Epoxy Esters as Plasticizers and Stabilizers for Vinyl Chloride Polymers

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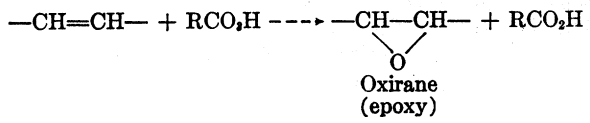
LEE P. WITNAUER, H. B. KNIGHT, W. E. PALM, R. E. KOOS, W. C. AULT, AND DANIEL SWERN

Eastern Regional Research Laboratory, Philadelphia 18, Pa.

FATS and most compounds derived from them by simple reactions have relatively low vapor pressures and limited solubility in and extractability with water, characteristics which are highly desirable in plasticizers. Moreover, fats are inexpensive and plentiful. The poor compatibility of these compounds with synthetic resins in general and poly(vinyl chloride) in particular has seriously restricted their use in the plasticizer field (*18*). With only a few exceptions, where fats or compounds prepared from them are used with synthetic resins, their function is to serve as diluents, lubricants, or plasticizer extenders.

The compatibility of long-chain compounds with poly(vinyl chloride) can be increased by the introduction of the three-membered oxirane ring into the molecule (*15, 19, 20, 28, 30*). This can be readily accomplished by the epoxidation of unsaturated fatty materials with organic peracids (*23, 24*), as shown in the accompanying equation. Although this reaction has been known for some time (*21*), practical, efficient, and high-yield procedures for carrying it out were developed only within the past 10 years (*13, 24, 25, 27*). Besides enhancing the compatibility of long-chain fatty compounds with poly(vinyl chloride), epoxidized fatty materials when used to the extent of 1 to 5% of the formulation have recently been shown to be excellent light stabilizers for poly(vinyl chloride) (*7, 10*).



About 5 years ago the first epoxy stabilizer, epoxidized soybean oil, became available commercially. Soybean oil was chosen for epoxidation because it was cheap and plentiful, it could be epoxidized to a relatively high oxirane content (5.8 to 6.0%), and its volatility loss from poly(vinyl chloride) was low. Epoxidized soybean oil cannot be used as a primary plasticizer, however, because its compatibility with poly(vinyl chloride) is poor owing to its large content of incompatible components (glyceride molecules containing a saturated, nonepoxidized acyl radical). In an attempt to obtain epoxy stabilizers which are also primary, solvent-type plasticizers, considerable industrial research effort has been expended in the preparation and evaluation of epoxidized esters of oleic acid, such as butyl epoxystearate and other alkyl epoxystearates, also derivable from inexpensive fat sources (tallow and grease). The compatibility of many of the simple alkyl epoxystearates is high, they impart good low temperature characteristics to poly(vinyl chloride), and they are efficient plasticizers, as shown by their effect on modulus, elongation, and tensile strength. These monomeric epoxy plasticizers, however, frequently have poor migration characteristics and their volatility is relatively high. When molecular weight or chain length of the alkyl group of the ester moiety is increased sufficiently to reduce volatility loss to a satisfactory level, compatibility and efficiency are adversely affected.

Another group which is known to increase the compatibility of long-chain compounds with poly(vinyl chloride) is the acetyl group. It was reasoned, therefore, that if both the acetyl and oxirane groups were present in the same molecule, efficient, primary plasticizers with relatively low volatility and migration loss should be obtained. This goal has been realized with the preparation of epoxidized diacetoglycerides from fats.

The interesterification of triacetin with fats is a convenient, high-yield reaction for replacing one or two of the long-chain radicals by acetyl groups, producing monoacetodiglycerides or diacetomonoglycerides (*11, 12*). Although the resulting products have greater compatibility with poly(vinyl chloride) than do the parent fats, mono- and diacetoglycerides are still not primary plasticizers (*17*). On the other hand, if the unsaturated long-chain radicals of diacetoglycerides are epoxidized, highly efficient, relatively nonvolatile, nonmigratory primary plasticizers are obtained, provided that the iodine number of the original fat is above about 70.

This paper describes the preparation and evaluation of this new class of epoxy plasticizers and stabilizers for poly(vinyl chloride)—namely, epoxidized diacetomonoglycerides. For completeness these have been compared with the commercially available epoxy plasticizer-stabilizers, as well as with some conventional plasticizers such as dioctyl phthalate [di(2-ethylhexyl)phthalate, DOP] and tricresyl phosphate (TCP). During the course of this work, a large number of other epoxy esters were prepared in an attempt to correlate the efficiency of epoxy esters as primary plasticizers with structure. The results of this last study are also included.

Some quantitative test data on the efficiency of various types of epoxy esters as plasticizers and stabilizers have recently been published. Greenspan and Gall (*15*) published data for poly(vinyl chloride) plasticized with methyl epoxystearate, butyl epoxystearate, epoxidized methyl and butyl esters of cottonseed and soybean oil fatty acids, epoxidized octyl, tetrahydrofurfuryl, and diethylene glycol monobutyl ether esters of soybean oil fatty acids, epoxidized ethylene glycol monobutyl ether ester of oleic acid, and epoxidized soybean oil. The formulations also contained a calcium-barium stabilizer. Terry and Wheeler (*30*) reported on poly(vinyl chloride-acetate), poly(vinyl chloride), poly(vinyl butyral), and poly(vinyl chloride-vinylidene chloride) plasticized with methyl epoxystearate, butyl epoxystearate, epoxidized methyl and butyl esters of cottonseed and soybean oil fatty acids, epoxidized octyl, tetrahydrofurfuryl, and diethylene glycol monobutyl ether esters of oleic acid, and epoxidized soybean oil. All plasticizers were not evaluated with all the resins; lead carbonate was also employed in many cases. Niederhauser (*19*) has suggested the use of epoxidized oils to stabilize chlorinated rubber. The results of these earlier investigations showed that some epoxy esters are excellent plasticizers as well as stabilizers. In several cases outstanding low temperature characteristics were observed; noteworthy compounds are butyl epoxystearate and the epoxidized monobutyl ether ester of oleic acid.

Epoxy esters were prepared and tested

Epoxidized soybean oil (A,B,C,D), hexyl epoxystearate, buty epoxystearate, sodium epoxystearate, dimerized linoleic acid, tall oil fatty acids, sorbitan trioleate, polyoxyethylene sorbitan trioleate, and iso-octyl, isodecyl, and tridecyl alcohols were commercial materials. Diacetomono-olein (prepared from pure oleic acid and excess glycerol followed by acetylation with acetic anhydride) (iodine number 58) and diacetomonoglycerides of soybean oil (iodine number 101) were obtained from R. O. Feuge of the Southern Regional Research Laboratory. Characteristics of the epoxidized esters are listed in Table I.

Table I. Characteristics of Epoxy Esters Used in Present Investigation

Epoxy Ester	n_D^{30}	Iodine No.	Oxirane Oxygen, %
Epoxidized soybean oil			
A	...	13	5.58
B	...	2.7	5.91
C	...	2.0	5.92
D	...	9	5.73
Epoxidized diacetomonoglycerides			
Of tallow	1.4508	1.8	1.66
Of lard	1.4518	2.3	2.28
Of cottonseed oil	...	2.2	3.57
Of soybean oil	...	2.4	4.55
Epoxidized diacetomono-olein	1.4542	3.4	3.54
Benzyl epoxystearate	1.4825	1.3	3.68
Butyl epoxystearate	1.4483	1.2	3.99
2-Chloroethyl epoxystearate	...	1.1	3.83
Cyclohexyl epoxystearate	1.4607	4.2	3.75
Dihydronopyl epoxystearate	1.4728	2.9	3.06
2-Ethylbutyl epoxystearate	1.4519	1.9	3.56
2-Ethylhexyl epoxystearate	1.4524	2.3	3.31
Methoxyethyl epoxystearate	1.4500	1.6	3.91
Isodecyl epoxystearate	1.4528	0.8	3.19
Iso-octyl epoxystearate	1.4520	1.1	3.39
n-Octyl epoxystearate	1.4520	2.5	3.30
Epoxyoctadecyl epoxystearate, m.p. 44–46°	1.4590 (50°)	3.5	5.28
Tridecyl epoxystearate	1.4556	0.7	2.90
Tetrahydrofurfuryl epoxystearate	1.4588	0.9	3.77
Phenyl epoxystearate	1.4812	5.2	3.78
Acetoxyethyl epoxystearate	1.4517	1.7	3.73
Butyl epoxytallate	1.4532	0.7	4.62
Glycidyl epoxystearate, m.p. 43–44°	1.4500 (50°)	1.1	8.0
Sorbitan triepoxystearate	1.4723	...	3.89
Polyoxyethylene sorbitan triepoxystearate	1.4672	...	1.81
Epoxidized glycerol monoricinoleate triacetate	1.4680	1.8	2.53
tert-Butylphenyl epoxystearate	1.4822	1.6	3.93[a]
Hexyl epoxystearate, commercial	...	1.4	3.64

[a] Calculated from reduction in iodine number.

Peracetic acid in acetic acid solution was furnished by Frank P. Greenspan, Buffalo Electrochemical Co. Sodium acetate was added just before use to neutralize any strong acid which might be present.

Epoxidized Diacetomonoglycerides of Tallow. A sodium methylate solution, prepared from 2.0 grams of metallic sodium and 25 ml. of methanol, was added to a stirred mixture of 400 grams of triacetin and 277 grams of tallow at 90° C. After 2 hours at 90° C., the reaction mixture was dissolved in ether and washed with water to remove catalyst and excess triacetin. The ether was distilled off and the triacetin not removed by water washing was separated by heating under vacuum. The yield of diacetomonoglyceride, a pale yellow oil, was 420 grams (iodine number 31 and saponification number 390).

To 50 grams of diacetomonoglycerides, 50 ml. of a 20% solution of peracetic acid in acetic acid was added dropwise with agitation at 20° to 30° C. (cooling bath required). After 3 hours the reaction mixture was poured into several volumes of cold water and extracted with ether. The ether solution was washed with water until free of acid and the ether was distilled off, the last traces under vacuum. The yield of epoxidized diacetomonoglycerides, a pale-yellow oil, was 43 grams [iodine number 1.8; oxirane oxygen (*29*) 1.66% (Table I)].

Epoxidized Diacetomonoglycerides of Lard. From 254 grams of lard, 411 grams of diacetomonoglycerides (iodine number 42 and saponification number 410) were obtained. From 50 grams of these and 60 ml. of 20% peracetic acid, 42 grams of epoxidized diacetomonoglycerides (iodine number 2.3 and oxirane oxygen 2.28%) were obtained (Table I).

Epoxidized Diacetomonoglycerides of Cottonseed Oil. The 90% commercial grade of monoglycerides of cottonseed oil was acetylated by heating and stirring with a 100% excess of acetic anhydride for 2 hours at 110° C. Hot water was slowly added and stirring was continued for 10 additional minutes to hydrolyze excess acetic anhydride. The aqueous layer was discarded and the upper layer was washed with water to remove acetic acid. The acetylated monoglycerides were then heated under vacuum to remove water. From 175 grams of these (iodine number 73 and saponification number 367) and 330 ml. of 20% peracetic acid, 174 grams of epoxidized diacetomonoglycerides (iodine number 2.2 and oxirane oxygen 3.57%,) were obtained as a colorless oil (Table I).

Epoxidized Diacetomonoglycerides of Soybean Oil. From 175 grams of diacetomonoglycerides of soybean oil and 420 ml. of 20% peracetic acid, 179 grams of epoxidized diacetomonoglycerides (iodine number 2.4 and oxirane oxygen 4.55%) were obtained as a yellow oil (Table I).

Epoxidized Diacetomono-olein. From 50 grams of diacetomono-olein and 55 ml. of 20% peracetic acid, 47 grams of epoxidized diacetomono-olein [iodine number 3.4 and oxirane oxygen 3.54% (calculated 3.65%)] were obtained as a colorless oil (Table I). For larger scale preparations olive oil was first converted to the diacetomonoglycerides, followed by molecular distillation and epoxidation of the main fraction (saponification number 355 and iodine number 60). As the olive oil used contained 85% oleic acid, the resulting epoxidized diacetomono-olein was only of moderate purity.

Epoxidized Glycerol Monoricinoleate Triacetate. Castor oil was acetylated with a 100% excess of acetic anhydride for 2 hours at 110° C., then, converted to diacetoglyceride as described. The reaction product, after removal of excess triacetin, was molecularly distilled. The fractions coming over from 140° to 180° C. at a pressure of 5 to 7 microns were combined and reacetylated to eliminate all free hydroxyl. The resulting product was a pale yellow oil [saponification number 425 (calculated 450) and iodine number 55.5]. From 200 grams of these and 400 ml. of 20% peracetic acid, 202 grams of epoxidized glycerol monoricinoleate triacetate (iodine number 1.8 and oxirane oxygen 2.53%) were obtained as a pale yellow oil.

Epoxidized Esters of Oleic Acid. The following esters were prepared in the conventional manner by direct esterification of oleic acid with the appropriate alcohol, using naphthalene-2-sulfonic acid as catalyst and benzene or toluene as the entraining agent for separation of water (*26*). The numbers in parentheses are the boiling point and pressure in millimeters, and iodine number; all distillations were conducted from an alembic flask. Benzyl oleate (176–8°/0.3; 65); butyl oleate (150°/0.03; 74); 2-chloroethyl oleate (150°/0.05; 75); cyclohexyl oleate (160–4°/0.3; 68); dihydronopyl oleate (180–200°/0.01; 54); 2-ethylbutyl oleate (139°/0.04; 69); 2-ethylhexyl oleate (152°/0.04; 63); methoxyethyl oleate (143°/0.2; 72); isodecyl oleate (165°/0.01–0.02; 55); iso-octyl oleate (157–8°/0.02–0.03; 59); *n*-octyl oleate (160°/0.01–0.03; 64); oleyl oleate (—; 95); tridecyl oleate (176°/0.0003; 50); and tetrahydrofurfuryl oleate (150°/0.03–0.04; 71). These esters and those described below were epoxidized as already described. Characteristics of the epoxidized esters are given in Table I.

Miscellaneous Esters. Phenyl oleate (168–170°/0.03–0.04; 71) and *tert*-butylphenyl oleate (not distilled; 64) were prepared by the reaction of oleyl chloride [from oxalyl chloride and pure oleic acid (*8*)] with phenol and *tert*-butylphenol, respectively, in pyridine solution. Acetoxyethyl oleate (161°/0.02; 71) was prepared by direct esterification of oleic acid with a 100% excess of ethylene glycol (using benzene as the azeotropic agent for

removal of water and naphthalene-2-sulfonic acid as catalyst), followed by acetylation of the crude reaction product with acetic anhydride using the procedure given. Butyl esters of tall oil fatty acids (150°/0.02; 110) were prepared by direct esterification of tall oil fatty acids, containing less than 2% of rosin fatty acids, with butanol. Glycidyl epoxystearate (160°/0.04; oxirane oxygen, 8%) was prepared by heating dry epichlorohydrin with sodium epoxystearate at 140° to 160° C. under pressure for

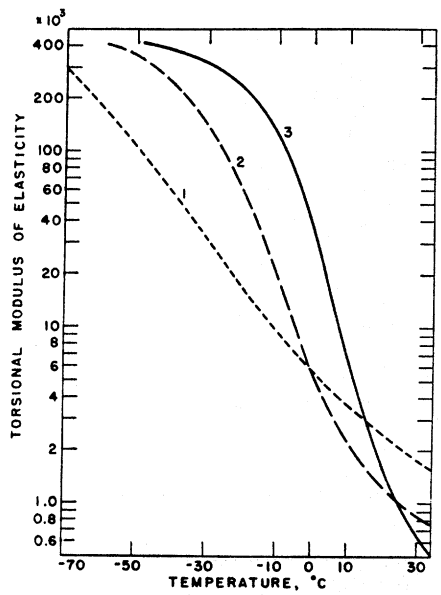


Figure 1. Change in modulus as a function of temperature for VYDR

Plasticized with 35% of (1) epoxidized aliphatic monoesters, (2) epoxidized aromatic monoesters, diesters, and diacetoglycerides, (3) epoxidized soybean oil

3 hours (*16*). Butyl chlorohydroxystearate was prepared by slowly adding butyl epoxystearate (51 grams) to a dioxane solution (1500 ml.) containing 24 ml. of concentrated hydrochloric acid. After 1 hour the reaction mixture was poured into 4 liters of water and the insoluble oil was dissolved in ether, washed acid-free, and dried. Evaporation of the ether resulted in a quantitative yield of desired product. Characteristics of the epoxy esters are given in Table I.

Evaluation of Epoxy Esters. The resin used in most of the investigations was a commercial copolymer (Vinylite VYDR) containing 95 parts by weight of vinyl chloride and 5 parts by weight of vinyl acetate. The standard recipe used was as follows:

Vinylite VYDR	64.5%
Plasticizer	35.0%
Stearic acid	0.5%

When di(2-ethylhexyl)phthalate (DOP) or tricresyl phosphate (TCP) was employed, 1% of lead carbonate was added as stabilizer.

The plasticizer was added to the dry mixture of VYDR and stearic acid just prior to milling. The milling was carried out on a 6 × 12 inch rubber mill at a temperature of 300° F. for approximately 8 minutes. The sheeted resin was then molded in a standard 6 × 6 × 0.075 inch mold. The mold containing the resin was first heated at 300° F. for 10 minutes without pressure, then pressured to 1000 pounds per square inch and held for an additional 10 minutes at the 300° F. molding temperature. The mold was then cooled under pressure until it was at approximately room temperature.

All test procedures are standard ASTM methods, with the exception of heat stability and migration. For the determination of tensile strength, ultimate elongation, and 100% modulus, dumbbell specimens were die-cut (*1*) from the molded sheets parallel to the milling axis. The measurements were made on an IP-4 Scott tester at a loading rate of 73 pounds per minute at 73° F. and 50% relative humidity. The specimens were equilibrated to these conditions for at least 24 hours prior to testing (*4*). Hardness was determined with the Rockwell hardness tester (*2*). Torsional modulus as a function of temperature was determined with the Clash-Berg Stiffness tester (*5*). Results are given in Figure 1. The apparatus was slightly modified by reducing the weight loads to increase its utility at higher temperatures (low modulus range). Brittle point was determined with a hand-operated brittle point tester (*3*).

Migration of the plasticizers from the resin was measured according to the procedure of Geenty (*14*) by burying a weighed test specimen in absorbent powder consisting of a hydrated silica (sold as "silica acid, analytical grade, 100 mesh"), and following the loss in weight as a function of time at 30° C. The basis of this method is the removal of plasticizer as soon as it diffuses to the surface. Figure 2 summarizes the results.

Volatility was determined by use of activated carbon (Columbia activated carbon 6- to 14-mesh) (*6*); the volatilized plasticizer was absorbed by the activated carbon in a closed container.

The various tests are summarized in Table II.

Light stability tests were conducted on molded specimens in an Atlas Twin Arc WeatherOmeter. The specimens were also subjected to temperatures of about 75° C. during their exposure. Samples were exposed for 24, 48, 72, 96, 144, and 192 hours and examined for changes in color, tensile strength, elongation, modulus, and solubility (Table III).

Heat stability tests were conducted on molded specimens in an air convection oven at 160° C. Samples were observed for color changes at 1-hour intervals for 7 hours and finally 24 hours. The effect of heat on the mechanical properties was also investigated. Changes in tensile strength, elongation, 100% modulus, and hardness were measured after exposures from 0 to 360 minutes at 140° C. in an air convection oven (Table IV).

Compatibility of epoxy esters was judged by observing milling characteristics and the lapse of time before exudation occurred during storage at room temperature.

Oxirane Oxygen Content of Milled and Molded Sheets. It was of interest to determine whether epoxy ester was destroyed during milling and molding. Oxirane oxygen determinations were run on samples of the milled and molded specimens by a modification of the usual procedure, which involved solution of the plasticized samples in dioxane or tetrahydrofuran prior to the addition of the hydrochloric acid–ether or hydrochloric acid–dioxane reagent. Table V summarizes the results.

Efficient plasticizers of low volatility and migration loss were obtained

Mechanical Properties. Table II shows the properties of VYDR plasticized with the epoxy esters investigated. For comparison, VYDR plasticized with di(2-ethylhexyl)phthalate and tricresyl phosphate is also included in the table. Comparable tensile strength, ultimate elongation, 100% modulus, and hardness are obtained with all the epoxy esters having molecular weights below about 460. Their efficiency appears to be comparable to that of di(2-ethylhexyl)phthalate, with the exception of monoesters of lowest molecular weight, such as butyl-, 2-ethylbutyl-, and hexyl epoxystearate, which are somewhat more efficient. Included in this group are epoxy compounds containing one, two, and three ester linkages. Dihydronopyl epoxystearate, with a molecular weight similar to the diesters, is less efficient, as evidenced by a somewhat higher tensile strength, 100% modulus, and hardness. This compound contains a single ester group but has a substantially higher molecular weight than the other monoesters. Increasing the molecular weight to 900 or above (epoxidized soybean oil) reduces the efficiency of the plasticizer slightly. In addition to a higher 100% modulus and greater hardness, the elongations at break are considerably less. The presense of a saturated or unsaturated ring in the epoxy compound (benzyl and cyclohexyl epoxystearate) appears to produce a slight decrease in the efficiency of the plasticizer.

Table II. Properties of Vinyl Copolymer (VYDR) Plasticized with Epoxy Esters

Epoxy Ester	Tensile Strength, Lb./Sq. Inch	Elongation, %	Modulus 100%, Lb./Sq. Inch	Hardness, Shore A, 10 Sec.	Stiffening Temp., ° C.	Brittle Point, ° C.	Migration Wt. Loss after 14 Days, %[a]	Volatility Wt. Loss, %[a]
Epoxidized soybean oil								
A	3090	290	1660	89	−17	−18	3.9	0.34
B	2800	260	1520	85	−19	−18	2.4	0.23
C	2800	200	1930	90	−13	− 6	2.4	0.20
D	2950	290	1690	90	−15	−12	...	...
Epoxidized diacetomonoglycerides								
Of tallow	2770	365	1230	85	−19	−20	...	...
Of lard	3120	400	1300	85	−21	−23	...	...
Of cottonseed oil	3160	410	1240	82	−23	−21	6.1	0.36
Of soybean oil	2920	400	1120	79	−26	−21	9.1	0.42
Epoxidized diacetomono-olein	3160	360	1490	84	−27	...	10.7	0.98
Benzyl epoxystearate	2960	370	1250	80	−39	−39	...	...
Butyl epoxystearate	2440	460	1010	78	−51	−55	22.3	3.55
Cyclohexyl epoxystearate	3050	350	1350	82	−36	−38	...	...
Dihydronopyl epoxystearate	3370	335	1650	90	−30	−39	...	...
2-Ethylbutyl epoxystearate	2730	350	1290	79	−55	...	22.7	1.50
Methoxyethyl epoxystearate	2830	370	1130	78	−45	−44	...	...
Isodecyl epoxystearate	2410	220	1640	91	...	...	...	...
Iso-octyl epoxystearate	2800	310	1550	87	...	...	...	...
Tetrahydrofurfuryl epoxystearate	2730	360	1010	75	−37	...	...	...
Phenyl epoxystearate	2850	410	1110	79	−33	...	...	...
Acetoxyethyl epoxystearate	2910	410	1030	79	−41	...	...	...
Butyl epoxytallate[b]	2860	380	1170	78	−41	...	...	...
Glycidyl epoxystearate	2290	340	920	75	−42	...	...	...
Epoxidized glycerol monoricinoleate triacetate	3310	360	1770	85	−17	...	...	...
tert-Butylphenyl epoxystearate	3060	270	1610	85	−21	...	...	...
Hexyl epoxystearate (commercial)	2575	300	1270	82	−47	−49	18.8	2.74
Controls								
Di-2-ethylhexyl phthalate + 1 pt. $PbCO_3$	3030	390	1300	84	−28	−24	6.0	1.09
Tricresyl phosphate + 1 pt. $PbCO_3$	3630	295	2010	90	0	+ 7	0.5	0.26

[a] Weight loss is actual loss in weight per 100 grams of milled and molded sheet.
[b] Epoxidized butyl esters of tall oil fatty acids.

To study the effect of two epoxy groups in a monoester of low molecular weight, glycidyl epoxystearate was prepared. Unfortunately, slight exudation was observed on the surface of the molded specimen after 72 hours. The tensile strength and 100% modulus of this sample, however, were the lowest obtained. It is doubtful whether the exudate was glycidyl epoxystearate, as the low temperature properties of this plasticizer indicate high compatibility. Apparently the sample contained a small amount of an incompatible impurity.

The properties exhibited by one epoxidized compound, epoxidized glycerol monoricinoleate triacetate, do not fall in line with the rest of the epoxy esters. Its molecular weight is approximately 510, only slightly greater than that of the epoxidized diacetoglycerides, yet its efficiency was the poorest of the epoxidized compounds investigated. Based on the data collected on the epoxidized acetoglycerides and other substances, a compound containing four ester groups and having a relatively low molecular weight should show good plasticizing efficiency. Analyses showed that the compound had the expected iodine number; its acid number, however, was 15.5, which was 5 to 8 times the acid number of the other epoxy compounds studied, and its oxirane content was unexpectedly low. The presence of free carboxyl groups results in a greatly reduced compatibility of the epoxy ester with VYDR.

Low Temperature Flexibility. Gradually decreasing the temperature to very low values causes all plasticized systems to become brittle and stiff. While the stiffness increases gradually, brittleness seems to occur at rather sharply defined temperatures. It has become common practice to measure either the brittle temperature or the stiffness in torsion, or both, as a function of temperature. The latter method was introduced by Clash and Berg (*9*), who empirically selected an apparent modulus of elasticity of 135,000 pounds per square inch as the borderline between a rigid and a nonrigid material. The temperature required to reach this value corresponds to the stiffening or Clash-Berg temperature. In Table II are given the stiffening temperatures for the VYDR specimens plasticized with epoxy esters, as well as the brittle points of some of the compounds investigated. There appears to be little difference in the two tests when applied to these plastic compositions.

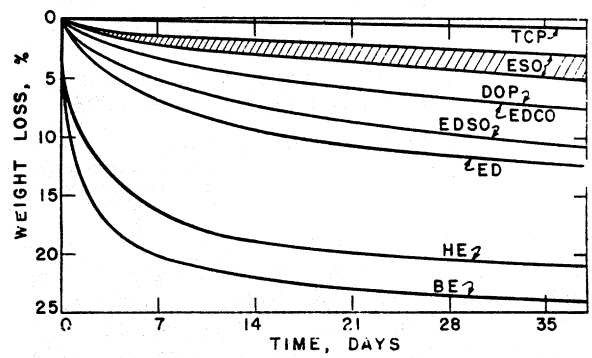


Figure 2. Migration loss as a function of time

TCP (tricresyl phosphate)
ESO (epoxidized soybean oils A to C)
DOP [di(2-ethylhexyl) phthalate]
EDCO (epoxidized diacetomonoglycerides of cottonseed oil)
EDSO (epoxidized diacetomonoglycerides of soybean oil)
ED (epoxidized diacetomono-olein)
HE (hexyl epoxystearate)
BE (butyl epoxystearate)

The data show that the epoxy monoesters have better low temperature flexibility than di(2-ethylhexyl)phthalate and considerably better than tricresyl phosphate. The epoxy triesters of low molecular weight (epoxidized diacetomonoglycerides of oleic acid and of soybean oil) are comparable to di(2-ethylhexyl)-phthalate, while the triesters of higher molecular weight (epoxidized soybean oil) show somewhat higher Clash-Berg temperatures, as might have been expected from the higher 100% modulus and the low elongations that they exhibit. The effect of branching on the low temperature flexibility is illustrated by a comparison of hexyl- and 2-ethylbutyl epoxystearates. The branched-chain compound has a stiffening temperature of −55° compared to −47° C. for the unbranched.

A close examination of the data for apparent modulus of elasticity in torsion *vs.* temperature reveals distinct differences among the epoxy esters (Figure 1). Aliphatic esters containing

a single ester and oxirane group are characterized by the smallest rate of change in modulus with temperature. The moduli of the formulations containing aromatic monoesters, aliphatic diesters, and the triesters of low molecular weight show a much greater dependence on temperature. The curve for di(2-ethylhexyl)phthalate shows a similar shape. A third type of change is characteristic of the triesters of high molecular weight. A narrow transition region exists in going from a rigid to the elastic state. A large change in modulus takes place over a relatively small temperature range. Tricresyl phosphate exhibits a similar type of curve. Although the compounds included in any one of the three types outlined above have the same shape of curve of the modulus *vs.* temperature, the curves are shifted along the temperature scale, depending on the flexibility of the material. The fact that a compound shows a good low temperature flexibility does not in itself mean that its rate of change in modulus will be small. For example, methoxyethyl epoxystearate has a stiffening temperature of −45° C., almost identical with that of hexyl epoxystearate (−47°), yet its curve is almost identical to that of di(2-ethylhexyl)phthalate.

Migration. For many uses of vinyl resins migration of the plasticizer is important because a loss of plasticizer is reflected in a loss in flexibility and other desirable characteristics, as well as in producing an undesirable effect on the surface with which the resin is in contact. The migration tendencies of some of the epoxy plasticizers are shown in Figure 2 and Table II. The epoxy esters of low molecular weight show a large migration, as would be expected. The weight loss after 14 days is approximately 20% for butyl-, hexyl-, and 2-ethylbutyl epoxystearates. The epoxy triesters of low molecular weight (epoxidized diacetoglycerides) show a weight loss of only 6 to 10%, which is in the same range as that found for di(2-ethylhexyl)phthalate.

The migration rate of triesters of high molecular weight (epoxidized soybean oil) is only slightly less than that of the triesters of low molecular weight and di(2-ethylhexyl)phthalate. None of the compounds approach the very low rate of migration of tricresyl phosphate.

Volatility. Another way in which a plasticized resin can lose plasticizer is through volatilization. The volatility of some of the epoxy esters incorporated in VYDR is shown in Table II. The epoxy plasticizers of low molecular weight have the largest percentage weight losses. Butyl and hexyl epoxystearates lose 3.6 and 2.7%, respectively, the loss decreasing with increasing molecular weight. The branched isomer of hexyl epoxystearate, 2-ethylbutyl epoxystearate, loses somewhat less, 1.5%. These compounds have a greater loss than di(2-ethylhexyl)phthalate (1.09%), but the loss for epoxidized diacetomono-olein is almost identical. The epoxidized diacetomonoglycerides of soybean and cottonseed oil, on the other hand, are one eighth to one ninth as volatile as butyl and hexyl epoxystearates, and one third that of di(2-ethylhexyl)phthalate. The weight loss of two of the epoxidized soybean oil samples was 0.2 and 0.3%, slightly less than that of the diacetomonoglycerides. Epoxidized soybean oil, epoxidized diaceto compounds, and tricresyl phosphate have similar volatilities.

Light Aging. The effect of light on the color, mechanical properties, and solubility of molded specimens was determined. The exposure was carried out in an Atlas Twin Arc Weather-Ometer. The specimens are necessarily heated during this exposure; temperatures range from 70° to 75° C. The specimens were examined at regular intervals, first for change in color. The time recorded was that at which the samples became distinctly yellow. At the end of 192 hours none of the epoxy compounds had developed a pronounced color, whereas di(2-ethylhexyl)phthalate and tricresyl phosphate had after 72 and 24 hours, respectively. Some of the specimens plasticized with epoxy esters had developed a slight yellow color after milling and molding (no heat stabilizer was used in the formulation). This always disappeared completely after exposure in the Weather-Ometer for a few hours. The surfaces of the plasticized sheets were examined periodically for tackiness, exudation, and blistering. After about 72 hours' exposure, most of the compounded sheets either had or developed a greasy surface; on some it was not immediately evident but showed up on standing at room temperature. The surface of the stock plasticized with di(2-ethylhexyl)phthalate became tacky after only 24 hours.

Because of the efficiency and stabilizing action of these epoxy plasticizers it was considered that an investigation of this undesirable characteristic was warranted. The incorporation of lead carbonate into the stocks did not eliminate this effect, but the addition of as little as 0.25% of disodium hydrogen phosphate or trisodium phosphate had a marked effect. For example, a stock plasticized with the relatively volatile butyl epoxystearate but containing 0.25% of disodium hydrogen phosphate showed no surface exudation after 264 hours and only relatively few blisters. The surface of the sheet had also retained high gloss, and no change in its stabilizing action was effected. After 4 months' standing at room temperature the sample still had not changed in appearance.

The effect of light on the mechanical properties is given in Table III for one member of each class of epoxy ester investigated. Similar data are included for a specimen containing di(2-ethylhexyl)phthalate. The per cent change in tensile strength of the specimens containing epoxy esters appears to depend on the molecular weight of the plasticizer and the length of exposure. The epoxy ester of low molecular weight, butyl epoxystearate, shows a decrease of 38%, epoxidized diacetomono-olein 20%, and epoxidized soybean oil less than 4% after exposure for 264 hours. Di(2-ethylhexyl)phthalate shows approximately the same decrease (32%) as do the epoxy compounds of lowest molecular weight.

A similar situation is observed for the decrease in elongation. Butyl epoxystearate and di(2-ethylhexyl)phthalate show about a 60% decrease, while epoxidized diacetomono-olein decreases about 35%. The epoxidized soybean oil sample shows no change. The change in 100% modulus ranges between 12 and

Table III. Effect of Light on Mechanical Properties

Epoxy Ester	Green				24 Hours				120 Hours				264 Hours			
	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.
Butyl epoxystearate	2680	330	1190	80	2450	300	1250	77	1850	210	1150	80	1660	170	1340	79
Butyl epoxystearate + 1 pt. $PbCO_3$	2650	355	1140	85	2700	330	1250	84	2250	255	1230	85	1700	150	1270	85
Epoxidized diacetomono-olein	3160	360	1490	84	2990	360	1550	84	2670	300	1650	86	2520	230	1810	87
Epoxidized soybean oil B	3020	310	1600	86	2810	280	1670	85	2710	280	1670	89	2910	310	1970	90
Control																
Di-2-ethylhexyl phthalate + 1 pt. $PbCO_3$	3270	330	1590	85	2850	250	1650	84	2340	200	1570	84	2240	135	1890	87

Table IV. Effect of Heat on Mechanical Properties

Epoxy Ester	Green				15 Minutes				90 Minutes				360 Minutes			
	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.	Tensile strength, lb./sq. inch	Elongation, %	Modulus 100%, lb./sq. inch	Hardness Shore A, 10 sec.
Butyl epoxystearate	2680	330	1190	..	2460	400	920	..	2180	310	1065	..	2130	270	1100	..
Butyl epoxystearate + 1 pt. $PbCO_3$	2620	350	1160	..	2340	300	1080	..	2085	435	830	..	1930	220	1100	..
Epoxidized diacetomono-olein	3160	360	1490	84	2820	390	1380	82	2800	385	1410	86	2600	330	1610	95
Epoxidized soybean oil B	3020	310	1600	86	2860	350	1420	85	2910	390	1550	85	2680	320	1570	86
Control																
Di-2-ethylhexyl phthalate + 1 pt. $PbCO_3$	3270	330	1590	..	2790	320	1330	..	2800	325	1335	..	2460	250	1350	..

22% for all the specimens. The addition of 1% of lead carbonate to the specimen plasticized with butyl epoxystearate slows down the rate of decrease in tensile and elongation; however, at the end of 264 hours its properties are almost the same as the specimen containing no lead carbonate.

The solubilities of the plasticized samples, after being aged in light, were investigated with the hope of learning whether degradation or cross linking was taking place and perhaps helping explain the changes in mechanical properties. The solubility of the specimens plasticized with epoxy esters and with di(2-ethylhexyl)phthalate was determined in tetrahydrofuran. The specimens containing epoxy esters were completely soluble even after 264 hours of exposure. Lead carbonate in the formulation had no apparent effect on the solubility. The specimens plasticized with di(2-ethylhexyl)phthalate, however, had very different solubility characteristics. The specimens were completely soluble after 24 hours of exposure, showed traces of gel at the end of 48 hours, had an insoluble surface layer at the end of 72 hours, and were almost completely insoluble at the end of 264 hours.

These results indicate that in the presence of an epoxy ester poly(vinyl chloride) probably does not cross link on exposure to ultraviolet light. If it does, chain degradation must also be a predominant reaction. This is not the case, however, when di(2-ethylhexyl)phthalate is used with lead carbonate as stabilizer; here, cross linking is predominating.

Heat Aging. The heat stability of the plasticized specimens as judged by color change varied considerably for different preparations of the same plasticizer. The majority of the transparent, almost colorless, plasticized sheets containing epoxy esters were transformed into transparent yellow or orange colored sheets after 7 hours at 160° C. The stocks plasticized with di(2-ethylhexyl)phthalate and tricresyl phosphate (1% lead carbonate) became intensely brown after 4 and 2 hours, respectively, under the same conditions. Most of the plasticized stocks were black and opaque at the end of 24 hours, with the exception of those containing epoxidized soybean oil, which were red and translucent, and those containing glycidyl epoxystearate, which were still transparent although colored orange.

Some of the samples became opaque after 1 hour's exposure and black and opaque after an additional 2 hours. Different preparations of the same plasticizer varied considerably in their heat-aging characteristic. One preparation of butyl epoxystearate became opaque and darkened after a 2-hour exposure to heat; another showed hardly any effect after an exposure of similar duration. After addition of 0.2% methyl oleate hydroperoxide to this sample it became opaque after 1 hour and had blackened at the end of 4 hours. The presence of small amounts of hydroperoxides apparently has a large effect on heat stability. The presence of trace amounts of other impurities may also result in instability; therefore, extreme caution must be exercised in considering the role that the epoxy group plays in the presence of heat. Some of the specimens after exposure to heat contained some exudate on their surface. This is considered in the discussion of the effects of light aging.

The effect of heat on the mechanical properties was also investigated. For this experiment the temperature was reduced to 140° C. The results are summarized in Table IV for one member of each class of epoxy ester investigated, and for a specimen plasticized with di(2-ethylhexyl)phthalate. The decrease in tensile strength ranges from about 10 to 25%, the greatest occurring with butyl epoxystearate and di(2-ethylhexyl)phthalate, and the smallest with epoxidized soybean oil. The change in elongation follows a similar pattern, except that the elongation of the specimen plasticized with epoxidized soybean oil shows no change. Combination of butyl epoxystearate and lead carbonate results in the largest ultimate decrease in elongation. Within the limits of the measurements the 100% modulus is unchanged for all the specimens, with the possible exception of the specimen containing di(2-ethylhexyl)phthalate, which is slightly less than that of the original.

The solubility of the exposed specimen was determined in tetrahydrofuran. Like the samples exposed to light the resins plasticized with epoxy esters are completely soluble after a 360-minute exposure at 140°. The specimens plasticized with di(2-ethylhexyl)phthalate are also completely soluble, exactly the opposite effect to that obtained for stocks subjected to light aging. These effects probably will be explained only when the mechanism of the degradation of poly(vinyl chloride) at elevated temperatures is found and all modes of action of a stabilizer are determined.

Oxirane Content of Milled and Molded Sheets. As shown in Table V, the epoxy compounds undergo no substantial loss in oxirane content as a result of these treatments. The apparent variation in oxirane content before and after milling and molding can be accounted for by variations in analysis and formulation. The results also indicate that there is no loss of plasticizer through volatilization during formulation at elevated temperatures.

Plasticization of Pure Poly(vinyl Chloride). Because of the

Table V. Analysis of Milled and Molded Sheets[a] of Epoxy Esters

Plasticizer	Epoxy Ester Content, %		
	Before milling and molding	After milling	After milling and molding
Epoxidized soybean oil			
A	35	35	35
B	35	35	36
C	35	36	35
D	35	35	Not run
Butyl epoxystearate	35	36	35
Hexyl epoxystearate	35	35	35
Epoxidized diacetomonoglycerides			
Of cottonseed oil	35	35	34
Of soybean oil	35	36	Not run

[a] Milling at 300° F. for 8 minutes; molding at 300° F. for 10 minutes without pressure and 10 minutes at 1000 lb. per sq. inch.

increasing tendency to utilize the homopolymer, poly(vinyl chloride), instead of a copolymer of vinyl chloride and vinyl acetate, a few epoxy esters were evaluated with Geon 101, a commercially available poly(vinyl chloride) resin. All of the resin-plasticizer mixtures could be easily milled between 300° and 330° F. The results of the evaluation tests are given in Table VI. The data are in line with those obtained when VYDR was used as the resin.

Table VI. Properties of Poly(vinyl Chloride), Geon 101[a], Plasticized with Epoxy Acid Esters

Epoxy Ester	Tensile Strength, Lb./Sq. Inch	Elongation, %	Modulus 100%, Lb./Sq. Inch	Low Temp. Flexibility, ° C.	Migration, Weight Loss after 72 Hr., %
Hexyl epoxystearate	2475	390	1310	−55	18.9
Epoxidized diacetomonoolein	2970	325	1740	−25	7.5
Epoxidized soybean oil A	3125	305	1875	−18	2.6
Control					
Di(2-ethylhexyl)phthalate + 1 pt. $PbCO_3$	2720	390	1405	−28	4.5

[a] Recipe. Geon 101, 100% poly(vinyl chloride), 63.5; stearic acid, 0.5; $PbCO_3$, 1.0; plasticizer, 35.

Small amounts of impurities reduce compatibility

One of the first requirements of any plasticizer is that it be compatible with the resin. This topic is discussed here, following discussion of other factors, because of the difficulties encountered when small amounts of impurities are present in the plasticizers.

The effect of the introduction of an oxirane group into a free acid or alcohol, such as oleic acid and oleyl alcohol, does not in itself render the compound compatible. For example, epoxystearic acid could not be milled into the resin. Epoxyoctadecanol, on the other hand, although it could be milled into the resin and appeared to be compatible on the mill at the elevated temperature, yielded a weak brittle specimen on cooling. Free carboxyl and hydroxyl groups, therefore, exert marked incompatibilizing effects.

In Table VII are listed some of the epoxy esters which were found to be incompatible at the 35% level. The sample of epoxidized sorbitan trioleate had an acid number of 22, which was 7 to 10 times that of the compatible epoxy plasticizers; in addition, the molecule contained free hydroxyl. Similarly, an incompatible epoxidized polyoxyethylene sorbitan trioleate was found to have a fairly high acid number and to contain free hydroxyl. The nopol epoxystearate sample had a low oxirane oxygen content, less than 0.8%, and a relatively high iodine number of 17, indicating incomplete oxidation. When an attempt was made to prepare glycidyl epoxysterate by the epoxidation of allyl oleate, the product had a high acid number (27) in addition to a high iodine number (52). The epoxidized methyl dilinoleate had an oxirane oxygen content of <1% and a high acid number (68). It appears from these observations that to obtain the best compatibility for epoxy plasticizers there should be relatively few, and, preferably, no free carboxyl or hydroxyl groups in the molecule.

The one halogen-containing epoxy compound investigated was 2-chloroethyl epoxystearate. The oxirane oxygen content, iodine number, and acid numbers were the expected ones for a compatible epoxy plasticizer; however, the compound was incompatible. A milled and molded sheet showed a large amount of exudation after 24 hours. The incorporation of 0.25% magnesia, however, resulted in compatibility; no exudate was evident on such a molded composition even after 6 months. The cause for this is not evident at the present time.

Some evidence is available that even extremely small amounts of impurities can produce pronounced effects on compatibility. This view was strengthened by the results obtained with one sample of presumably pure butyl epoxystearate, prepared in this laboratory, which showed exudation immediately after molding with VYDR. It was shown that incompatibility was caused by the presence of small amounts (<0.2%) of a water-insoluble peroxide. The effect of prolonged heating of samples containing small amounts of peroxidic impurity was to render a clear specimen opaque. This is indicative of incompatibility. It should be remembered, however, that these compatibility experiments are based on observations made with 35% by weight of plasticizer.

An attempt was made to determine the aliphatic chain of highest molecular weight that could be joined to epoxystearic acid before incompatibility resulted. 2-Ethylbutyl epoxystearate was one of the most efficient epoxy plasticizers investigated and had extremely good low temperature flexibility. Hexyl epoxystearate and 2-ethylbutyl epoxystearate were similar in plasticizing properties. Iso-octyl epoxystearate was not as efficient as hexyl epoxystearate. Exudation was observed on the surface after standing a few weeks at room temperature. Increasing the number of carbon atoms in the alkyl chain to ten (isodecyl epoxystearate) resulted in a further apparent decrease in efficiency. Exudate was observed on the surface of the molded specimen after 24 hours. It is impossible to say with absolute certainty whether the length of the chain or trace impurities cause the exudation in this case. On the other hand, tridecyl epoxystearate and epoxyoctadecyl epoxystearate were incompatible within the resin.

Table VII. Incompatible Compounds (35% Level)

Compound	Remarks
Butyl oleate Butyl stearate Vinyl oleate Epoxidized sorbitan trioleate Epoxidized polyoxyethylene sorbitan trioleate Nopol epoxystearate Tridecyl epoxystearate	Did not blend with resin
Epoxidized allyl oleate	Milled and molded well; profuse exudation after 1 hour
Epoxidized methyl dilinoleate 2-Chloroethyl epoxystearate	Profuse exudation after 24 hours

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A new class of primary epoxy plasticizers, epoxidized diacetomonoglycerides, promising with vinyl chloride polymers, was prepared from fats and studied.

Certain of these are comparable or superior to di(2-ethylhexyl) phthalate and are light stabilizers. None was effective as a heat stabilizer. The commercially available epoxidized oils and esters were also examined.

To broaden the study and obtain information on the relationship of structure to plasticizing ability, approximately 25 additional compounds were prepared. The outstanding members of this last group, with respect to low temperature characteristics and efficiency, are 2-ethylbutyl epoxystearate, epoxidized butyl esters of tall oil, and methoxyethyl, acetoxyethyl, glycidyl, tetrahydrofurfuryl, cyclohexyl, phenyl, and benzyl epoxystearate.