The variation in linolenic acid content from 1 to 14% may influence the selection of species for certain uses.

Variations in oil content from 11% (possibly not fully mature) to 39% and in hydroxy acid content from 45% to 74% suggest that the development or selection of plant types suitable for present production and harvesting methods is feasible.

Acknowledgments

The authors are grateful to C. A. Glass for infrared analysis of the oils, to R. L. Cunningham for technical assistance, and to Drs. A. S. Barclay, R. E. Perdue, and H. S. Gentry of the Crops Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Maryland, for supplying samples for analysis.

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[Received June 7, 1961]

The Oxyethylation of 9, 10-Octadecanediols and 9, 10-Dihydroxystearonitrile. Nonionic Soaps[1]

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The alkali-catalyzed reaction of ethylene oxide with the *meso-* and *dl*-forms of 9,10-octadecanediol and with *threo*-9,10-dihydroxystearonitrile was carried out in an apparatus that was equipped with automatic controls for temperature and pressure.

The earlier consumption found for the *dl*-form compared to the *meso* is attributed to intramolecular hydrogen bonding. A characteristic constant for the distribution of products is calculated.

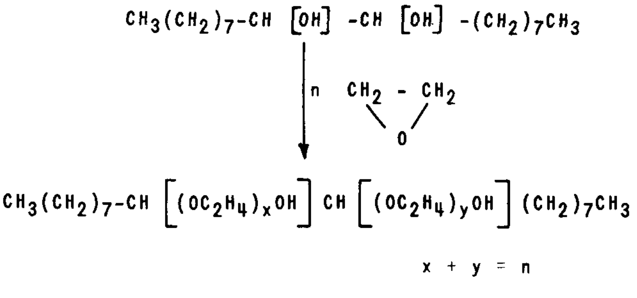
The products formed are nonionic surface-active agents with the hydrophilic portion at the middle rather than at the end of the hydrophobic chain. Properties were primarily determined by the value of n, the average number of oxyethyl groups. Optimum emulsifying properties were found at n = 4; optimum wetting at n = 12.

The oxyethylated nitriles were hydrolyzed to the corresponding "nonionic soaps," which have typical nonionic characteristics; unlike soap they are not easily precipitated by hard water or various metal ions.

THE REACTION of ethylene oxide with mono- or dihydroxystearic acids under the usual conditions of alkaline catalysis seems to occur exclusively at the carboxyl group (1,17), and the product is a mixture of monoesters, diesters, and polyethylene glycols (6,19). This appears to be true even with the corresponding methyl esters; in each case there is practically no reaction of ethylene oxide at the secondary hydroxyl groups.

To avoid the presence of competing groups, *meso-* and *dl*-9,10-octadecanediols were used as model compounds to investigate the alkali-catalyzed reaction of ethylene oxide with fat-based secondary glycols.

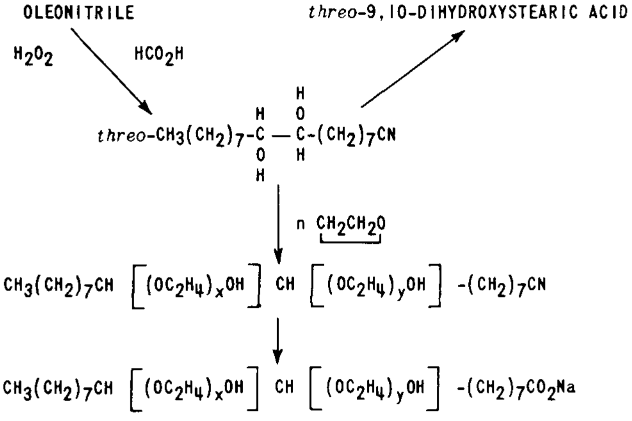
The *meso-* and *dl*-9,10-octadecanediols were oxyethylated under controlled conditions (1.4 atms. pressure of ethylene oxide, 160°, 4 mole % KOH) to a selected average number, n, of oxyethyl groups (n = 4, 8, 12, 16):



$$CH_3(CH_2)_7\text{-}CH\,[OH]\,\text{-}CH\,[OH]\,\text{-}(CH_2)_7CH_3 \xrightarrow{n\ CH_2-CH_2\ (O)} CH_3(CH_2)_7\text{-}CH\,[(OC_2H_4)_xOH]\,CH\,[(OC_2H_4)_yOH]\,(CH_2)_7CH_3$$

$x + y = n$

threo-9,10-Dihydroxystearonitrile was oxyethylated in a similar manner (n = 4, 6, 8) and hydrolyzed to the corresponding nonionic soap:



$$\text{OLEONITRILE} \xrightarrow{H_2O_2,\ HCO_2H} threo\text{-}CH_3(CH_2)_7\text{-}\overset{H}{\underset{OH}{C}}\text{—}\overset{OH}{\underset{H}{C}}\text{-}(CH_2)_7CN \rightarrow threo\text{-9,10-DIHYDROXYSTEARIC ACID}$$

$$\xrightarrow{n\ CH_2CH_2O} CH_3(CH_2)_7CH\,[(OC_2H_4)_xOH]\,CH\,[(OC_2H_4)_yOH]\,\text{-}(CH_2)_7CN \rightarrow CH_3(CH_2)_7CH\,[(OC_2H_4)_xOH]\,CH\,[(OC_2H_4)_yOH]\,\text{-}(CH_2)_7CO_2Na$$

Nonionic Soap

9,10-Octadecanediols

meso-9,10-Octadecanediol, m.p. 129.4–130.5° and *dl*-9,10-octadecanediol, m.p. 78.5–79.4°, were made from nonyloin (19). The ditosylate of the *meso*-glycol, m.p. 56.2–57.0°, was found to melt lower than the ditosylate of the *dl*-glycol, m.p. 64.6–65.6°; this is an anomalous relationship though not without parallel (14). The ditosylates were reconvertible in high yield to the original glycols by means of potassium acetate, followed by hydrolysis.

threo-9,10-Dihydroxystearonitrile

Commercial oleonitrile was redistilled; and middle fractions, b.p. 140–145°/0.05 mm., n_D^{30} 1.4564–1.4568 [reported (7) 1.4566], iodine value 96.2 (calcd. 96.3) were used for hydroxylation. Oleonitrile was treated with 98% formic acid and 30% hydrogen peroxide (12) to give the hydroxy-formate, hydrolyzed under mild conditions to *threo*-9,10-dihydroxystearonitrile, m.p. 74.7–75.7°, yield 45–50%. To prove structure a sample was hydrolyzed with 10% aqueous alcoholic

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[1] Presented at the Annual Meeting, American Oil Chemists' Society, St. Louis, Mo., May 1–3, 1961.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

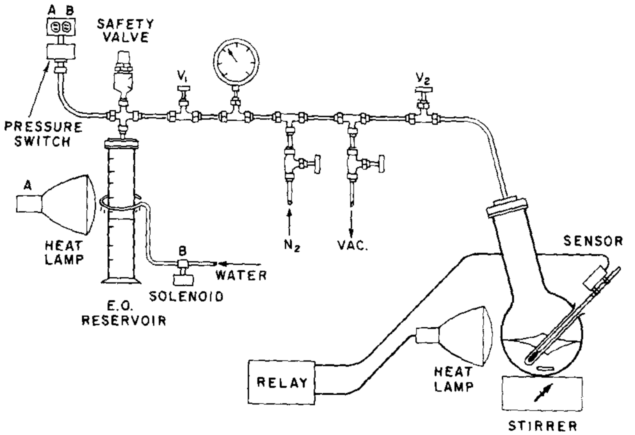

Fig. 1. Apparatus for oxyethylation under constant pressure, temperature, and stirring rate, with measured level of liquid ethylene oxide.

sodium hydroxide to an acid, m.p. 93.4–94.8°, shown by melting-point, mixed melting-point, and infrared spectrum to be *threo*-9,10-dihydroxystearic acid (16).

Reaction with Ethylene Oxide

Typical Oxyethylation. The graduated reservoir was charged with liquid ethylene oxide and attached to the apparatus shown in Fig. 1. With valve 2 closed it was freed of air by the alternate introduction of nitrogen and boiling of ethylene oxide under vacuum; finally valve 1 was closed. A 500-ml. reaction flask, containing a 23-mm.-long, glass-enclosed magnetic stirring bar, was charged with 11.25 g. (0.0393 mole) of *dl*-9-10-octadecanediol and 104.7 mg. of 85% KOH (4 mole %). With valve 2 open the glycol and catalyst were purged of air and water by heating and stirring at 140° with the alternate introduction of nitrogen and evacuation (*ca.* 25 mm.) for several cycles.

The volume of liquid ethylene oxide in the reservoir was now read (45.0 ml.), the nitrogen and vacuum valves were closed, and valve 1 was opened. The temperature of the magnetically stirred reaction mixture was brought to and maintained at 160° by the sensor and heat lamp whereas the pressure of ethylene oxide gas was maintained at 6.7-lb. gauge or at about 21 lb. total pressure by alternate heating and cooling of the reservoir as controlled by the pressure-sensitive switch. The progress of oxyethylation was followed by the decreasing volume of liquid ethylene oxide, density taken as 0.87 g./ml. After 90 min. the reaction was stopped for a weight check at 95% of the desired uptake. A final brief reaction gave 31.75 g. of a product with 11.9 oxyethylene units per mole of original octadecanediol. The weight increase of the reaction flask, which checked with the decrease in the reservoir volume, was taken as the final measure of oxide combined. After neutralization of the catalyst in isopropyl alcohol solution, this solvent was removed by vacuum evaporation.

Removal of Parent Diol. In the case of products containing sufficient surviving parent glycol to interfere seriously with water solubility, this residual diol was destroyed by oxidation. A major part of the *meso*-diol could be removed first by crystallization.

For example, *meso*-9,10-octadecanediol oxyethylated to n = 4.00 was found to contain 20.30% unreacted octadecanediol. By crystallization of the product mixture (31 g.) from ether at 0° and then at −20°, 5.50 g. of *meso*-octadecanediol, out of 6.29 g. expected, was removed. The remaining product in 175 ml. of ether was shaken repeatedly with 4.0 g. (7 equivalents/equivalent) of periodic acid in 250 ml. of water, with which it formed an emulsion. After 1.3 hr., 100 ml. of a saturated solution of potassium iodide were added; the iodine was immediately reduced with thiosulfate solution. After boiling off the ether and heating the mixture to 60°, the aqueous layer was saturated with sodium sulfate and separated. After three more washings at 60° with saturated solutions of sodium sulfate the organic layer was freed from nonaldehyde by distillation at 0.05 mm., leaving an oxyethylated product devoid of parent diol.

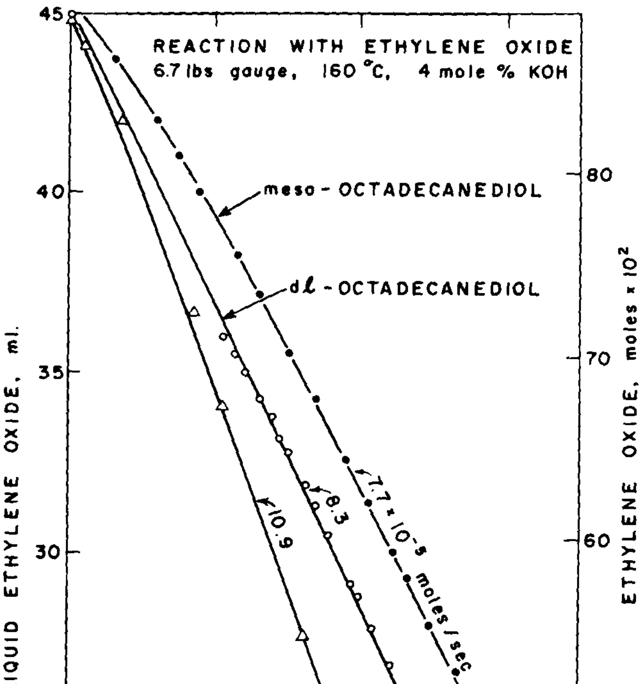

Fig. 2. Reaction rates in oxyethylation of *meso*- and *dl*-9,10-octadecanediols and *threo*-9,10-dihydroxystearonitrile. Plot of reservoir ethylene oxide *vs.* time.

Oxyethylation of threo-9,10-Dihydroxystearonitrile. Preparation of Nonionic Soaps. The possibility that oxyethylation would involve the nitrile group was shown to be minor by a preliminary experiment in which equimolar amounts of *dl*-9,10-octadecanediol and stearonitrile were treated with 6 moles of ethylene oxide; 96.3% of the stearonitrile was recovered unchanged.

threo-9,10-Dihydroxystearonitrile was accordingly caused to react with 4-, 6-, and 8-molar proportions of ethylene oxide under the same conditions used for the octadecanediols. The resulting oxyethylated nitriles were converted to nonionic soaps by refluxing in aqueous alcohol with excess alkali, conversion to a solution of the carboxylic acid by ion exchange, exact neutralization to pH 9, and rotary evaporation of solvent.

Reaction Rates

The oxyethylation apparatus was convenient for kinetic measurements, which were made in the course of several preparations. In such cases the stirring rate was controlled at 1,900 rpm by operating the magnetic stirrer through a voltage stabilizer and variable transformer; speed was checked several times by a stroboscopic tachometer (5). Typical results in the oxyethylation of *meso-* and *dl*-9,10-octadecanediol and *threo*-9,10-dihydroxystearonitrile with respective rates 7.7, 8.3, and 10.9 x 10^{-5} moles/sec., are shown in Fig. 2. Aside from slight initial curvature these compounds gave straight-line plots of ethylene oxide (ml. or moles) *vs.* time, as reported for n-octadecanol (17). This was to be expected under conditions of constant ethylene oxide pressure and constant molar concentrations of catalyst and hydroxy groups.

Consumption of Parent Diol

Weibull and Nycander (13) showed that the distribution of products in the oxyethylation of water, methanol, ethanol, ethylene glycol, and ethoxyethanol is described by the equations:

$$v = c \ln n_{oo}/n_o - (c-1)\left(1 - n_o/n_{oo}\right)$$

$$n_i/n_{oo} = c^{i-1}/(c-1)^i \left\{ n_o/n_{oo} - \left(n_o/n_{oo}\right)^c \sum_{j=0}^{i-1} 1/j! \left[(c-1)\ln n_{oo}/n_o\right]^j \right\}$$

in which

N_i = molecule with i added ethylene oxide molecules
m = number of moles of ethylene oxide consumed
n_{oo} = number of moles of starting compound
n_o = number of moles of surviving starting compound
n_i = number of moles of N_i in reaction product
k_i = velocity constant for reaction of N_i with ethylene oxide
k_o = velocity constant for reaction of starting compound with ethylene oxide
c = k_i/k_o = distribution constant
v = m/n_{oo} = average number of moles of ethylene oxide per mole of starting compound

The base-catalyzed oxyethylation of long-chain primary alcohols (20) obeys the Weibull-Nycander equations with distribution constants c of about 3.

The amount of parent octadecanediol remaining at various degrees of oxyethylation was determined by the periodate method (10) and recorded in Table I. It is seen that, at comparable degrees of oxyethylation, less *dl* than *meso*-diol survives in each case. Although the amounts of various individual oxyethylated products were not determined, the quantity of residual glycol was used in the first equation to calculate an approximate distribution constant. Thus for *meso*-9,10-octadecanediol a distribution constant of 6 to 8 is suggested; for the *dl*-diol, about 3.

Distillation of a reaction product of 90.64 g. of *dl*-octadecanediol and 3.0 moles per mole of ethylene oxide (n, or v = 3) was undertaken to obtain further data on the distribution of products. With a spinning band column (28 theoretical plates) 30 2- to 4-g. fractions were collected before decomposition was appreciable. Although no pure individual products were isolated, the proportion of touching oxyethylene derivatives (i = 0 and 1, 1 and 2, etc.) in each fraction was assigned on the basis of carbon analyses. The results are plotted in Fig. 3 in comparison with a Weibull-Nycander distribution calculated for v = 3, c = 3, and Poisson distribution for v = 3; c, by definition, = 1 (20). The experimental curve resembles the Weibull-Nycander more than the Poisson distribution.

TABLE I
Surviving Starting Glycol

Substance oxyethylated	Degree of oxyethylation, n, or v	Surviving starting glycol, %	Distribution constant,[a] c = k_1/k_o
9,10-Octadecanediol			
meso	4.00	20.30	7.5
dl	4.00	10.48	3.3
meso	7.87	6.40	6.4
dl	8.09	1.78	3.2
meso	12.12	2.14	6.0
dl	11.86	0.39	3.1
meso	16.26	1.44	7.5
dl	16.01	<0.1	....
9,10-Dihydroxystearonitrile			
threo	4.03	5.90	2.2
threo	8.03	1.40	2.8

[a] Calculated from $v = c \ln n_{oo}/n_o - (c-1)(1 - n_o/n_{oo})$.

Under alkaline catalysis the acidity of parent alcohol compared with the derived ether alcohols is considered to be an important factor (13). Since the ether-alcohol products must be quite similar in the two octadecanediol series, the earlier consumption (and lower distribution constant) of the *dl*-diol suggests that the *dl*-diol possesses a proton somewhat more easily removed by catalyst anion than that of the *meso*-compound. This supposition is indirectly supported by conformational comparison and infra-

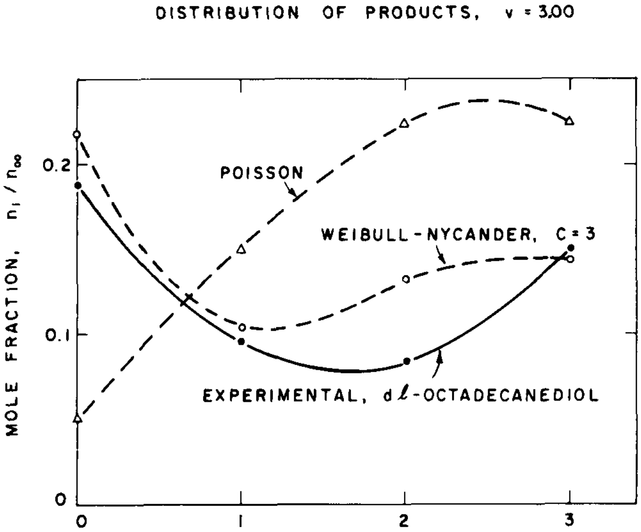

FIG. 3. Distribution of products in oxyethylation of *dl*-9,10-octadecanediol to v = 3.00 compared with Poisson distribution, and with Weibull-Nycander distribution calculated for c = 3.

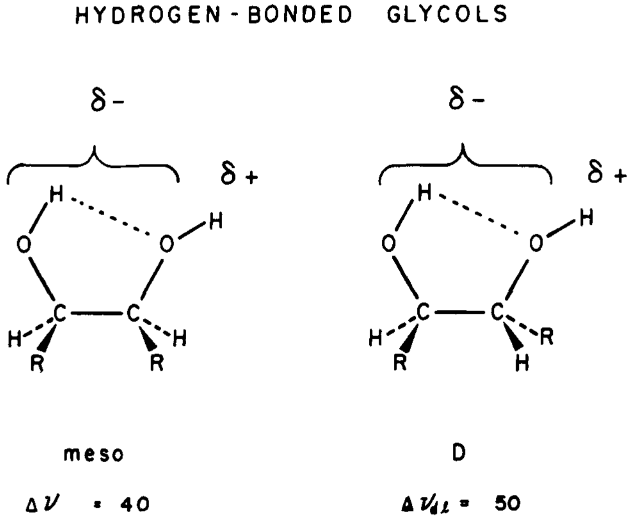

FIG. 4. Intramolecularly hydrogen-bonded conformations of *meso-* and *asymmetric*-9,10-octadecanediols.

TABLE II

Surface-Active Properties

Surface-active agent	Average number of oxyethyl groups, n	Cloud point, 1%	Wetting time,[a] 0.1%, sec.	Surface and interfacial tension, 0.1% dynes/cm.		Foam height(8), immediate, 0.25%, 60°, mm.	Emulsion stability,[b] 2% in light petrolatum	Detergency[c] 60°, 300 ppm △ R	
				S.T.	I.T.			0.25%	0.05% +0.2% builder
Oxyethylated 9,10-octadecanediols									
meso	4[d]	......[e]	25.0	26.0	1.6	15	4 days	....	....
dl	4[d]	......[e]	87.0	26.0	1.9	7	2 days	....	....
meso	8[d]	......[e]	17.0	26.6	1.7	40	1500 sec.	....	....
dl	8[d]	......[e]	23.0	26.9	2.2	40	510 sec.	....	....
meso	12[d]	51.5°	6.1	26.9	2.1	100	140 sec.	....	....
dl	12	48.5°	6.3	27.5	2.4	105	190 sec.	12	27
meso	16	83.0°	14.0	28.7	3.5	100	70 sec.	....	....
dl	16	83.0°	15.0	30.1	4.1	125	80 sec.	13	26
Oxyethylated *threo*-9,10-dihydroxystearonitriles	4	......[e]	19.0	31.4	5.0	0	200 sec.	8	27
	6	......[e]	14.0	34.8	7.4	0	200 sec.	8	28
	8	34.2°	8.8	33.1	3.7	2	100 sec.	8	26
Nonionic soaps	4	......[f]	29.0	31.4	5.0	65	90 sec.	15	26
	8	......[f]	300.0	33.1	3.7	30	80 sec.	14	26
Oxyethylated									
oleic acid	15	82.0°	49.0	33.2	6.5	30	1200 sec.	14	26
stearic acid	15	79.0°	106.0	34.4	6.5	2	1200 sec.	14	23
oleyl alcohol	10	57.0°	30.0	30.4	4.7	40	1750 sec.	14	24
octadecanol	10	68.0°	103.0	34.5	6.8	50	2100 sec.	16	23

[a] Shapiro standard tape method (9). [b] Atlab emulsion tester, time for 10% separation from emulsion of 25 ml. 2% solution in mineral oil with 25 ml. water. [c] Launder-Ometer, A.C.H. standard soiled cotton. △ R = increase in reflectance after washing = 16 and 25, respectively, for Na dodecyl sulfate. Builder = 25% $Na_4P_2O_7$, 25%, $Na_5P_3O_{10}$, 48.75% Na_2CO_3, 1.25% CMC (11). [d] Purified by removal of unreacted diol. [e] Too turbid for cloud-point determination. [f] No cloud point below 100°.

red data. From Fig. 4, contrasting intramolecularly hydrogen-bonded conformations of the octadecanediols, it is apparent that interaction between the eclipsed alkyl groups R would impair the strength of the hydrogen bond of the *meso*-diol. However the more favorable transoid relation of the alkyl groups would permit stronger H-bonding in the D, or L glycol. Since the stronger H-bond would more strongly attract electrons of the adjacent hydroxyl group, it should more effectively enhance the acidity of that group. Kuhn has shown (4) that dilute carbon tetrachloride solutions of glycols exhibit two infrared absorption bands in the 3-micron region; the separation between which, $\triangle\nu$, indicates the strength of the hydrogen bond. Such measurements made on the present compounds resulted in $\triangle\nu$ of 40 and 50 cm.$^{-1}$ for *meso*- and *dl*-9,10-octadecanediol [compared to 43 and 53 cm.$^{-1}$ reported for *meso*- and *dl*-6,7-dodecanediol (4b)]. Electron attraction by hydrogen bonds was similarly recognized in a study of the basicity of glycols toward hydrogen chloride (2).

Surface-Active Properties

Surface-active and related properties were determined for the oxyethylation products of *meso*- and *dl*-9,10-octadecanediol, *threo*-9,10-dihydroxystearonitrile and the nonionic soap. Products containing about 2% or more of the unreacted octadecanediols (Table I) were purified by the removal of starting material before measurements were made. Properties are shown in Table II.

Products from octadecanediols and the dihydroxystearonitrile, at n = 4, had limited solubility in water but were dispersible. The nonionic soaps (n = 4 and n = 8) were easily soluble and gave clear solutions. At n = 8 oxyethylated diols gave turbid solutions, but the oxyethylated dihydroxystearonitrile gave a clear solution. All compounds were quite soluble at n = 12 and n = 16.

Cloud point, wetting time, surface and interfacial tension, foam height, emulsion stability, and detergency values are recorded in Table II and compared with values for related nonionic surface-active agents.

Wetting time was measured by the Shapiro standard binding tape method (9). Optimum wetting properties were observed at n = 12 for the oxyethylated octadecanediols. The oxyethylated dihydroxystearonitrile may have optimum wetting properties at n = 8; in contrast, the corresponding nonionic soap has no wetting properties. The oxyethylated diols have the lowest surface and interfacial tension values at low values of n (n = 4) and greatest foam height at high values (n = 16). The foam is not permanent and falls rapidly.

Emulsifying properties were measured with the Atlab emulsion tester. Emulsions made from a 2% solution of the surface-active agent in 25 ml. of mineral oil (U.S.P. light petrolatum) and 25 ml. of water were shaken for 3 min., and the time required for 10% of the emulsion to separate as the aqueous phase was recorded. Oxyethylated 9,10-octadecanediol with 4 oxyethyl groups was found to have exceptional emulsifying properties under these conditions. A spontaneous emulsion formed on pouring the 2% solution into water. Aqueous solutions did not form stable emulsions.

Detergency was measured in the Launder-Ometer at 60° in hard water of 300 ppm, using A.C.H. standard soiled cotton. Built solutions, 0.05% with respect to the surface-active agent and 0.20% with respect to the builder [25% $Na_4P_2O_7$, 25% $Na_5P_3O_{10}$, 48.75% Na_2CO_3, 1.25% CMC (11)], were better detergents than unbuilt 0.25% solutions. With the exception of the oxyethylated dihydroxystearonitriles, which did not form clear solutions at 0.25% concentration in hard water at 60°, detergency was about equal to that for the other nonionic detergents listed, and equal to that for sodium dodecyl sulfate, the values for which were 16 and 25.

The nonionic soaps (n = 4, n = 8) had the salt-forming characteristics of soap but in other respects

TABLE III

Metal Ion Stability of Nonionic Soaps[a]

$C_8H_{17}CH[(OC_2H_4)_xOH]CH[(OC_2H_4)_yOH](CH_2)_7CO_2Na$

Number of oxyethyl groups, x+y=n	Mg^{++}	Al^{+++}	Ca^{++}	Fe^{++}	Ni^{++}	Cu^{++}	Zn^{++}	Ba^{++}	Pb^{++}
4	100	10	100[b]	5	100[b]	6	14	100[b]	15
8	100	100[c]	100	11	100[d]	11	100[e]	100	100[f]

[a] Metallic ion stability = 10 x no. of ml. of 1% metal salt solution tolerated by 10 ml. of 1% surface-active agent (3).

[b,c,d,e,f] Cloud points 27°, 34°, 45°, 52°, 50°, respectively.

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.

Acknowledgment

The authors are grateful to Robert E. Maydole for elemental analyses.

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[Received August 4, 1961]

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

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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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