appeared to have typical nonionic characteristics. Calcium stability values (15) were greater than 1,800.

Metal ion stability values (3) for the nonionic soaps are recorded in Table III. Increase in the number of oxyethyl groups markedly improved the stability to Al^{+++}, Zn^{++}, and Pb^{++}. On heating the test solution of the metal soap above room temperature, the listed cloud points were observed.

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Reactivation of Alumina Used in Bleaching of Off-Colored Cottonseed Oils

J. C. KUCK, W. A. PONS, JR., and V. L. FRAMPTON, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

Spent alumina recovered from bleaching cottonseed oil with activated alumina can be reactivated by simple incineration at 400–700°C. and remoistening to at least 10% moisture content. The cycle of bleaching and regeneration may be repeated indefinitely with only nominal mechanical losses of alumina. Losses of refined oil by entrainment in activated alumina need be only 0.5%.

IT IS ESTIMATED that the value and usefulness of about 25% of the cottonseed oil produced in the United States is impaired because of the presence in the oil of red color bodies that are not removed by the conventional refining and bleaching processes. An improvement in the color of such oils would help to channel them into end uses where the use of cottonseed oil is on the decline (1).

Pons, Kuck, and Frampton (2) demonstrated that activated alumina may be used to bleach badly off-colored cottonseed oils. The present report is concerned with the reactivation of the spent alumina recovered from the bleaching operation.

Materials and Methods

The study was limited to four off-colored refined cottonseed oils. Oils *A* and *C* were obtained by laboratory refining crude oils which had been stored in the laboratory at ambient temperatures for several years. The refining was by use of appropriate A.O.C.S. methods (3). Oils *B* and *D* were refined oils of commercial origin.

The activated alumina used was received in pellet form and of commercial origin. The pellets were ground in a ball mill to a powder fine enough to pass through a 400-mesh sieve, and the powder was moistened to 14.7% moisture content. Moistening was accomplished by storage over water in a desiccator. The procedure offered by Pons *et al.* (2) was followed in conducting bleaching tests with activated alumina under atmospheric or reduced pressure (0.5 mg. Hg.).

A.O.C.S. official bleaching earth (natural fuller's earth) (3) was used as a reference bleaching agent.

Color indices were determined by the method of Pons, Kuck, and Frampton (4).

Experimental

Reactivation of Spent Alumina. The results from preliminary experiments indicated that the organic matter which was strongly absorbed on the spent alumina could be eliminated from the alumina by simple incineration. In a more detailed study, 1,500 g. of a badly off-colored oil (Oil *C*) were bleached with 150 g. of activated alumina; the mixture was heated at 225°C. for 5 min. The slurry was filtered on a Buchner funnel. The filter cake, which was washed with petroleum ether (b. 68–71°C.) and air dried, served as a stock supply of spent alumina.

Seven-gram portions of the spent alumina were spread to a depth of 2 mm. in flat-bottom porcelain dishes (67 mm. x 67 mm. x 13 mm. deep), and heated in a muffle furnace at different temperatures and for differing periods of time (Table I). The several portions were then cooled and moistened to a moisture content of 10% or more before they were used in the bleaching tests (2) reported in Table I.

It is known that the adsorption on activated alumina of the color bodies in off-colored cottonseed oil follows the Freundlich adsorption isotherm (2). The isotherm may be expressed by the equation:

$$R - C = EdC^n$$

where *R* is the color index of the refined oil, *C* the color index of the bleached oil, *E* the quantity of alumina used per unit weight of oil, and *d* and *n* are constants. The values of *n* for the variously activated alumina preparations, calculated from the data in Table I are also recorded in that table.

The rate of change of the color index with respect

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[1] One of the laboratories of the Southern Utilization Research and Development Division of the Agricultural Research Service, U. S. Department of Agriculture.

TABLE I

Reactivation of Spent Alumina—Effect of Temperature and Time of Incineration on Bleaching Efficiency

Adsorbent		Per cent adsorbent in bleaching			n	dC/dE[b]
		2	4	6		
		Color index of bleached oil[a]				
Natural earth (A.O.C.S.)		......	64.0	......	......	......
Original activated alumina		46.3	35.6	33.0	3.03	−3.11
Reactivated alumina						
Temp. (°C.)	Time (min.)					
	0	73.9	72.2	68.1	16.7	−0.54
400	60	54.6	42.9	40.5	3.13	−3.02
450	30	52.0	40.5	38.4	3.33	−2.85
	60	50.4	39.0	35.7	2.63	−3.56
500	30	48.4	39.7	37.0	3.44	−2.76
	60	47.1	37.0	36.5	3.45	−2.75
550	15	51.1	39.9	36.6	2.50	−3.71
	30	47.8	37.3	34.6	2.63	−3.56
	60	50.0	39.7	37.0	3.03	−3.11
600	15	48.4	40.6	39.0	3.44	−2.76
	30	51.8	40.6	36.2	2.61	−3.59
	60	49.2	39.9	36.1	3.03	−3.11
700	15	50.7	37.6	34.7	2.63	−3.56
	30	47.8	38.8	36.8	3.33	−2.85

[a] Refined oil color—127.0.

[b] Values for dC/dE when the color index of the bleached oil is 20, and the quantity of alumina used is 2% by weight of the refined oil.

TABLE II

Bleaching Power of Reactivated Alumina

Adsorbent	Color index of bleached oil			
	Oil A[a]	Oil B[a]	Oil C[b]	Oil D[b]
Natural earth (A.O.C.S.)	52.0	36.0	64.0	46.7
Alumina reactivation cycles				
0	36.0	26.2	38.7	27.2
1	37.6	38.2	45.1	35.3
2	39.8	25.6	43.3	34.0
3	39.2	28.3	40.1	31.0
4	41.1	29.2	42.8	28.9
5	38.1	41.2	46.0	31.5
6	39.6	30.7	45.2	30.8
7	38.0	30.1	45.3	33.1
8	39.6	31.6	42.9	29.9
9	39.6	36.9	44.0	29.3
10	39.3	27.4	42.9	28.0
11	38.2	......	......	32.7
12	......	......	......	32.5
13	......	......	......	32.4
14	......	......	......	33.4
15	......	......	......	27.0

[a] Bleached under atmospheric condition.

[b] Bleached under reduced pressure, 0.5 mm. Hg.

to the quantity of alumina used was calculated for each preparation by the relationship

$$\frac{dC}{dE} = -\frac{(R-C)C}{E[C+(R-C)n]}$$

and the values for dC/dE are reported in Table I. The color index of the bleached oil and the quantity of alumina used for the calculations of the rates appearing in Table I were 20 and 2%, respectively.

No pattern evolved from these studies to relate the activity of the reactivated alumina to the manner of reactivation. Apparently the differences in n and in dC/dE for the several reactivations arose because of experimental error, and all that is necessary for the reactivation is that all of the adsorbed oil and pigments be burnt off.

Successive Reactivations of Spent Alumina. Five hundred grams of a stock supply of off-colored refined cottonseed oil was mixed with 50 g. of activated alumina, and the mixture was heated at 225°C. for 5 min. The mixture was then filtered and the excess oil was washed from the filter cake with petroleum ether. The cake was then heated at 550°C. for 30 min., cooled, and stored over water in a desiccator until the moisture content was 10% or more. Aliquot fractions of the reactivated alumina were used to bleach samples of each of four different oils; 2 g. of alumina were used for 50 g. of oil. The mixtures of oil and reactivated alumina were heated at 225°C. for 5 min. under either atmospheric conditions (Oils *A* and *B*) or under reduced pressure (Oils *C* and *D*). The samples were filtered on a Buchner funnel under reduced pressure, and the color index of the filtered oils was determined. The spent aluminas from the filter cakes were combined with the remainder of the stock supply of reactivated alumina, and the entire lot of alumina was mixed with 500 g. of the stock oil and heated at 225°C. for 5 min. This cycle of bleaching and reactivation was repeated 15 times. The data recorded in Table II indicate that the regeneration cycle may be repeated indefinitely.

The moisture content of the reactivated and moistened alumina preparations ranged from 12.7 to 22.5%. There was no apparent relationship between the moisture content in this range and the capacity of each activated alumina to remove the color bodies from the oil. Evidently, it is only necessary that the moisture content of the activated alumina be more than 10% for it to serve as a good bleaching agent for cottonseed oil (2).

The losses of alumina that accrue during the bleaching and reactivation operations appear to be nominal. For example, when the experiment was carried out with 50.0 g. of alumina, 67.4% of the alumina was recovered after 14 successive bleaching and regeneration cycles in tests with Oil *D* (Table II). This corresponds to a mechanical loss of 2.3% of alumina per bleaching and regeneration cycle in a small laboratory scale operation that involved many transfers of sample material. It may be assumed that the losses in a large scale operation would be less.

A portion of the oil adsorbed on the spent alumina can be recovered by extracting it with petroleum ether. The oil so recovered is a bleached oil. For example, the combined petroleum ether washings of the filter cakes obtained in a series of tests with Oil *B* yielded an oil with a color index of 39.6. This may be compared with an average color index of 31.6 for Oil *B* bleached with activated alumina, and with 36.0 for this oil bleached with fuller's earth. Comparable values were 39.8 for Oil *D* recovered from entrainment in the spent alumina, 31.1 for the oil bleached with activated alumina, and 46.7 for the oil bleached with fuller's earth. Evidently the oil recovered from spent alumina by petroleum ether extraction may be regarded as a bleached oil.

Recovery of Oil from Spent Alumina. The quantities of oil constituents that are irretrievably lost on the alumina may be seen from the data given in Table III. In these experiments 200 g. of oil were bleached with 8 g. of activated alumina or 8 g. of A.O.C.S. Official Earth and the slurries were filtered under reduced pressure (1 mm. Hg.) on a Buchner funnel. The filtration was continued for 30 min. after the oil level reached the level of the filter cake. Each cake was then washed with five 75-ml. portions of petroleum ether (b. 68–71°C.). The solvent was removed from the extracted oil by distillation under reduced pressure. The weight of recovered bleached oil was determined.

The quantities of oil constituents recovered from the filter cake and of constituents irretrievably lost on the filter cake were also determined by the method of Rich (5). The data are reported in Table III.

The oil recovery data indicate that with the laboratory method employed, oil retention on spent

TABLE III

Oil Recovery from Alumina Filter Cake

Adsorbent	Oil recovery			Oil constituents per 100 g. of adsorbent[a]		
	As bleached oil	Extracted from cake with petroleum ether	Total oil recovered	Total in cake	Extracted with petroleum ether	Residual in cake
	g.	g.	%	g.	g.	g.
Alumina[b]	195.4	3.6	99.5	34.7	20.4	14.3
Alumina	195.2	3.1	99.2	36.2	20.3	15.9
Alumina	195.1	3.5	99.3	......	......	......
Natural earth, A.O.C.S.	195.8	3.2	99.5	26.3	13.8	12.5

[a] Determined by method of Rich (5).
[b] Bleached under reduced pressure, 0.5 mm.

alumina is about 35% the weight of the absorbent used. This compares favorably with data obtained with the same method for oil retention on natural earths of commercial origin, namely 26–33% (5). By solvent extraction of spent alumina the oil retention can be reduced to 15%, thus allowing a total recovery of 99.5% of the refined oil as bleached oil.

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Evaluation of Cottonseed Meals Prepared by Extraction with Acetone-Hexane-Water Mixtures[1]

G. E. MANN, F. L. CARTER and V. L. FRAMPTON Southern Regional Research Laboratory,[2] New Orleans, Louisiana, and A. B. WATTS and CHARLES JOHNSON, Department of Poultry Industry, Louisiana State University, Baton Rouge, Louisiana

Eleven cottonseed meals have been prepared by batch extractions of a given lot of cottonseed with various acetone-hexane-water mixtures using several different extraction schedules. These meals, together with eight meals of commercial origin and a commercial soybean meal, have been subjected to chemical evaluation and assayed for protein quality using the growing chick as a test animal. In general the acetone-hexane-water meals were superior to the commercial cottonseed meals for promoting the growth of the chicks and, considering all the meals, a linear correlation was obtained between the logarithm of the weight gains and the available lysine contents of the meals. The free and total gossypol contents of the cottonseed meals appeared to have little or no influence on the growth rates.

UNDUE APPLICATION OF HEAT during the processing of cottonseed has an adverse effect upon the nutritive quality of the meal proteins (1,2). This has been attributed to: a) the destruction of part of the lysine of the seed proteins (3); b) the binding of the *epsilon* amino groups of a portion of the lysine by gossypol and other meal constituents (4,5). Lysine bound in this manner is not available to nonruminant animals (6).

Evidence developed by Frampton *et al.* (7) indicates that the variation in nutritive quality for broilers noted among commercial cottonseed meals is largely accounted for by variations in the lysine contents of the meals, and that the influence of the gossypol contents of the meals is too small to be statistically measured. While the effects of gossypol and gossypol derivatives on the growth of broilers may be subject to question, it has been established that the presence of these compounds is undesirable from other nutritional aspects. For example, these substances are responsible for some of the abnormalities that occur in stored shell eggs produced by hens fed cottonseed meals (8). Moreover, gossypol and gossypol derivatives may be implicated in the mortalities that occur among swine receiving diets containing certain cottonseed meals (9).

To achieve the desired end of obtaining cottonseed meals low in gossypol without application of heat, King, Kuck, and Frampton (10) have proposed the use of a solvent mixture composed of acetone, hexane, and water (A:H:W; proportions by volume, 53:44:3) for the extraction of raw (or mildly-treated) cottonseed flakes. Meals prepared using this solvent proved to be low in gossypol and high in available lysine. (The term "available lysine" refers to the meal lysine having free *epsilon* amino groups as determined (13) by use of 2,4-dinitrofluorobenzene.) Preliminary feeding tests indicated that they were superior to conventional cottonseed meals in promoting the growth of young animals.

This report describes further the use of A:H:W solvents for the preparations of cottonseed meals. The extraction variables investigated included the composition of the A:H:W mixtures, the time of contact between the cottonseed flakes and the first portion of solvent, and the total number of solvent passes used. All meals were characterized chemically and tested for their growth-promoting properties using the chick as a test animal. For comparison eight other meals, primarily of commercial origin, were assayed along with the A:H:W meals.

Experimental

Seed and Flakes. The single lot of delinted seed was stored at 60°F., and from time to time portions were hulled and separated using standard mill ma-

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[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.