did not prove, that other spectroscopic isomers were absent.

As punicate isomerized, a definite maximum for *alpha* eleostearate was observed, analogous to the maximum for conjugated *cis, trans* linoleate observed during isomerization of *cis, cis* linoleate (1). The concentration of the *alpha* isomer then decreased to the equilibrium value while that of the *beta* isomer rose steadily to the equilibrium value.

As *alpha* eleostearate isomerized, the *beta* isomer increased regularly to its equilibrium content. Punicate concentration apparently went through a slight but definite maximum, greater than the final low equilibrium value.

As *beta* eleostearate isomerized, the content of the *alpha* and punicate isomers increased regularly to equilibrium values.

As previously mentioned, no bands between 10 and 11 μ were observed during the isomerization of any of the three isomers studied other than those which could be attributed to these isomers. If one assumes from this observation that spectroscopic isomers other than the three already characterized by secondary 10–11 μ bands are absent during equilibration, the structure of punicate may be deduced to be *ctc*. This follows from the fact that punicate has only one *trans* double bond (weakest 10.1 μ band) leaving *cct (tcc)* and *ctc* as alternate structures. The *cct (tcc)* structures would be expected to give a *tct* structure as one of the primary products of isomerization, which might be expected to have other secondary bands in the 10–11 μ region. Since no such bands were observed, this structure seems less probable than the alternate *ctc* structure. On the other hand, the *ctc* punicic structure should give the observed maximum of the *alpha* isomer *(ctt)* during its isomerization. The synthetic proof of the structure of punicate by Crombie made this presumptive "proof" of little consequence. However the apparent absence of other isomers in the equilibrium would also mean that the center double bond (at least if *trans*) does not readily isomerize; otherwise the equilibrium should contain some of all six spectroscopic species.

Speculation as to the cause of this presumed inactivity of the center double bond to *cis, trans* isomerization led to the following suggestion by M. M. Kreevoy of the University of Minnesota: when a double bond forms the intermediate complex or activated state with the catalyst, it loses much of its double bond character. If this occurs on an "outer" double bond of a conjugated triene, the two remaining double bonds are still conjugated and the resonance due to their conjugation should give appreciable stability to this intermediate. When the "center" double bond forms the intermediate complex, conjugation is essentially lost so this unstabilized form would be less probable than that from an "outer" double bond. This leads to the interesting prediction that isomerization of an isomer with a *cis* center double bond might lead to a mixture of the *tct, cct, tcc*, and *ccc* isomers with none of the known isomers, each of which has a *trans* center double bond. The all-*cis* isomer would be the most interesting one to isomerize since it should have no bands in the 10–11 μ region by analogy to the *cis, cis* linoleate. The *cct (tcc)* isomer should be the first to appear, followed by the *tct* isomer.

Summary

Methyl *beta* eleostearate, *alpha* eleostearate, and punicate isomerize readily with iodine and light to an equilibrium mixture of 2.6% punicate, 33% *alpha* eleostearate, and 64% *beta* eleostearate. The course of isomerization is in agreement with the following structures: *ttt* for *beta* eleostearate, *ctt* for *alpha* eleostearate, and *ctc* for punicate. These structures have been proven *via* synthesis by Crombie and Jacklin. There is some evidence that the center double bond of a conjugated triene isomerizes less readily than the outer double bonds.

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Bleaching of Off-Colored Cottonseed Oils[1]

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The adsorption of fixed red pigments from refined off-colored cottonseed oil by several adsorbents is described by the empirical Freundlich adsorption isotherm. Numerical values for the coefficient and the exponent in the Freundlich equation were determined for several oils and several adsorbents. Activated alumina was found to be a superior adsorbent for removing the red color bodies. It was observed that the variations from oil to oil in the numerical values of the coefficient and the exponent of the Freundlich equation were smaller for the several aluminas than they were for the other adsorbents studied. The particle size and moisture contents of the alumina, and the temperature of activated adsorption were of importance in determining the effectiveness with which the red color bodies were removed from the oils. The conditions required for optimum bleaching with alumina had no detectably adverse effect on oil quality.

THE VALUE and usefulness of about 25% of the cottonseed oils produced in the United States are impaired because of the presence in the oil of red pigments that are not removed by the conventional refining and bleaching processes. The evidence developed during the past several years suggests very strongly that the alkali-fast, red color bodies in off-colored oils are derivatives of gossypol and that they

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may arise in crude cottonseed oil while it is in storage. The red color bodies may also occur in seed that has been stored improperly or that has been damaged in the field before harvest.

The present communication is concerned with the removal by use of adsorbents of the red color bodies from refined oils.

Materials and Methods

A bleachable, prepressed, solvent-extracted cottonseed oil and several screw-pressed cottonseed oils were obtained from commercial sources and refined by A.O.C.S. Official Method Ca 9a-52 (1). In addition, an off-colored oil was prepared by adding gossypol (0.5%) to a high-quality commercial salad oil (refined, bleached, winterized, and deodorized) for the purpose of comparing the behavior of gossypol derivatives produced in cottonseed oil in this manner (4) with the red color bodies that occur in off-colored cottonseed oils of commercial origin. The gossypol-oil solution was heated for 16 days at 60°C. to fix the color. Unreacted gossypol was then removed from the oil by extraction with aqueous sodium carbonate (5).

The adsorbents used are listed in Table I. All were of commercial origin except aluminum silicate, which was synthesized in the laboratory, and the A.O.C.S. official bleaching earth.

TABLE I
Relative Efficiency of Adsorbents for Red Color Bodies in Refined Off-Colored Cottonseed Oil

Adsorbent [a]	Particle size (mesh)	Color index of bleached oil
None	......	125.0
Natural earth (A.O.C.S.)	......	62.3
Acid activated earth (commercial)	......	52.8
Magnesium oxide—chromatographic grade	−400 M	53.2
Magnesium trisilicate—chromatographic grade	−400 M	42.5
Silicic acid—chromatographic grade	−400 M	74.5
Zinc carbonate—reagent grade	Powdered	75.8
Calcium alumino silicate—synthetic	−400 M	79.5
Sodium alumino silicate—synthetic	−400 M	65.0
Aluminum hydroxide—reagent grade	......	80.9
Aluminum silicate—adsorbent grade	−400 M	51.5
Calcined alumina—commercial, grade No. 1	−325 M	66.9
Calcined alumina—commercial, grade No. 3	−325 M	61.0
Calcined alumina—commercial, grade No. 14	−325 M	76.7
Hydrated alumina—commercial, grade No. 31	−400 M	76.7
Hydrated alumina—commercial, grade No. 730	5–10 micron	52.9
Activated alumina—chromatographic grade	−400 M	35.0
Activated alumina—commercial, grade No. 1	−400 M	33.4
Activated alumina—commercial, grade No. 3	−400 M	32.8
Activated alumina—commercial, grade No. 101	−400 M	28.0

[a] Four parts by weight of adsorbent per 100 parts of oil.

It has been shown (2,3,7) that the Freundlich adsorption isotherm describes the activated adsorption of cottonseed oil pigments on fuller's earth when the reduction in color intensity, obtained on treating the oil with the earth, is assumed to be proportional to the quantity of pigments removed, and the color intensity of the oil after treatment is assumed to be proportional to the concentration of the pigments after equilibrium conditions are established. The color indices, r and c of the refined and of the bleached oils, respectively, were determined by the method described by Pons, Kuck, and Frampton (6). The differences, $r - c = x$, were used in the Freundlich equation,

$$\frac{x}{m} = kc^n$$

where x is the reduction in color intensity, c the color intensity after treatment, m the quantity of adsorbent used, and k and n are constants.

In the usual investigations of adsorption phenomena the quantity of adsorbent is held constant while the initial solute concentration is varied. However, in the experiments carried out in this investigation, the initial solute concentration (color intensity of refined oil) remained constant while the quantity of adsorbent was varied.

The technique for adsorption bleaching was essentially that described in the A.O.C.S. Official Method Cc 8a-52 for cottonseed oil, but the temperature and time of treatment were varied.

Results

Data obtained from tests with the adsorbents listed in Table I indicate that of all those used, activated alumina was the most effective one for the removal of fixed red pigmentation from refined off-colored cottonseed oils.

Activated allumina was chosen for special attention. Variables studied for its use were bleaching temperature, time of contact between oil and alumina, and moisture content and particle size of alumina. The data (Table II) demonstrate that 225°C. is the best temperature and that maximum adsorption of the color bodies occurs when the moisture content of the alumina is 10% or more and the surface area of this adsorbent is increased by grinding. Under these conditions the time of contact for adsorption is relatively short. Increasing it from 5 to 25 min. gave practically no improvement in bleached oil color.

The relative effectiveness of activated alumina, used under optimum conditions, and of natural bleaching earth, used under conditions described in A.O.C.S. Official Method Cc 8-52, is illustrated in Figure 1. It is evident that the activated alumina is many times more effective than the earth in removing the alkali-fast, red color bodies.

Adsorption Isotherms. That the Freundlich adsorption isotherm is followed in the adsorption of the red color bodies is demonstrated by the regressions of log x/m on long c, plotted in Figure 2, for six adsorbents. The intercept on the ordinate is the logarithm of the coefficient k in the Freundlich equation, and the slope is equal to the exponent n. The calculated values for constants k and n obtained with several adsorbents used in bleaching a refined off-colored oil

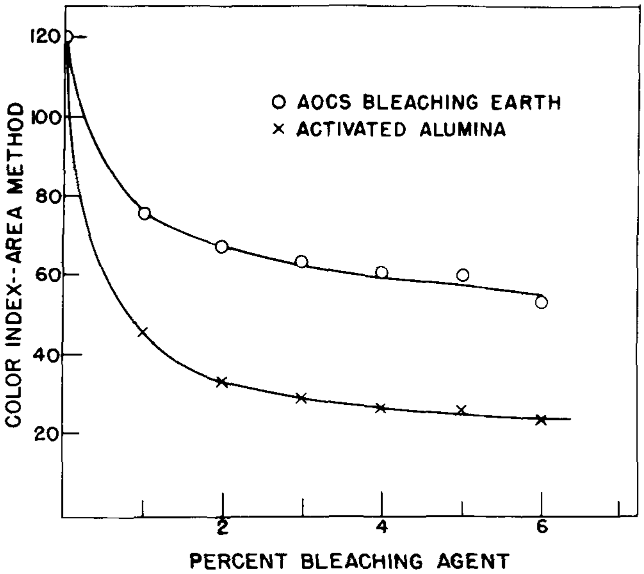

Fig. 1. Comparison of the relative effectiveness of activated alumina and A.O.C.S. official bleaching earth in removing alkali-fast color bodies from refined off-colored cottonseed oil.

TABLE II

Variables Affecting Adsorption of Red Color Bodies from Refined Oil by Activated Alumina

Oil temperature		Contact time at 225°C.		Moisture content of alumina[b]		Particle size of alumina[c]		
°C.[a]	Color index	Min.	Color index	%	Color index	Retained on mesh	Passed through mesh	Color index
26	74.7	5	31.1	Dry	46.1	200	100	56.2
75	66.5	10	32.7	1.41	47.1	270	200	48.6
120	64.4	15	32.9	4.69	40.7	320	270	42.5
150	64.1	20	33.4	5.64	37.7	......	400	35.0
200	48.0	25	31.7	6.72	37.0	......	......	......
225	31.1	....	....	10.42	33.7	......	......	......
260	30.1	....	....	13.36	33.2[d]	......	......	......
				14.37	32.6[d]			

[a] Five minutes to reach temperature; 5 min. bleaching at temperature specified.
[b] Bleaching at 225°C. for 5 min.
[c] Bleaching with alumina containing 10% moisture at 225°C. for 5 min.
[d] Equilibrium moisture content when aluminas were stored over water.

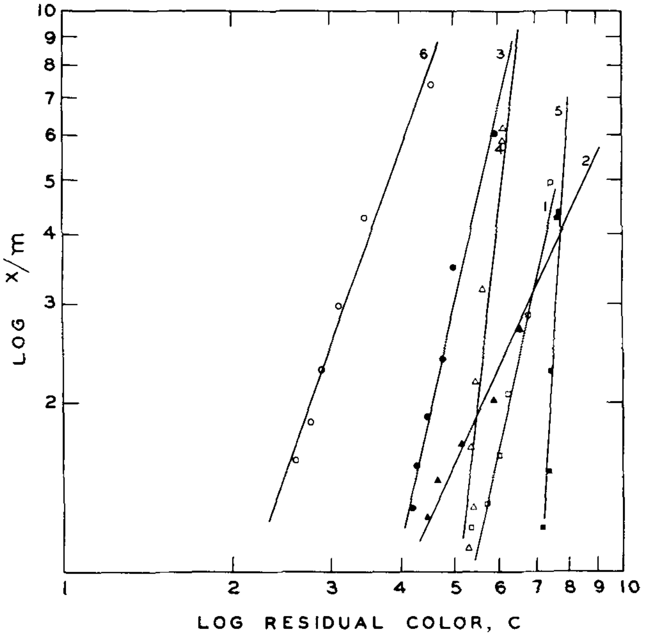

FIG. 2. Freundlich adsorption isotherms for the adsorption of alkali-fast color bodies from a refined off-colored cottonseed oil on: (1) A.O.C.S. official bleaching earth; (2) acid activated earth, (3) magnesium silicate; (4) aluminum silicate; (5) sodium alumino silicate; (6) activated alumina.

TABLE III

Adsorption Constants of Adsorbents Used to Bleach Refined Off-Colored Cottonseed Oil[a]

Adsorbent	Freundlich constants		Grams adsorbent per 100 g. of oil to attain color index of:	
	k	n	20.0	30.0
Natural earth (A.O.C.S.-Official)	0.00067	4.35	765.0	119.0
Activated earth (A.O.C.S.)	0.055	2.09	43.1	16.5
Magnesium trisilicate	0.0026	4.38	184.5	28.1
Aluminum silicate	3.59×10^{-7}	9.10	∞	∞
Sodium alumino silicate	9.94×10^{-14}	15.29	∞	∞
Activated alumina—No. 101 (—400 mesh)	0.117	2.78	12.4	3.6
Activated alumina—No. 1 (—400 mesh)	0.263	1.75	11.3	5.0
Activated alumina—No. 3 (—400 mesh)	0.249	1.79	11.7	5.1
Activated alumina—No. 20 (—100; +200 mesh)	0.018	2.71	91.1	27.6
Activated alumina—No. 20 (—200; +270 mesh)	0.080	2.00	32.8	13.2
Activated alumina—No. 20 (—270; +320 mesh)	0.152	1.78	20.0	8.8
Activated alumina—No. 20 (—400 mesh)	0.230	1.68	14.2	6.5

[a] Refined oil off-colored. Color index = 124.8.

are recorded in Table III. In the case of activated aluminas the values for k are higher and for n lower than those calculated for the other adsorbents.

These adsorption constants were used to calculate the quantities (Table III) of each of the several adsorbents required to reduce the color index of a refined off-colored oil from 125 to 30 and also to 20. Smaller quantities of alumina are required to attain these bleach colors.

The numerical values of the coefficient k and the exponent n of the Freundlich equation for alumina No. 20 varied with particle size (Table III); the values for k increased while those for n decreased with increasing fineness of the adsorbent. The values of k and n for the four aluminas of commercial origin were all of the same order of magnitude.

The coefficient and exponent vary with the type of oil (2,3), as may be observed from the data obtained on bleaching several refined off-colored cottonseed oils with either A.O.C.S. official natural bleaching earth or activated alumina (Table IV). The variation among the constants for the alumina was less than for the earth.

A further demonstration of the greater effectiveness of activated alumina in removing the alkali-fast red color bodies is found in the data obtained on bleaching several oils with both adsorbents (Table V). Two additional points of interest may be noted: a) the red color bodies formed on adding gossypol to a high quality of salad oil have a much greater affinity for the alumina than for the natural bleaching earth; and b) there is little improvement in the color of oils H and N (bleached by either adsorbent) when the bleached oil is deodorized.

Removal of Green Pigments. Although activated

TABLE IV

Comparison of Bleaching Efficiency of Adsorbents for Several Refined Off-Colored Cottonseed Oils

Refined oil		Adsorbent	Adsorption constants		Grams of absorbent per 100 g. of oil to attain color index of:	
No.	Color index		k	n	20.0	30.0
A	125.0	Natural earth (A.O.C.S.)	0.00067	4.35	765.0	119.0
B	130.0	Natural earth (A.O.C.S.)	0.0037	3.72	227.0	45.6
C	147.0	Natural earth (A.O.C.S.)	0.0396	2.36	62.5	22.2
D[a]	105.0	Natural earth (A.O.C.S.)	1.17	2.11	1.7	0.6
A	125.0	Activated alumina No. 20[b]	0.230	1.68	14.2	6.5
B	130.0	Activated alumina No. 20[b]	0.257	1.81	12.3	5.3
C	147.0	Activated alumina No. 20[b]	0.262	1.97	12.4	5.1
D[a]	105.0	Activated alumina No. 20[b]	0.103	6.76	0.8	0.2

[a] Prime grade, bleachable.
[b] —400 mesh; 5-min. bleach at 225°C., atmospheric conditions.

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	28.8
			45.4[c]	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	15.7
			7.0[c]	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		
		Natural earth[e]	Alumina	
			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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