ity. Alkylbenzene B gives fairly good colors by all three sulfonation techniques but high oil contents, while Alkylbenzene D gives low oils when oleum sulfonated but high oil content and a poor color when SO_3-air sulfonated. Alkylbenzene G gives fair colors but high oils by the oleum methods and a poor color on SO_3-air sulfonation. On the other hand, Alkylbenzenes A and E gave good colors and low oils by all three sulfonation procedures.

It is evident that sulfonate quality obtainable from any particular alkylbenzene is greatly influenced by method of sulfonation. Variation in alkylbenzene most strongly affects the colors of SO_3-air sulfonates and the oil contents of continuous oleum sulfonates. However, the two effects are apparently not related, as the same alkylbenzenes are not necessarily poor in both qualities. Except for the above-mentioned relation, no effective general correlations between alkylbenzene inspections and sulfonate quality appear to exist. Thus, it is not yet possible to accurately predict alkylbenzene sulfonation performance without actual sulfonation tests. Small-scale sulfonation methods as described in this paper are therefore most useful in predicting sulfonate quality.

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Bleaching of Refined Cottonseed Oil with Modified Alumina Adsorbents[1]

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Abstract

Activated aluminas, modified by treatment with inorganic and organic acids were tested for their efficiency as bleaching agents and for their ability to eliminate the response of refined cottonseed oil to the Halphen test. The best of these adsorbents, an alumina containing catalytic amounts of adsorbed sulfurous acid, is a bleaching agent that is effective in removing problem pigments from off-colored cottonseed oils, and is superior to activated aluminas in removing green chlorophyll-like pigments. Oils bleached with the catalytic adsorbent are negative to the Halphen test, and are free of sulfur.

Study of the rate of reduction in the Halphen test response as a function of bleaching time and temp indicated that sulfurous acid treated alumina has a pronounced catalytic effect. The Halphen test response is eliminated during a 30 min bleaching period at 225C. Deodorization conditions employed had little effect on Halphen test reduction.

Introduction

ADSORPTION BLEACHING of refined cottonseed oil is practiced for the purpose of removing objectionable red, yellow, and green color bodies from the oil. However, the Bentonites and Fullers earths normally used for this purpose have little, if any, affinity for the refractory red color bodies which occur in about 25% of the domestically produced oils (7). Such oils are termed "off-color" refined oils.

Finely ground activated alumina was found recently to be superior to both Natural and acid activated Fullers earths for removing the red "problem" pigments from off-color refined cottonseed oils (7). Alumina, however, must be employed in conjunction with small amounts of activated carbon to remove the green chlorophyll-like pigments which occur in some refined oils (7).

Cottonseed oil, and the seed oils of seeds from many plants of the order *Malvales,* give a positive Halphen test. These oils turn red when they are heated in the presence of sulfur and carbon disulfide (1,4). It is generally assumed that this test is specific for fatty acids containing a cyclopropene ring.

Although the removal of the Halphen test response is not generally an objective of the bleaching process, adsorbents which are efficient both for the removal of objectionable pigments, and the Halphen test response, would materially broaden the scope of the bleaching process.

In the studies reported here, on the evaluation of acid modified aluminas, a catalytic sulfurous acid-treated alumina adsorbent was found to be efficient for removing green chlorophyll-like pigments as well as objectionable red and yellow pigments from refined cottonseed oil. Oils bleached with this adsorbent were found to be negative to the Halphen test, and free of sulfur.

Materials and Methods

The several modified alumina adsorbents used in the present study were prepared from a commercial activated alumina which was ground in a ball mill to pass a 400 mesh screen. The particle size distribution of this stock alumina, and of official AOCS Natural Earth (1) are reported in Table I. Fifty-g por-

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[1] Presented at the AOCS Meeting in New Orleans, 1962.

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TABLE I
Particle Size Distribution of Adsorbents

Particle size range	Size distribution[a]	
	Stock alumina	AOCS Natural earth
	%	%
0–1 μ	3.4	0.5
1–3 μ	9.6	1.6
3–5 μ	13.5	1.4
5–8 μ	40.5	6.0
8–11 μ	25.5	75.0
11–15 μ	8.5	11.8
Over 15 μ	0.0	3.7

[a] Determined by the Andreason sedimentation pipette, distilled water as suspension media (5).

tions of the ground alumina were suspended for one hr in 500 ml of 5–10% aqueous solutions of the acids or salts as listed in Table II. The adsorbent was recovered by filtration and air dried to about 15% moisture.

The acidity of each preparation was determined by suspending 1-g portions in 10 ml of distilled water for 1 hr, after which the pH of the aqueous phase was determined using a glass electrode.

Bleaching efficiences of all alumina adsorbents were determined in glass equipment. One hundred g of refined oil and 4.0 g of adsorbent were introduced into a 300 ml, three-neck, round bottom flask equipped with a vacuum tight stirrer, and evacuated to 0.5–1.0 mm Hg pressure. The suspension was heated to 225C for 30 min, with stirring, and cooled to 50C before exposure to the atmosphere. The adsorbent was removed by filtration. Comparable bleaching experiments were conducted with AOCS Official Natural Earth (1), but at a bleaching temp of 120C.

Bleached oils were steam deodorized at 200–225C for 1 hr in glass laboratory equipment (3).

The color index proposed by Pons, Kuck, and Frampton (8) was used to determine the proportion of the total pigments removed from the oils. The color indices, divided by 10, yield values of the same order of magnitude as the conventional Lovibond red colors (8).

Appropriate AOCS methods were used for the determination of oil acidity, I.V., conjugated diene and triene, and isolated *trans* isomers, as well as the chlorophyll-like pigments of the bleached oils (1). Because of the change in the absorption characteristics of the green pigments in the alumina-bleached oils, as compared with Fullers earth-bleached oils, the AOCS Method Cc 13d-55 was modified in that absorbance measurements at 610, 650, and 690 mμ were used in the determination of the concentration of green chlorophyll-like pigments.

TABLE II
Effect of Acid Treatments of Activated Alumina on Bleaching Efficiency

Treatment of activated alumina	pH of adsorbent	Properties of bleached oil			
		Acidity-calc. as oleic acid	Color index $\times 10^{-1}$	Reduction in Halphen test	Chlorophyll
		%		%	ppm
None	9.23	0.06	2.16	18.1	0.73
Acid treatment					
Hydrochloric	3.96	0.36	3.10	98.6	0.004
Sulfuric	4.10	0.71	2.88	93.0	......
Sulfamic	3.85	0.35	2.91	91.9	......
Phosphoric	3.60	0.54	3.22	81.3	0.30
Sulfurous	4.00	0.52	2.80	100.0	0.13
Oxalic	4.58	0.29	3.09	79.0	......
Citric	3.03	0.30	3.45	78.8	0.19
Sorbic	3.15	0.11	5.39	93.0	......
Acetic	4.38	0.06	2.92	82.5	0.47
Carbonic	7.73	0.10	2.33	52.1	0.41
Boric	6.73	0.21	3.38	86.6	0.39
Salt treatment					
Sodium sulfite	8.60	0.04	3.39	100.0	0.66
Sodium bisulfite	5.10	0.30	3.40	100.0	0.24

The method of Deutschmann and Klaus (4) was used in determining the intensity of the Halphen test. Fractional reduction in this assay induced by the treatment was obtained from the ratio of the absorbance values per unit wt of treated and refined oils, respectively.

Results and Discussion

In the absence of adsorbent, heating refined cottonseed oil at 225C under reduced pressure for 1–3 hr destroys heat sensitive pigments of the oil, but has little effect on the fixed red pigments (Table III). Prolonged heating also promotes a gradual reduction in the Halphen test response of the oil (Fig. 1, Curve 1).

The adsorption of the red problem pigments on normal activated alumina (Table II) is almost instantaneous, while the destruction of the heat-sensitive pigments catalyzed by alumina is slower. About a 30 min bleaching period is required to eliminate the heat-sensitive pigments. This effect is suggested by the virtual equivalence of the bleached and deodorized oil colors after 30 min. bleaching period. In agreement with previous observations (7), normal activated alumina has little effect on reducing the concentration of green pigments.

The data (Fig. 1, Curves 1 and 2) suggest that normal activated alumina exerts a mild catalytic

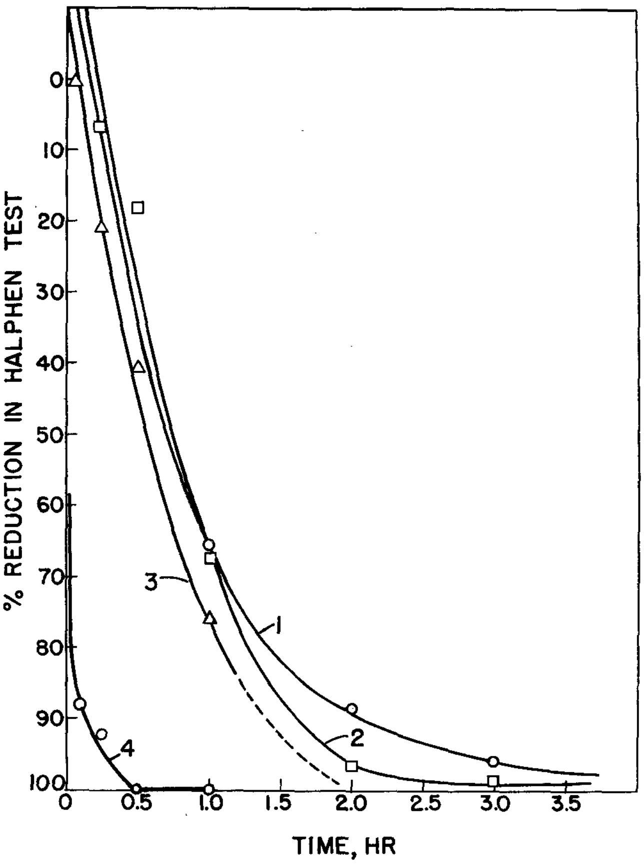

FIG. 1. Rate of reduction in Halphen test response of treated cottonseed oils. (1) Refined oil heated at 225C under vacuum; (2) Refined oil bleached with 4.0% of normal activated alumina at 225C under vacuum; (3) Alumina bleached oil (Curve 2) after steam deodorization for 1 hr at 200C; and (4) Refined oil bleached with 4.0% of sulfurous acid-treated alumina at 225C under vacuum.

TABLE III

Heat Treatment of Refined Cottonseed Oil—Catalytic Effect of Normal Activated Alumina

Adsorbent and conditions[a]	Bleach time	Color index × 10^{-1}		Halphen reduction		Chlorophyll pigments	
		Bleached oil	Deodorized oil[c]	Bleached oil	Deodorized oil[c]	Bleached oil	Deodorized oil[c]
	min.			*%*	*%*	*ppm*	*ppm*
None[b]	0	17.22	......	0.0	......	0.91	......
None[b]	60	4.92	......	65.6	......	0.26	......
None[b]	120	4.36	......	88.5	......	0.23	......
None[b]	180	4.40	......	95.8	......	0.37	......
AOCS Natural Earth	30	3.80	3.66	54.4	71.2	0.04	0.0
Activated alumina	5	3.62	2.24	14.2	21.2	0.83	0.81
Activated alumina	15	2.74	2.16	6.7	0.2	0.70	0.74
Activated alumina	30	2.16	2.10	18.1	40.3	0.73	0.73
Activated alumina	60	2.08	2.00	67.3	75.7	0.66	0.68
Activated alumina	120	2.20	......	96.7	......	0.58	......
Activated alumina	180	1.93	......	98.1	......	0.58	......

[a] 4.0% Adsorbent, vacuum bleaching (0.5 mm Hg) at 120C for earth, and 225C for alumina.
[b] Refined oil, heated at 225C for indicated times under vacuum.
[c] Bleached oils steam deodorized 1 hr at 200C.

effect on the reduction in Halphen response beyond that which may be attributed to the heat treatment alone. It may be noted that heating periods in excess of 2–3 hr were required for substantial, but not complete, reduction in Halphen test response. Steam deodorization had little effect on further reduction in the Halphen test intensity.

Modified Aluminas. Acid modifications of activated alumina produced marked changes in the properties of alumina, as may be noted from the data recorded in Table III. Most of these modified adsorbents exhibited a pronounced catalytic effect on reducing the intensity of the Halphen test, as compared with normal activated alumina. Another effect was the improved adsorption of the green chlorophyll-like pigments. Most of the treated aluminas were not as effective as activated alumina for removal of total pigmentation from the refined oil.

Sulfurous Acid Treated Alumina. Among the adsorbents listed in Table III, sulfurous acid-treated alumina gave the best results in terms of a low color index, low green pigment and low Halphen response. Accordingly, this adsorbent was selected for further study.

Suspending activated alumina in a saturated aqueous solution of sulfurous acid (7–9%), followed by air drying of the filtered adsorbent, produced a modified adsorbent which contained the equivalent of 0.22% SO_2, as determined by the Monier-Williams method (2). The sulfurous acid is weakly adsorbed, since heating the treated alumina at 100C for 1 hr reduced the SO_2 content to 0.03%.

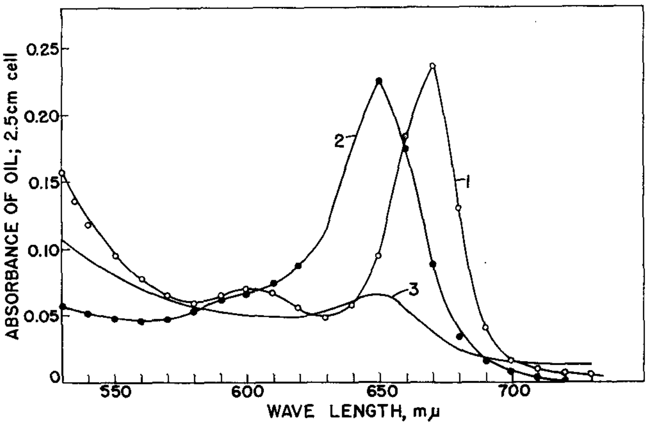

FIG. 2. Effect of normal activated and sulfurous acid-treated aluminas on the chlorophyll pigments of refined cottonseed oil. (1) Refined oil only; (2) Refined oil bleached with 4.0% of normal activated alumina; and (3) Refined oil bleached with 4.0% of sulfurous acid-treated alumina.

That the action of sulfurous acid-treated alumina in reducing the Halphen response is catalytic may be inferred from the calculation of the molar ratio of malvalic acid to SO_2. At an adsorbent concentration of 4%, and assuming a concentration of 1–3% of Halphen positive fatty acid in the oil (9,10), the calculated molar ratio varies between 77:1 and 26:1. These molar ratios do not suggest a stoichiometric reaction between SO_2 and the cyclopropene ring of malvalic acid. Moreover, the oil was found to be free of sulfur, odorless, and of bland taste. Although the bubbling of SO_2 through a refined oil, followed by vacuum de-gassing and steam deodorization, yielded an oil that was also negative to the Halphen test, it contained 0.55% total sulfur, was darkly colored and had a distinctive musty or straw-like odor.

Green Pigment Removal. A comparison of the effect of both activated and sulfurous acid-treated alumina on the adsorption of the green pigments from cottonseed oil is illustrated by the absorption spectra shown in Figure 2. A sample of commercially refined cottonseed oil (Curve 1) exhibits a principal absorption max at 670 mμ. The absorption max at 670 mμ has been attributed by O'Connor et al. (6) to pheophytin, a chlorophyll degradation product. Treatment of the oil with activated alumina (Curve 2) causes a shift in the principal absorption max from 670–651 mμ, but the intensity of the absorption remains essentially unchanged. This shift suggests that a change in the structure of the green pigment occurred, and that little, if any, is removed. Bleaching the refined oil with sulfurous acid-treated alumina also resulted in a corresponding shift of the absorption max, but there was a considerable decrease in the absorbance at 651 mμ.

The optimum conditions for maximum bleaching

TABLE IV

Influence of Treatment Conditions on Bleaching Efficiency of Sulfurous Acid-Treated Alumina

Adsorbent	Bleaching conditions			Properties of bleached oils		
	Adsorbent	Temp	Time	Color index	Halphen reduction	Chlorophyll
	%	*C*	*min*	× 10^{-1}	*%*	*ppm*
H_2SO_3-Alumina	4.0	125	30	10.22	26.5	0.17
H_2SO_3-Alumina	4.0	150	30	8.95	30.3	0.27
H_2SO_3-Alumina	4.0	175	30	7.59	47.3	0.24
H_2SO_3-Alumina	4.0	225	30	2.65	100.0	0.13
H_2SO_3-Alumina	1.0	225	30	4.57	72.9	......
H_2SO_3-Alumina	2.0	225	30	4.27	94.5	......
H_2SO_3-Alumina	3.0	225	30	3.57	93.1	......
H_2SO_3-Alumina	4.0	225	30	2.65	100.0	0.13
H_2SO_3-Alumina	4.0	225	5	3.36	88.2	0.10
H_2SO_3-Alumina	4.0	225	15	3.14	92.2	0.12
H_2SO_3-Alumina	4.0	225	30	2.80	100.0	0.13
H_2SO_3-Alumina	4.0	225	60	2.84	100.0	0.13

efficiency, reduction of the intensity of the Halphen test, and green pigment removal with sulfurous acid-treated alumina occur at a bleaching temp of 225C, and for a heating time of 30 min (Table IV). An indication of the effectiveness of sulfurous acid-treated alumina on reducing the intensity of the Halphen test is found in the data plotted in Figure 1, Curve 4.

The removal of the green pigments seems to be almost instantaneous as may be seen from the data in Table IV.

Mixed Adsorbents. Mixtures composed of activated and sulfurous acid-treated alumina are better bleaching agents than either adsorbent alone. Bleaching experiments in which the ratio of activated alumina to sulfurous acid-treated alumina varied from 0–100% (Table V) indicate that a mixture composed of equal parts of activated and sulfurous acid-treated alumina is the best for the combined effects of bleaching (removal of the red, yellow, and green pigments) and reduction in the intensity of the Halphen test. Actually, bleaching efficiency for red and yellow pigments was almost equal to that obtained with activated alumina alone. Bleaching time, however, must be increased to 60 min to eliminate the response to the Halphen test. Apparently, the rate of reduction in the intensity of the response to the Halphen reagent and efficiency of removal of the green pigments are both more dependent on the relative proportions of the adsorbents in the mixture than is the total bleaching efficiency.

TABLE V

Bleaching Cottonseed Oil with Mixed Alumina Adsorbents—Effect of Relative Proportions

Composition of mixed adsorbent		Bleaching conditions			Bleached oil properties		
Normal alumina	H_2SO_3 treated alumina	Adsorbent	Temp	Time	Color index	Halphen reduction	Chlorophyll
%	%	%	*C*	*min*	×*10⁻¹*	%	*ppm*
100	0	4.0	225	30	2.16	18.1	0.73
90	10	4.0	225	30	2.26	67.0	0.34
75	25	4.0	225	30	2.33	96.4	0.27
50	50	4.0	225	15	2.53	95.1	0.19
50	50	4.0	225	30	2.15	97.3	0.19
50	50	4.0	225	60	2.33	100.0	0.20
0	100	4.0	225	30	2.80	100.0	0.13

Application to Commercial Oils. Results of treatments of four commercially refined cottonseed oils of different origins with both natural earth and sulfurous acid-treated alumina are compared in Table VI. Oils A and B were badly off-colored oils, oils C and D were bleachable oils. Reduction in the Halphen test response ranging from 31.5–95.7% of that found in the refined oils were found for natural bleaching earth. On the other hand, the reduction in the response to the Halphen test was 100% in each case for the oils bleached with sulfurous acid-treated alumina.

TABLE VI

Comparative Bleaching Experiments with Commercial Refined Cottonseed Oils

Refined oil No.	Type of oil	Adsorbent used for bleaching	Bleaching oil properties		
			Color index	Halphen reduction	Chlorophyll
			×*10⁻¹*	%	*ppm*
A	Expeller	None	13.39	0.0	0.71
A	Expeller	Natural earth	6.34	56.1	0.006
A	Expeller	H_2SO_3-alumina	2.73	100.0	0.071
B	Screw-pressed	None	10.76	0.0	0.34
B	Screw-pressed	Natural earth	4.36	31.5	0.004
B	Screw-pressed	H_2SO_3-alumina	2.61	100.0	0.041
C	Pre-press, solvent	None	11.40	0.0	0.42
C	Pre-press, solvent	Natural earth	2.40	95.7	0.001
C	Pre-press, solvent	H_2SO_3-alumina	1.11	100.0	0.012
D	Pre-press, solvent	None	12.15	0.0	0.70
D	Pre-press, solvent	Natural earth	1.50	98.2	0.001
D	Pre-press, solvent	H_2SO_3-alumina	1.46	100.0	0.079

Without exception, the oils bleached with treated alumina were lighter in color than the comparable earth-bleached oils. Removal by both absorbents of the green chlorophyll-like pigments was substantially complete.

Oil Properties. Properties of a typical commercially refined oil bleached with sufurous acid-treated alumina and with natural bleaching earth, and followed by steam deodorization, are compared in Table VII.

TABLE VII

Properties of Cottonseed Oil Bleached with Sulfurous Acid-Treated Alumina

Oil property	Control-refined oil	Bleached and deodorized oil	
		Natural earth	H_2SO_3-treated alumina
Color index, × 10⁻¹	12.15	1.08	1.05
Halphen reduction, %	0.0	71.2	100.0
I.V.	110.2	109.9	109.9
Conjugated diene, %	none	0.38	0.59
Conjugated triene, %	none	0.02	0.04
Isolated trans isomers, %	3.2	3.7	4.3
Tocopherols, %	0.049	0.049	0.040

The sulfurous acid-treated alumina induced no detectable change in unsaturation. In contrast with the earth-bleached oil, however, minor amounts of diene conjugation and isolated trans isomers were found for the alumina-bleached oil. The tocopherol contents were essentially unchanged by treatment of the oil with treated alumina. The results of these studies on the properties of the oil confirm previous reports that activated alumina does not markedly affect the physical and chemical properties of cottonseed oil (7).

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