Inheritance of linolenic and linoleic acids in soybean seeds appeared to be quantitative rather than qualitative (Table I). Because of the lack of parents differing widely in linolenic and linoleic acid contents and the consequent overlapping in acid percentage of some members, it was not possible to estimate the number of gene pairs exerting a cumulative effect on the production of the two acids. Harosoy x P.I.85671 exhibited well the blending of characteristics of the two parents in the F_1 generation, followed by the complete range of variation in the F_2 population from the one parental series of values to the other. In some instances, plants that extended beyond the parental extremes and indicated transgressive segregation were obtained.

Some evidence was found for a dissimilarity in the manner of inheritance of the two acids, particularly in F_2 plants of P.I.80476 x P.I. 85671. The frequency distribution pattern for plants grown in the greenhouse was different for the two acids (Figure 1). Moreover plants grown in the field showed a considerable amount of transgressive segregation to low percentages of linolenic acid. This was not true for linoleic acid (Table I).

The lack of completely effective selection in F_2 to obtain F_3 plants with low amounts of linolenic acid (Table IV) was probably due to environment. The high variability among single plants in these data show the need for replicated plots when evaluating for linolenic and linoleic acids.

Comparison of field and greenhouse data from F_2 plants of P.I.80476 x P.I.85671 demonstrated the presence of an influential factor in the field which destroyed the close correlation ($P<1\%$) between the amounts of linolenic and linoleic acids found in seeds grown in the greenhouse (Figures 2-C and 2-D). The F_2 plants in both instances came from the same F_1 population.

The nearly perfect correlation between the two acids in Harosoy from the greenhouse was decidedly lessened in the field environment (Figures 2-A and 2-B). The regression coefficient of linoleic on linolenic acid for Harosoy was 3.3 whereas that for F_2 members of P.I.80476 x P.I.85671 was 7.2; both values are for plants grown in the greenhouse. Thus, if any kind of equilibrium between the two acids was operative through their interconversion, an increase in one relative to the other was not the same in different populations. However the high correlation between the two acids clearly showed their association rather than their independence during the fat-deposition period.

Barker and Hilditch (17) concluded that the more unsaturated oils from sunflower seeds were a result of slow development and ripening of the seeds and consequent slow fat production. They considered temperature and probably the amount of direct sunlight incident on the ripening seed heads as the most important factors controlling the rate of seed development and hence the composition of the fat. A similar inverse effect of temperature on fat unsaturation was noted for soybean seeds by Howell and Collins (8). They also found a positive correlation between the proportions of linolenic and linoleic acids (6). It may be that the light intensity or quality reaching the developing soybean seeds and temperature effects in the present work was responsible for the close correlation between the acids in seeds from the greenhouse in contrast to those from the field.

Acknowledgment

The authors acknowledge the assistance of H.E.W.N. Sturm in the early phase of this study and the technical assistance of Mrs. Judy Davey in the analytical work.

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[Received April 7, 1960]

Safflower Oil Adducts as Plasticizers[1,2]

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Eleven esters and epoxides of adducts of conjugated linoleic acid with maleic and acrylic acids, and eight esters and epoxides of adducts of vegetable oils with acrylic and maleic esters were evaluated as plasticizers for polyvinyl chloride (PVC), acrylonitrile rubber, and polyvinylidene chloride, and in PVC plastisols. The dimethyl ester of the acrylic adduct of linoleic acid and its epoxide were the most promising as plasticizers for PVC and in PVC plastisols as their performance compared favorably with that of controls. In polyvinylidene chloride however these adducts had a slight adverse effect on color stability. The vegetable oil adduct esters and epoxides were incompatible with PVC but had extremely good compatibility with acrylonitrile rubber. In general, they performed like the

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[1] Paper VII in a series entitled "Reactions of Conjugated Fatty Acids." Presented at Fall Meeting, American Oil Chemists' Society, New York, N.Y., October 17–19, 1960.

[2] The evaluation studies were conducted at Battelle Memorial Institute, Columbus, O., under contract with the U.S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the Northern Regional Research Laboratory.

[3] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

petroleum type of plasticizers but were less volatile and less easily extractable.

ADDUCTS of conjugated linoleic acid or esters can be prepared conveniently by reaction of nonconjugated safflower fatty acid or esters with dienophiles in the presence of catalytic amounts of selenium (4). Preliminary tests (1) suggested that these adducts and their epoxidized derivatives might have promise as plasticizers for polyvinyl chloride. The purpose of this paper is to summarize the results of evaluation studies of selected adduct esters and their epoxides as plasticizers for polyvinyl chloride, polyvinylidene chloride, and acrylonitrile rubber and in polyvinyl chloride plastisols. Preparation and evaluation of certain esters and epoxides of adducts obtained by direct reaction of dienophiles and vegetable oils are also described.

Experimental

Preparation of Adducts and Epoxides

Conjugated Linoleic Acid Adduct Esters and Epoxides. Preparation and properties of these materials have been described previously (4).

The following products were prepared: 2-ethylhexyl, *n*-butyl, and methyl triesters of the maleic adduct; 2-ethylhexyl and methyl diesters of the acrylic adduct; epoxides of the preceding products; and epoxidized *n*-butyl diester of the acrylic adduct.

Vegetable Oil Adduct Esters and Epoxides. Adducts were prepared directly from safflower, soybean, and linseed oils by reaction with di-*n*-butyl maleate and *n*-butyl acrylate in the presence of sulfur dioxide or anthraquinone as catalyst. Three moles of dienophile were used per mole of polyunsaturated fatty triglyceride present in the oil. Properties of the adducts and their epoxides are given in Table I.

TABLE I

Properties of Vegetable Oil Adduct Esters and Epoxides

Materials	n_D^{30}	Iodine value	Oxirane oxygen, %
Adducts of vegetable oils			
Di-*n*-butyl maleate adduct of safflower oil	1.4750	66.2	0.0
Di-*n*-butyl maleate adduct of soybean oil	1.4730	60.5	0.0
Di-*n*-butyl maleate adduct of linseed oil	1.4790	54.1	0.0
n-Butyl acrylate adduct of safflower oil	1.4755	80.4	0.0
Epoxidized adducts of vegetable oils			
Di-*n*-butyl maleate adduct of safflower oil	1.4742	41.2	0.7
Di-*n*-butyl maleate adduct of soybean oil	1.4705	15.6	1.7
Di-*n*-butyl maleate adduct of linseed oil	1.4797	7.3	1.3
n-Butyl acrylate adduct of safflower oil	1.4732	19.5	2.7

Maleate Oil Adducts. These adducts were prepared by a previously described procedure (2). After the recovery of unreacted dienophile, the products were used without further treatment.

Acrylate Oil Adducts. A medium pressure, stainless steel, hydrogenation reactor was charged with 750 g. of safflower oil (equivalent to 0.62 mole of trilinolein), 240 g. (1.87 moles) of *n*-butyl acrylate, and 37.5 g. (5% based on weight of oil) of anthraquinone. Air was flushed from the reactor with nitrogen. The reactor was then closed, nitrogen was introduced to a pressure of 20 p.s.i., and the reactor was heated to 250°C. for 1 hr. During heating the internal pressure reached 80 p.s.i. The reactor was then cooled immediately with a stream of cold water. The reaction mixture was dissolved in 700 ml. of heptane and chilled over-night at 0°C. Separated anthraquinone was removed by filtration, and the solution was stripped of all volatile material by distillation, first at atmospheric pressure and then *in vacuo* at 180°–190°C. Yield of the viscous, yellow residue was 950 g.

Epoxidation of Oil Adducts. The oil adducts were epoxidized with hydrogen peroxide and an ion-exchange resin as catalyst by use of a published procedure (3) with minor modifications. These modifications were drop-by-drop additions of hydrogen peroxide and (except for the acrylate adduct) maintenance of the reaction mixture for 6 hr. at 75° to 80°C. Unlike epoxidation of acrylate adducts, epoxidation of maleate adducts was not noticeably exothermic. Because of the exothermic nature of epoxidation of acrylate adducts, the reaction mixture spontaneously rose to a temperature of 98°C. after an induction period of 0.75 hr. The temperature was then reduced to 75° to 80°C. and held for only 4 hr. Color of the epoxidized products was substantially lighter than that of the original oil adducts. On the basis of reduction in iodine value, reaction with the residual unsaturation of the oil adducts took place to the extent of 33.8–84.5% during epoxidation.

Evaluation Studies

The experimental products were evaluated as plasticizers in a) a polyvinyl chloride (PVC) composition; b) a PVC plastisol; c) a polyvinylidene chloride composition; and d) an acrylonitrile rubber. All products were evaluated in PVC and nitrile rubber. Two were examined in the plastisol and one in polyvinylidene chloride.

Polyvinyl Chloride Study. The following composition was employed:

Polyvinyl chloride (Geon 101)	100
Plasticizers	50
Barium-cadmium stabilizer	0.5

The stabilizer was reduced from the customary two to three parts to accentuate differences in the stabilizing action of individual plasticizers. Milling and molding procedures were those recommended by commercial resin manufacturers. Molded specimens were tested according to applicable ASTM methods. Controls were formulated with dioctylphthalate and two commercial epoxy type of plasticizers.

Plastisol Study. A uniform paste was prepared from 100 parts by weight of PVC and 65 parts of plasticizer by mixing in a 250-ml. beaker with a laboratory stirrer, fitted with a shearing-type agitator. Samples were examined for changes in viscosity after various periods of aging at 78°F. and 50% relative humidity. Viscosities were measured with a Brookfield viscometer, Model LVF, operating at 6 r.p.m.

Polyvinylidene Chloride Study. Polyvinylidene chloride resin (100 parts) was dissolved in enough methyl ethyl ketone to form a 35% solution. Films (3 mil dry thickness) were drawn down on glass plates. After the films had air-dried over-night, they were oven-dried at 300°F. for 5 min. and subsequently heat-aged in a circulating-air oven at 300° for 30 min. Films were examined at 5-min. intervals for change in color or clarity and for evidence of incompatibility.

TABLE II
Performance Data on PVC Compositions Containing Linoleic Adduct Esters and Epoxides

Plasticizer	100% Modulus, p.s.i.		Ultimate tensile strength, p.s.i.		Ultimate elongation, %		Set at break, %		Hardness, Shore D		Brittle point, °C.
	Unaged	Aged[a]	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	
Trimethyl ester of maleic adduct	2070	2290	3410	3070	330	300	45	40	46	47	−5
Dimethyl ester of acrylic adduct	1640	1710	3100	2300	380	210	69	23	40	45	−28
Epoxidized dimethyl ester of acrylic adduct	1720	1690	3140	2800	310	300	40	42	40	45	−11
Di-2-ethylhexyl phthalate[b]	1660	1850	2850	2880	325	320	60	55	40	45	−28
Epoxidized vegetable oil[b]	2040	2150	2990	2750	325	320	65	80	47	50	−18
Isooctyl epoxystearate[b]	1450	1410	2800	2300	370	310	83	74	40	40	−51

[a] Aged in metal block heater at 212°F. for 7 days. [b] Control plasticizer.

Nitrile Rubber Study. The following composition was employed:

Acrylonitrile (40%) rubber (Hycar 1001)	100
Carbon black (Continex SRF)	60
Zinc oxide	5
Stearic acid	1.5
Sulfur	1.5
Plasticizer	20
Benzothiazyl disulfide	1.5

Milling, curing, and testing were conducted according to applicable ASTM methods. Control plasticizers were di-2-ethylhexyl sebacate and commercial petroleum type and polymeric epoxy type of plasticizers.

Discussion

A copy of a manuscript giving a detailed account of evaluation of the 19 experimental plasticizers included in this study has been filed with the Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, N.J. Evaluation data in this paper are confined therefore to the more promising materials.

Polyvinyl Chloride Study. The linoleic adduct esters and epoxides, with the exception of the 2-ethylhexyl derivatives, showed good compatibility with PVC. The oil adduct esters and epoxides were incompatible with PVC. The results of tests of compositions containing the more promising linoleic adduct esters and epoxides are shown in Table II. Relative rating indices for these experimental plasticizers are given in Table III. One product not listed in these tables, the tri-*n*-butyl ester of the maleic adduct, rated first in light stability and third in brittle point (−25°C.); however ratings on other characteristics were comparatively low. Of the three experimental products included in these tables, two, both derivatives of the acrylic adduct, compare favorably with the controls. Although it is unlikely that the characteristics listed in Table III would have equal importance in any specific application for a plasticizer, the ratings were averaged for each plasticizer as a rough measure of their overall performance. On this basis the acrylic adduct plasticizers appeared to be equal to or better than the controls.

Plastisol Study. Only the trimethyl ester of the maleic adduct of linoleic acid and the dimethyl ester of the acrylic adduct of linoleic acid were included in this study. Di-2-ethylhexyl phthalate was the control. Viscosity changes of the plastisols are shown in Figure 1. Both of the experimental plastisols showed better viscosity stability than did the control.

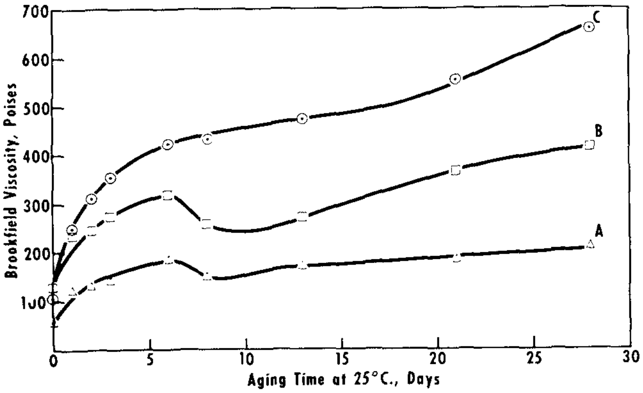

FIG. 1. Viscosity characteristics of PVC plastisols containing conjugated linoleic acid adducts: A. Dimethyl ester of acrylic acid adduct. B. Trimethyl ester of maleic acid adduct. C. Di-2-ethylhexyl phthalate (control).

Polyvinylidene Chloride Study. The experimental plasticizer selected for this study was the epoxidized dimethyl ester of the acrylic adduct of linoleic acid. It was found to be completely compatible with the polymer at the 10% and 20% levels. Control plasticizers were di-2-ethylhexyl phthalate and isooctyl epoxystearate. As judged by color stability during heat aging of the plasticized resin, the experimental plasticizer was less effective than di-2-ethylhexyl phthalate but more effective than isooctyl epoxystearate. It would be necessary to utilize a heat stabilizer with the experimental plasticizer in order to compensate for the slightly harmful effect of this plasticizer on heat stability.

Nitrile Rubber Study. Of the 11 conjugated linoleic acid adduct esters and epoxides, seven showed

TABLE III
Rating of Most Promising Linoleic Adduct Esters and Epoxides as Plasticizers for PVC

Plasticizer	Relative rating index[a]									
	Efficiency	Set at break	Brittle point	Heat stability	Light stability	Volatility	Extraction			Average
							Water	Gas	Oil	
Trimethyl ester of maleic adduct	7	2	7	8	3	8	7	6	1	5+
Dimethyl ester of acrylic adduct	2	6	2	6	8[b]	1	1	3	7	4
Epoxidized dimethyl ester of acrylic adduct	4	1	6	3	2	5	3	2	3	3
Di-2-ethylhexyl phthalate[c]	3	3	2	5	7	3	2	1	5	3+
Epoxidized vegetable oil[c]	8	5	4	2	2	2	6	5	2	4
Isooctyl epoxystearate[c]	1	8	1	1	2	7	1	8	8	4+

[a] Best = 1. [b] Plasticizer exuded. [c] Control plasticizer.

TABLE IV
Performance Data on Nitrile Rubber Compositions Containing Experimental Plasticizers

Plasticizers	300% Modulus, p.s.i.		Ultimate tensile strength, p.s.i.		Ultimate elongation, p.s.i.		Brittle point, °C.
	Unaged	Aged[a]	Unaged	Aged	Unaged	Aged	
Controls							
None	2970	......	3380	3420	400	210	—32
Polymeric epoxy	1420	......	2950	3110	600	260	—26
Petroleum type	1670	3210	3020	3300	550	310	—28
Di-2-ethylhexyl sebacate	1650	3300	3190	3410	530	210	—32
Linoleic adducts							
Trimethyl ester of maleic adduct	1620	3180	3100	3360	560	335	—27
Dimethyl ester of acrylic adduct	1480	2970	3170	3110	600	320	—32
Epoxidized dimethyl ester of acrylic adduct	1380		3130	2880	620	340	—29
Oil adducts		2740					
Safflower dibutyl maleate adduct	1510	2800	2430	2980	490	320	—18
Linseed dibutyl maleate adduct	1620	2830	2570	2830	500	310	—29

[a] Aged in metal block heater at 212°F. for 7 days.

TABLE V
Rating of Most Promising Adduct Products as Plasticizers for Nitrile Rubber

Plasticizer	Relative rating index[a]					
	Efficiency	Compression set	Volatility	Extraction		Brittle point
				ASTM oil No. 1	Ref. fuel B	
Controls						
None	10	4	11	16	4	1
Polymeric epoxy type	2	10	10	17	9	6
Petroleum type	5	2	13	15	10	4
Di-2-ethylhexyl sebacate	3	1	14	6	6	1
Linoleic adducts						
Trimethyl ester of maleic adduct	3	1	3	8	2	5
Dimethyl ester of acrylic adduct	2	1	9	11	1	1
Epoxidized dimethyl ester of acrylic adduct	1	6	9	1	3	3
Oil adducts						
Safflower dibutyl maleate adduct	4	3	2	2	16	9
Linseed dibutyl maleate adduct	5	8	4	12	15	3

[a] Best = 1.

good compatibility with acrylonitrile synthetic rubber. The remaining four, which included the epoxidized tri-2-ethylhexyl ester and the tri-*n*-butyl ester of the maleic adduct and the epoxides of the di-2-ethylhexyl ester and the di-*n*-butyl ester of the acrylic adduct, were only partially compatible. All of the vegetable oil adduct esters and epoxides showed good compatibility. As judged by appearance and feel of the specimens, compositions plasticized with the vegetable oil adduct products were "drier" than some plasticized with compatible linoleic adduct esters and epoxides. Performance data and relative rating indices for the more promising experimental plasticizers are given in Tables IV and V. It is evident that the experimental plasticizers compared favorable to the control plasticizers. The dimethyl ester of the acrylic adduct equalled or exceeded any of the controls.

Considered as a group, the vegetable oil adduct esters and their epoxides were generally similar in performance to the petroleum type of control except that they were less volatile and less readily affected by ASTM oil No. 1. The lowest brittle point was observed with the linseed dibutyl maleate adduct.

All of the plasticizers tested, both experimental and control, showed approximately equivalent behavior in tests for contact and migration staining.

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[Received September 9, 1960]

Water Absorption of Soybeans

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The rate of water absorption of U.S. and Japanese soybeans has been measured at 10° and 25°C. and at initial moisture levels ranging from 7.5 to 14.0%. The principal controlling factor in absorption of water is the seed coat. However the rate of water absorption of sound whole beans is also influenced by the initial moisture level in the beans; the lower the moisture the slower the rate of water absorption. The presence of hard beans also reduces the rate of water absorption. U.S. soybeans usually have lower moisture and contain more hard ones than do Japanese beans. These factors are attributed to the climatic differences of the two countries. No fundamental differences were found in the rate of water absorption of U.S. and Japanese soybeans.

THE RATE OF WATER ABSORPTION of soybeans is controlled by their seed coat; a pinhole or a crack in the coat greatly increases the absorption rate.

Brown, Stone, and Andrews (2) of the Tennessee Agricultural Experiment Station described a labo-

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[1] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.