin (Geon 101)	**100**
Epoxy plasticizer	**55 to 60**
Cadmium-barium stabilizer	**1.5**

Speed and ease of fluxing were observed. Milled sheets so prepared were then examined for bleed, clarity, tear resistance, and flexibility. No bleed was observed in milled sheets or Plastisol castings, 2 parts of Geon 121 to 1 part of plasticizer.

Modulus at 100% elongation, ultimate tensile strength, and ultimate per cent elongation were determined with a modified Dillon tensile tester, by the standard ASTM method for rubber and related materials. Dumbbell specimens were die-cut from molded 75-mil sheets and prior to testing were conditioned for 24 hours at 25° C. and 50% relative humidity. Shore hardness was determined as the Durometer reading after 10-second contact with a 75-mil molded sheet. Efficiency per cent plasticizer, the percentage of plasticizer required to give a Durometer hardness of 75 ± 2 and a modulus at 100% elongation of 1500 ± 100 pounds per square inch (except where noted), was interpolated from hardness and modulus at 100% elongation. Low temperature flexibility was determined by the Clash and Berg method (*1*). The performance of milled sheets of poly(vinyl chloride) plasticized with epoxyhexahydrophthalates is approximately equivalent to that of dioctyl phthalate (Table III).

Table III. Poly(vinyl Chloride) Plasticized with Epoxyhexahydrophthalate Esters[a] (Milled Sheets)

	Modulus at 100% Elong., 25° C., P.S.I.	Ultimate Tensile Strength, P.S.I. at 25° C.	Elong., % at 25° C.	Shore Hardness Dur., 25° C.	Efficiency, %		C. & B. Low Temp. Flex., ° C.
					Hardness[b]	Modulus[c]	
Di-2-ethylhexylphthalate	1490	2660	320	76	54	54	−33
Epoxyhexahydrophthalates							
Di-*n*-butyl	**1570**	**3000**	**270**	**74**	**54**	**59**[d]	**−14**
Di-*n*-hexyl[e]	**930**	**2420**	**360**	**68**	**53**	**49**	**−28**
Di-2-ethylhexyl	**1720**	**2960**	**340**	**76**	**57**	**59**	**−28**
Diiso-octyl	**1770**	**2840**	**300**	**78**	**58**	**60**	**−24**
Di-*n*-decyl[e]	**1380**	**2520**	**330**	**75**	**60**	**58**	**−26**
***n*-Butyl decyl**	**1520**	**2810**	**350**	**75**	**55**	**55**	**−26**

[a] 55 parts of plasticizer per 100 parts of resin and 1.5 parts of cadmium-barium stabilizer, except where noted.

[b] Shore dur. hardness at 75 ± 2.

[c] Modulus 100% elongation at 1500 ± 100 p.s.i.

[d] Modulus 100% elongation at 1300 ± 100 p.s.i.

[e] 60 parts of plasticizer.

Table IV. Permanency of Plasticized Sheet[a]

	24 Hours Carbon Volat., 70° C.	After 10 Days at 25° C.		Migration Test	
		Water	Oil	Varnish	Lacquer
Di-2-ethylhexylphthalate	**1.7**	**0.2**	**11.6**	**VS**	**VS**
Epoxyhexahydrophthalates					
Di-*n*-butyl	**11.2**	**6.6**	**4.1**	**SA**	**SA**
Di-*n*-hexyl[b]	**..**	**0.9**	**..**	**..**	**..**
Di-2-ethylhexyl	**1.1**	**0.1**	**8.0**	**N**	**N**
Diiso-octyl	**1.2**	**0.5**	**7.6**	**N**	**N**
Di-*n*-decyl[b]	**..**	**0.8**	**..**	**..**	**..**
***n*-Butyl decyl**	**3.9**	**0.9**	**9.4**	**N**	**N**

VS = very slight; SA slight adhesion, 1 month; N none, 2 weeks.

[a] 55 parts of plasticizer per 100 parts of resin and 1.5 parts of cadmium-barium stabilizer, except where noted.

[b] 60 parts of plasticizer.

Plasticizer permanency was determined by measurement of losses in air, water, and oil (Table IV). Migration tests were conducted with lacquered and varnished surfaces. Milled sheets, 3 × 6 × 0.004 inch, were used in the two latter tests.

Carbon volatility was determined by ASTM D 1203-55. A sample disk, 2 inches in diameter × 0.010 inch, of the plastic is immersed in activated granular carbon. The sample is sandwiched between two loadings of the activated carbon in a vented container and placed in a water bath for 24 hours at 70° C. Then the samples are removed from the container, allowed to cool to room temperature, brushed free of all carbon, and conditioned. The weight loss is computed as per cent of original weight of the sample.

Plasticizer extracted by water was determined by immersion of weighed milled sheet samples in distilled water at 25° C. over 10 days. The water was changed five times at regular intervals over the test periods. The sheets were then dried at 70° C. for 2 hours and reweighed, and the per cent loss in weight was calculated.

Plasticizer extracted by oil was determined by immersion of the weighed milled sheet samples in 100 ml. of white medium-heavy mineral oil at 25° C. over 10 days. The oil was changed three times during the test period. The samples were washed with hexane, followed by petroleum ether, dried, and reweighed, and the per cent loss in weight was calculated.

Migration tests were run by fastening milled test sheet strips with thumbtacks to a white nitrocellulose lacquered surface, and to a varnished surface. The effects of the plastic specimens on the respective finishes were recorded after 1, 2, 3, and 12 weeks.

Heat stability tests were conducted at 177° C. in an air circulating oven using 1 × 1 × 0.030 inch samples, prepared on a roll mill using a 10-minute milling cycle. Test samples were periodically removed and assigned a numerical color value on the American Public Health Association platinum cobalt color scale.

Samples were exposed to ultraviolet light for 50 hours using a slight modification of ASTM method D 620-49. The value of 50 on the APHA scale is approximately equivalent to a very pale lemon color; 100 is a pale lemon and 125 a pale orange color. Values of 350 to 500 range from a claret red to a very dark red. No color change, embrittlement, or bleeding was observed.

Similarly, long-term compatibility tests were conducted wherein plasticized sheets were stored in the dark for 8 months and separately exposed to diffused light (sample suspended behind a glass window exposed to sunlight). None of the samples showed evidence of bleed on exposure to ultraviolet light. The di-2-ethylhexylepoxyhexahydrophthalate showed a slight bleaching under ultraviolet light. No color change was observed in any of the other hexahydrophthalates or the blank di-2-ethylhexylphthalate. No bleed was observed after storage of plasticized sheets in the dark or on exposure to diffused light. The superior stability of epoxyhexahydrophthalate plasticized poly(vinyl chloride) to high temperature is shown in Table V.

Plastisols prepared from 2 parts of Geon 121 to 1 part of plasticizer, wherein the plasticizer was varied to include di-2-ethylhexyltetrahydrophthalate, di-2-ethylhexylepoxyhexahydrophthalate, and the chlorohydrin of the latter, showed no evidence of bleed.

Discussion of Results

The epoxyhexahydrophthalates are excellent primary plasticizers for poly(vinyl chloride) resins, approximately equivalent to dioctylphthalates. Efficiencies are somewhat greater than that of dioctyl phthalate. Hand, drape, clarity, and flexibility are good to excellent. Poly(vinyl chloride) films or sheets plasticized with epoxyhexahydrophthalates showed good permanency. The volatility of the C_8 alkyl derivatives is approximately that of dioctyl phthalate. Losses in water are low. No staining is shown in the migration tests. Oil extraction is somewhat lower than that of dioctyl phthalate. Epoxyhexahydrophthalates show excellent compatibility with poly(vinyl chloride) at primary use levels. Even at these high concentrations no evidence of bleed was observed in ultraviolet light or after prolonged exposure to diffused light, in contrast to the tendency to bleed observed with certain epoxy triglycerides at high levels of use on exposure to diffused light.

Table V. Stability of Plasticized Films to Heat and Ultraviolet Light[a]

	Heat Stability, 177° C.	
	Color[b]	Time, min.
Di-2-ethylhexylphthalate	50	70
	500	80
	Black	120
Epoxyhexahydrophthalates		
Di-*n*-butyl	..	..
Di-*n*-hexyl[c]	125	210
Di-2-ethylhexyl	125	210
Diiso-octyl	100	210
Di-*n*-decyl[c]	100	210
n-Butyl decyl	350	210

[a] 55 parts of plasticizer per 100 parts of resin and 1.5 parts of cadmium-barium stabilizer, except where noted.

[b] American Public Health Association platinum cobalt.

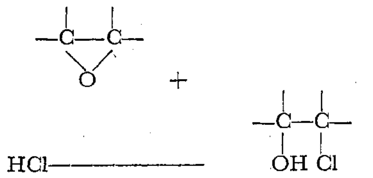
[c] 60 parts of plasticizer.

Epoxy fatty acid ester plasticizers generally carry a number of impurities possessing little or no plasticizing action, which dilute the epoxy plasticizer efficiency and compatibility, particularly at primary use levels. These include saturated esters that are difficult to separate from the final reaction product, as well as small quantities of unreacted, unsaturated esters. The latter material is poorly compatible with poly(vinyl chloride) resins. Epoxyhexahydrophthalates are derived from synthetic raw materials and, therefore, are obtainable as well defined chemical entities of high purity. The unsaturated analog is itself a good plasticizer with excellent compatibility. Further, the chlorohydrin of the epoxyhexahydrophthalates—i.e., the product formed on absorption of hydrochloric acid by the epoxy plasticizer—is in turn compatible with the poly(vinyl chloride) resin, in marked contrast to the chlorohydrins obtained from epoxy fatty acid ester plasticizers. Bleeding under diffused light exposure, sometimes observed with specific epoxy plasticizers at high use levels, has been theorized as possibly resulting from formation of an incompatible chlorohydrin.

Epoxyhexahydrophthalate plasticizers act as stabilizers for poly(vinyl chloride) resins, protecting them against degradation caused by heat and light. As such they can be classified as plasticizers with inherent stabilizing action or stabilizers with plasticizing properties. When epoxyhexahydrophthalate ester plasticizers are used with metallic stabilizers—e.g., cadmium soaps—this quality is greatly enhanced. In approximately 1-hour exposure at 177° C. poly(vinyl chloride) films plasticized with di-2-ethylhexylphthalate will show a very pale lemon color, becoming dark red in 80 minutes and black in 2 hours. The epoxyhexahydrophthalate plasticized films under the same conditions of test will show a pale lemon color after 210 minutes' exposure (Table V). No color changes were observed on exposure to ultraviolet light for 50 hours or after 8 months' exposure to diffused sunlight. Good heat and light performance was obtained even at partial replacement levels for conventional plasticizers—e.g., dioctyl phthalate.

The unique stabilizing action of the epoxyhexahydrophthalate esters is attributable to the epoxy group in the plasticizer molecule. This can be explained by modern theory, according to which degradation of a poly(vinyl chloride) polymer under heat or light action proceeds initially by a dehydrochlorination; this leads to a polyene structure. Initial degradation is believed to be a random splitting out of hydrochloric acid from the polymer structure. This hydrochloric acid further catalyzes polymer degradation or breakdown. Double bond formation contributes to color, with further color formation resulting from oxidative attack at the site of the double bond giving rise to carbonyl groups.

Stabilization systems for chlorinated polymers are dependent upon the addition of a stabilizer which removes the released hydrochloric acid and/or reacts with the double bond of the formed polyene. The epoxy group in the hexahydrophthalate is an excellent hydrochloric acid scavenger and reacts thus:



The pickup of hydrochloric acid by the epoxide results in diminished color formation and retarded polymer degradation. Where the conditions of poly(vinyl chloride) processing or end use exposure are mild, the epoxyhexahydrophthalate ester plasticizers may be used alone. More generally they are employed with less than the conventional amount of metallic stabilizer to protect against heat and light action.

Literature Cited

(1) Clash, R. F., Jr., Berg, R. M., Ind. Eng. Chem. **34,** 1218 (1942).
(2) Gall, R. J., Greenspan, F. P., *Ibid.*, **47,** 147 (1955).
(3) Gall, R. J., Greenspan, F. P., *J. Am. Oil Chemists' Soc.* **34,** 161 (1957).
(4) Gill, J. E., Munco, J., *J. Chem. Soc.* **1952,** p. 4630.
(5) Greenspan, F. P., Gall, R. J., Ind. Eng. Chem. **45,** 2722 (1953).
(6) Greenspan, F. P., Gall, R. J., *J. Am. Oil Chemists' Soc.* **33,** 391 (1956).
(7) Greenspan, F. P., Gall, R. J., U. S. Patent **2,692,271** (1954).
(8) *Ibid.*, **2,801,253** (1957).
(9) Niederhauser, W. D., Koroly, J. E., *Ibid.*, **2,485,160** (1949).
(10) Phillips, B., Starcher, P. S., *Ibid.*, **2,794,030** (1957).
(11) Swern, D., Findley, T. W., Billen, G. N., Scanlan, J. T., *Anal. Chem.* **19,** 414 (1947).
(12) Terry, D. E., Wheeler, D. H., U. S. Patent **2,458,484** (1949).
(13) Witnauer, L. P., Knight, H. B., Palm, W. E., Koos, R. E., Ault, W. C., Swern, D., Ind. Eng. Chem. **47,** 2304 (1955).

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