TABLE V
Comparison of Natural Earth and Activated Alumina for Bleaching Off-Colored Commercial Cottonseed Oils

Refined oil		Type of oil	Color index of bleachable oils	
No.	Color index		Natural earth[a]	Alumina[b]
E	128.0	Refined and bleached oil + gossypol (heated)	117.0	40.3
F	219.0	Screw-pressed (commercial)	82.6	56.9
G	125.0	Screw-pressed (commercial)	62.3	30.2
H	147.0	Screw-pressed (commercial)	56.5 45.4[c]	28.8 28.3[c]
I	130.0	Screw-pressed (commercial)	52.6	31.5
J	171.0	Screw-pressed (commercial)	48.3	35.9
K	104.0	Screw-pressed (commercial)	46.3	30.6
L	101.0	Screw-pressed (commercial)	35.4	32.3
M	134.0	Screw-pressed—under refined (commercial)	26.0	19.9
N	105.0	Prepressed—solvent prime bleachable	14.1 7.0[c]	15.7 5.1[c]

[a] A.O.C.S. earth, 4 g./100 g. oil, standard A.O.C.S. bleach method.
[b] No. 101 alumina, 4 g./100 g. oil, 5-min. bleach at 225°C.
[c] After deodorization.

alumina has reasonable affinity for red fixed pigments of gossypol origin, it was found that this adsorbent had little, if any, effect on the removal of the green pigments sometimes encountered in cottonseed oils. These green pigments are effectively removed from cottonseed oil by activated charcoal (2,3). The data reported in Table VI indicate that treatment of the oil with about 0.6% activated charcoal, following bleaching with alumina, effectively removes green pigments. The oils which were treated with alumina and charcoal had no significant absorption in the chlorophyll region (620–670 mμ) and were free of any visual appearance of green color.

TABLE VI
Removal of Green Pigments—Alumina Bleaching of Refined Off-Colored Cottonseed Oil

Adsorbent (g./100 g. oil)		Color index	Adsorbent (g./100 g. oil)		Color index
Activated alumina[a]	Charcoal[b]		Activated alumina[a]	Charcoal[b]	
4.0	None	49.4	1.0	0.6	59.5
4.0	0.2	36.2	2.0	0.6	46.2
4.0	0.4	34.9	3.0	0.6	37.3
4.0	0.6	32.3	4.0	0.6	32.3
4.0	0.8	32.7	5.0	0.6	30.9
4.0	1.0	33.0	6.0	0.6	28.8

[a] Activated alumina No. 20 (—400 mesh).
[b] Activated charcoal, vegetable oil grade.

Properties of Bleached Oil. The temperature required for the most effective use of activated alumina in bleaching off-colored cottonseed oils (225°C.) is considerably higher than that normally used in conventional bleaching with natural earth (100–120°C.). That this higher temperature has no apparent adverse effect on the oil is shown by the data recorded in Table VII, where a comparison is made of properties of an oil bleached with activated alumina and natural bleaching earth. Alumina had no detectable effect on the unsaturation, natural antioxidants (tocopherols), fatty acid isomerization, or oil stability. It was further observed that the amount of oil entrained in both the activated alumina and the natural earth is about the same.

TABLE VII
Comparison of Alumina and Natural Earth Bleaching on Oil Characteristics

Property	Refined oil	Bleached oil		
			Alumina	
		Natural earth[e]	Atmospheric bleach	Vacuum bleach
Color index	105.8	14.3	15.8	16.8
Oil retention of adsorbent,%[a]	......	25.1	25.2	......
Iodine number[b]	104.5	104.7	104.4	104.4
Refractive index, n_D 25°C.	1.4698	1.4699	1.4700	1.4699
Unsaponifiable matter, %[b]	0.57	0.53	0.59	0.55
Neutral oil, %[b]	99.7	99.5	99.7	99.6
Tocopherols, %[c]	0.053	0.055	0.056	0.056
Peroxide number–before deodorization[b]	34.2	20.2	24.8	23.6
Peroxide number–after deodorization[b]	0.0	0.0	0.0	0.0
Stability–after deodorization, hrs.[d]	22.5	36.0	40.5	35.0
Stability–after deodorization, hrs.[d]	139.0	80.0	69.0	67.0
Absorptivity:				
268 Mμ–triene conjugation	0.400	0.255	0.681	0.570
233 Mμ–diene conjugation	0.019	0.222	0.115	0.076
315 Mμ–tetraene conjugation	0.0015	0.0083	0.0083	0.00065

[a] Vacuum filtration, 1 hr. at 100°C., filter cake extracted with ether.
[b] By applicable A.O.C.S. methods (1).
[c] See reference (9).
[d] Oven stability-time at 100°C. to attain peroxide number of 100 (8).
[e] A.O.C.S.

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Divinyl Sulfone-Eleostearate Adducts as Plasticizers for Nitrile Rubber

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Four divinyl sulfone-eleostearate adducts were synthesized and compared with dibutyl sebacate as plasticizers for nitrile rubber. Three of these, the adducts of methyl *alpha*-eleostearate, its hydrogenated derivative, and that of tung oil, were found to be satisfactory primary plasticizers. The stocks prepared from the unhydrogenated adducts were superior in plasticizing efficiency to those prepared from their hydrogenated derivatives. The divinyl sulfone-tung oil adduct yielded a rubber which met the low-temperature flexibility requirements (−40°C.) of the automotive industry.

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THE DIELS-ALDER reaction of divinyl sulfone and eleostearic acid has been investigated recently in this laboratory, and evidence was adduced to show that the addition product is a transannular sulfone (1). Since monocyclic adducts of the eleostearates are satisfactory plasticizers for polyvinyl chloride (2,3,4,5) and also nitrile rubber (6), it became of interest to determine what influence the bicyclic compound would have on plasticizing properties. Accordingly the divinyl sulfone adducts of tung oil and methyl *alpha*-eleostearate, as well as their hydrogenated derivatives, were prepared and tested as plasticizers for vinyl chloride-vinyl acetate copolymer and nitrile rubber. Although these compounds were found to be incompatible with polyvinyl chloride, they had desirable properties when employed as plasticizers for nitrile rubber. It is the purpose of this paper to describe the preparation of these adducts and their properties as plasticizers for nitrile rubber.

Experimental

Starting Materials. Domestic tung oil containing 75.2% of trienoic acids was employed: I.V. (hydrogenation), 228.0; n_D^{20}, 1.5195.

Commercial divinyl sulfone was used without further purification: b.p., 102°C./10 mm.; sp. gr. 20/20° C., 1.1788; n_D^{20}, 1.4788.

Methyl esters of tung oil fatty acids containing 82% *alpha-* and 3% *beta*-methyl eleostearates[2] were prepared by methanolysis of tung oil as described in a previous publication (4): b.p., 162–4°C./10 microns; n_D^{25}, 1.5003.

Preparation of the Plasticizers. In the following preparations no attempt was made to produce the pure adducts since this, as previously reported (1), is a matter of some difficulty. Only simple procedures were employed in the isolation of the adducts because it was desirable to have a practical method for the preparation of suitable plasticizers.

Divinyl Sulfone-Methyl alpha-Eleostearate Adduct. A 337.0-g. quantity of the methyl esters of tung oil fatty acids, 150 ml. of divinyl sulfone, and 0.5 g. of hydroquinone were stirred with a magnetic stirrer and heated between 150 and 180°C. for 8 hrs. under a blanket of nitrogen gas. Excess divinyl sulfone was removed by vacuum-stripping on a steam cone, employing nitrogen as a sweep-gas. Unreacted methyl esters of tung oil fatty acids were distilled off under vacuum, leaving 329.7 g. of the light yellow, slightly turbid adduct which could not be distilled. The residue was filtered twice while hot through a bed of Hyflo Super Cel, yielding 284.7 g. of a clear, slightly viscous material.

Anal. Calcd. for $C_{23}H_{38}O_4S$: S, 7.8; OCH_3, 7.5; I.V., 123.6. Found: S, 6.8; OCH_3, 7.1; I.V. (hydrogenation), 119.8; n_D^{25}, 1.5048.

Divinyl Sulfone-Tung Oil Adduct. This material was prepared by a similar procedure, as described above, in which 384.0 g. of tung oil, 150 ml. of divinyl sulfone, and 1.0 g. of hydroquinone were heated at 100–150°C. for 6 hrs. Excess divinyl sulfone was removed by vacuum stripping on a steam cone with nitrogen as a sweep-gas. After filtering the product twice through a bed of Hyflo Super Cel while keeping the funnel and the material hot, 279.5 g. of a clear and viscous adduct were recovered which contained 4.8% of sulfur and had an I.V. (hydrogenation) of 115.3.

Hydrogenation of the Adducts. A procedure described previously for the preparation of other saturated tung oil adducts (5) was followed for the hydrogenation of the two divinyl sulfone adducts described in this paper. Three 35.0-g. samples of each addition product were hydrogenated at room temperature in a shaking type of hydrogenation apparatus with 3.0 g. of 10% palladium-carbon catalyst and 150 ml. of solvent. Ethyl acetate was employed as a solvent for the divinyl sulfone-methyl *alpha*-elostearate adduct and acetone for the divinyl sulfone-tung oil adduct. The theoretical amount of hydrogen required for complete saturation of the ethylenic bonds was taken up after 1 to 1½ hrs. of hydrogenation. After the catalyst was filtered off and the solvent removed, the remaining products were quite viscous.

Evaluation Procedures. The four divinyl sulfone-eleostearate adducts described above were screened as plasticizers for nitrile rubber, using the following formulation:

Nitrile rubber (Hycar 1042—33% acrylonitrile)	100.0 parts
SRF Black	60.0 "
Zinc oxide	5.0 "
Stearic acid	1.5 "
Sulfur	1.5 "
Benzothiazyl disulfide	1.5 "
Plasticizer	20.0 "

Cure: 30 min. at 310°F.(154.4°C.)

The details of the procedures followed in the milling, curing, preparation of test specimens, and the various tests employed in the evaluation of the plasticizers have been described previously (8). The plasticizers were rated as compatible if the formulations showed no active bleeding or contact smearing during the 190 days of observation.

TABLE I

Physical Properties of Nitrile Rubber (Hycar 1042) Plasticized with Divinyl Sulfone-Eleostearate Adducts

Plasticizers	Ultimate elongation (%)		300% Modulus (p.s.i.)		Tensile strength (p.s.i.)		Hardness Shore A (10 sec.)	Weight loss[a] (%)	Volume change[b] (%)	Brittle point (°C.)	Compatibility (days)[c]
	Unaged	Aged[a]	Unaged	Aged[a]	Unaged	Aged[a]					
Divinyl-sulfone adducts											
Methyl α-eleostearate	770	610	900	1460	2330	2380	44	0.42	26.7	—32	190
Tung oil	820	650	750	1170	2080	2050	43	0.36	35.3	—40	190
Hydrogenated divinyl sulfone adducts											
Methyl α-eleostearate	700	510	1040	1720	2380	2310	44	0.49	26.4	—36	190
Tung oil	680	510	1040	1620	2120	2190	44	0.41	35.9	—40	21[d]
Dibutyl sebacate (control)	640	510	1080	1840	2180	2460	44	5.55	20.0	—50	190

[a] Aged in forced draft oven at 212°F. for 48 hrs.
[b] Immersed 72 hrs. in mixed solvent at 78°F.
[c] Indicated no exudation during time specified.
[d] Smeared on contact.

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[2] The amount of eleostearates present was determined by the method of Hoffmann *et al.* (7).

Discussion

Table I presents the data obtained in the plasticizer screening tests for the divinyl sulfone-eleostearate adducts compounded with nitrile rubber. All of the experimental adducts milled satisfactorily in the nitrile rubber formulation. The hydrogenated divinyl sulfone-tung oil adduct however became incompatible as shown by exudation after 21 days of shelf aging. The divinyl sulfone adducts of methyl *alpha*-eleostearate and of tung oil were superior to the hydrogenated counterparts and to the control, dibutyl sebacate, in plasticizing efficiency, *i.e.*, lower modulus and greater elongation. Moreover the divinyl sulfone-tung oil adduct yielded a rubber which met the low-temperature flexibility requirements (−40°C.) of the automotive industry. All the compositions containing the experimental adducts exhibited modulus, elongation, and weight loss properties which were either comparable to or better than the control, plasticizer formulation. When subjected to the accelerated aging tests, the divinyl sulfone-methyl *alpha*-eleostearate adduct and its hydrogenated counterpart produced rubber stocks which had satisfactory low-temperature brittle points.

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ABSTRACTS .... R. A. REINERS, Editor

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H. S. Liles, Louise R. Morrow, and E. G. Perkins

• Fats and Oils

THE EFFECT OF METHOD OF CARE ON THE FRYING LIFE OF FAT. M. Elizabeth Rust and Dorothy Harrison (Depts. of Institutional Management and Foods and Nutrition, Kansas State Univ., Manhattan). *Food Tech.* 14, 605-609 (1960). The purpose of this study was to determine the effect of 4 methods of care used in restaurants on the length of the frying life and deteriorative changes in the fat. Regardless of method of care, there was a significant negative correlation between the acid number of the fat and the acceptability of French fried potatoes. The method of care significantly affected the viscosity of the fat and the percentage weight loss of fat and potatoes during frying. In general, there was little correlation between values for a chemical and a physical method used to determine the percentage of fat in the fried potatoes.

EFFECT OF CHEMICAL ADDITIVES ON THE SPREADING QUALITY OF BUTTER. I. THE CONSISTENCY OF BUTTER AS DETERMINED BY MECHANICAL AND CONSUMER PANEL EVALUATION METHODS. J.G. Kapsalis, J.J. Betscher, T. Kristoffersen, and I.A. Gould (Dept. of Dairy Tech., Ohio Agr. Exp. Station, Columbus). *J. Dairy Sci.* **11**, 1560-69 (1960). An instrument, the Consistometer, was perfected for measuring spreadability (by a knife) and hardness (by a wire) of butter. The instrument differentiated between butters with 120 to 500 g. of hardness and 260 to 1,542 g. of spreadability. Such butters ranged between easy to difficult to spread on the basis of a consumer panel evaluation. Evaluation of 109 commercial butter samples obtained from 14 different states located in different parts of the country revealed a high degree of correlation between the instrument and the consumer panel. The results indicated that the most desirable butter consistency from the consumer's standpoint represents a range on the Consistometer of 400 to 900 g. resistance to the knife, or 140 to 200 g. resistance to the wire, under the conditions of the study.

SPECTROPHOTOMETRIC DETERMINATION OF STERCULIC ACID. A.J. Deutschman, Jr., and I.S. Klaus (Dept. of Agri. Biochem., Univ. of Arizona, Tucson). *Anal. Chem.* 13, 1809-10 (1960). The cyclopropene configuration present in sterculic and malvalic acids has been found to be toxic to non-ruminants. The reaction conditions for carrying out the Halphen test for this structure have been studied and a procedure is proposed that results in reproducible color development. The reaction has been used as the basis for a spectrophotometric determination of the cyclopropene structure. The absorbance curve of the solution is presented. Purified sterculic acid was used for the preparation of a standard absorbance curve at 505 mμ. Standard error estimate is $\pm 0.2 \times 10^{-4}$ gram of sterculic acid in 10 ml. of solution with an accuracy of ± 10% at 95% confidence at the mid-point of the range for which the procedure is suggested.

EMULSIFYING AGENTS IN SHORTENING AND PROCESS OF PRODUCING SAME. H.H. Young and K.H. Spitzmueller (Swift & Co.). *U.S. 2,963,371.* A shortening composition consists of a major amount of glyceridic material having shortening properties and a small amount of the mixture produced by the reaction between *beta*-propiolactone and fatty acids having from about 6 to about 22 carbon atoms.

USE OF ORTHO-PHTHALIC-ETHYLENE GLYCOL POLYESTER IN GAS LIQUID CHROMATOGRAPHIC ANALYSIS OF FATTY ACID ESTERS. B.M. Craig (Prairie Regional Lab., Natl. Res. Council, Saskatoon, Saskatchewan, Can.). *Chem. and Ind.* **1960**, 1442. The polyester was dissolved in chloroform and applied to 40–60 mesh acid washed C-22 firebrick in the ratio of 1 to 4.5 w/w. An 8 ft. by 3/16 in. O.D. column was operated at 215° with a helium flow-rate of 50 ml. per minute to separate the methyl esters of rapeseed oil in 40 minutes. The separation factor for oleic/stearic was 1.11. The "polarity" of the packing with the *ortho*-phthalic polyester can be altered by mesh size of solid and by the ratio of liquid to solid phase. This polyester shows limited bleeding at 225°. It has three to six times the capacity of the aliphatic polyesters making it useful in preparative work.

PRODUCTION OF A SMOOTH, UNIFORM, AIR-FREE ALUMINUM STEARATE GREASE. J.F. Richards and R.A. Thompson, Jr. (Esso Res. & Eng. Co.). *U.S. 2,962,440.* Aluminum stearate (1 to 7 parts by weight) is dispersed in mineral lubricating oil (25 to 75% of the total 100 parts of oil) and heated to 250 to 450°F. The dispersion is then cooled to about 120°F. or lower under an absolute pressure of about 0 to 7.7 p.s.i.a. with stirring and the balance of the oil is added.

ALKALI FUSION PRODUCTS OF CYCLOHEXENONES IN LUBRICANT MANUFACTURE. A.J. Morway and J.H. Bartlett (Esso Res. & Eng. Co.). *U.S. 2,962,441.* In a lubricating oil is dispersed (a) a mixture of 2 to 75 molar proportions of a C_1 to C_6 fatty acid, 0.05 to 5.0 molar proportions of a C_6 to C_{30} fatty acid, and 1 molar proportion of a cyclic hexenone and (b) an alkali or alkaline earth metal base. The dispersion is heated to a temperature of about 400 to 700°F. and held for about ½ to 2 hours.

PAN OIL COMPOSITION AND PROCESS OF MAKING SAME. H. Brody and A.E. Fahlen (Swift & Co.). *U.S. 2,963,372.* The described pan dressing consists of an edible fatty material having in-