hexanal, and octenal have recently been isolated from an oxidized emulsion of ammonium linoleate (4). However the off-flavor material present in a sample of oil which has barely become inedible on an organoleptic scale has never been investigated. A sample of peanut oil of such an organoleptic quality was therefore examined. The volatile components responsible for the off-flavor were removed by de-gassing (5), and were found to consist almost entirely of aldehydes. These were investigated by gas chromatography, and also as their dinitrophenyl-hydrazone derivatives by paper chromatography, and shown to consist very largely of a mixture of hexanal and the two isomeric trans-trans- and cis-trans-decadienals. The latter two compounds were also isolated from oxidized peanut oil by Hoffmann (6). Hexanal and decadienal have been isolated many times from autoxidized oils and it therefore appears that the aldehydes formed in the initial stages of oxidation, and which constitute the off-flavors, are similar to those produced during gross oxidation. A similar mechanism of decomposition of hydroperoxides would therefore appear to operate in the two cases.

It is therefore surprising at first sight that the present work shows that antioxidants can suppress gross oxidation but cannot prevent the development of sufficient of the off-flavor aldehydes to render the oil inedible. However it must be remembered that very small amounts of aldehydes are sufficient to give a very strong off-flavor (7). Moreover the advantageous behavior of antioxidants in peanut oil purified on alumina suggests the presence of factors antagonistic to antioxidants, and it seems probable therefore that the suppresion of oxidation in a normally processed vegetable oil involves a number of factors of which the action of the antioxidants is only one.

The surprising improvement of quality of oils by treatment with alumina during the refining process will be the subject of a further communication.

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Keeping Properties of Edible Oils. Part II. Refining by Treatment with Alumina [1]

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A new refining technique is described in which the normal earth-bleaching process is replaced by a treatment of the neutral oil, in light petroleum solution, on a column of activated alumina. The products are generally of somewhat improved color and have considerably longer keeping times compared with conventional oils. The application of the process on the semi-large scale is described.

IN THE REFINING of edible oils the bleaching process plays an important part in removing not only the color, but also the soap remaining from neutralization, flavored impurities, various off-flavor precursors, and other trace components. Oils for edible use are bleached almost exclusively by diatomaceous earth, or in a few cases with activated carbon. In a previous paper (1) it was shown that the addition of antioxidants to an oil conventionally processed in the factory led to no improvement in quality. However when the bleaching process was replaced by a treatment of the oil in petrol on a column of activated alumina, the addition of antioxidant led to an oil with a considerably longer keeping time. An investigation has been made of this process of treating oils on alumina in order to determine whether the quality improvement is of general application to various oils, particularly groundnut and soybean oils, and also whether the process would be suitable for application in the factory.

Refining Methods

Neutralization. The neutralization process used varied according to the type of oil, and generally followed that normally employed for the particular oil in the factory. In general caustic soda was used in a batch process, the oil being water-washed and dried prior to bleaching. Frequently oils already neutralized in the factory were employed for further refining purposes.

Bleaching. Samples of neutralized oil were divided and the separate parts treated either by the bleaching process usually employed in the factory, or by the alumina column method. For simulation of factory bleaching conditions the oils were stirred with 2% of activated diatomaceous earth for 30 min. under nitrogen at 110C. The oil was then rapidly filtered and deodorized similarly to the other sample of oil, which had been treated on the alumina column (see below).

Treatment on Alumina. A number of methods of alumina treatment have been used but that given below, the so-called "standard method," has been used in most of the laboratory work and has been shown to give satisfactory results. Unless statements are made to the contrary, alumina treatment in this text will imply treatment by this standard method. Rather large quantities of solvents and alumina are used in this method but later work has shown that economies can be effected.

The alumina column was prepared by pouring the alumina, previously activated by heating at 400C, into a glass tube of the required length. Neutralized and dried oil (250 g.) was dissolved in light petroleum, boiling point 40-60C (750 ml.), and the solution passed through a column of 500 g. of alumina, the length of the column being approximately 45 cm. After elution of the solution of oil in petroleum the column was finally washed with light petroleum, boiling point 40-60C (1,500 ml.), and the washings combined with the main solution of treated oil. The

solvent was distilled from the oil which was then deodorized in the same manner as the oil obtained by conventional bleaching.

Deodorization. Oils obtained after either bleaching or treatment with alumina were deodorized by heating in a current of steam at 180C for 3 hr. under a pressure of 1 mm. of mercury. When required, antioxidant was added immediately after deodorization, and normally a quantity of about 0.02% was found to impart optimum stability to the oil.

Assessment of Quality of Edible Oils

Accelerated storage tests, such as the Swift and the oxygen absorption tests, are unrealistic as they bring about artificial deterioration of oils at much higher temperatures than those which are involved under practical storage conditions; moreover, they show little correlation with the organoleptic properties on normal storage (1). The oils, after deodorization, were stored in the dark at room temperature in bottles with loose fitting screw caps, and were tasted at weekly intervals. The taste was assessed by a score on a scale from 8 to 0. A score of 8 was given to a bland oil of superior quality, and a score of 3 represented the borderline between an edible and an inedible oil. The keeping time of an oil is defined as the time elapsing between its preparation in a fresh condition and its deterioration to score 3. The standards set in such an assessment are those used in margarine factories for judging the suitability of a particular batch of oil for incorporation in margarines. These standards are very high and result in keeping times for normally refined oils usually between 1 and 6 weeks. Assessments by skilled tasters result in remarkably uniform and reproducible results with a given sample of oil.

Results

Comparative Effects of Earth-Bleaching and Treatment on Alumina. Table I shows the results of subjective assessment of a number of oils. In most cases the results represent the average of a large number of separate experiments on different batches of oil. It is apparent that in most cases a very considerable percentage improvement in quality has been achieved by treatment on alumina, particularly when combined with the addition of antioxidant. However the degree of improvement of an oil depends on the original quality of the crude oil even in the case of treatment with alumina. Thus keeping times of alumina-treated peanut oil have varied between 4 and 12 weeks. However the limited improvement of a poor oil is usually of as much, or more importance than the greater improvement of a better quality oil. Table I rather underestimates the efficacy of the new process, as in a few cases oils have not responded to the process; in these cases the oils were usually of particularly good quality and were presumably free of the impurities which would normally be removed on the alumina column.

The results are given in Table I for one particular antioxidant, butylated hydroxyanisole. However similar results have been found with propyl gallate, butylated hydroxytoluene, and mixtures of antioxidants. In all cases given in Table I the color of the oils refined on alumina was lighter than corresponding samples refined using bleaching earth.

An attempt was made to treat neutralized peanut oil on a column of bleaching earth, but the absorptive

TABLE I
Comparative Effects of Earth Bleaching and Alumina Treatment

Oil	Antioxidant	Keeping time (weeks)	
		Earth bleached	Alumina treated
Peanut oil (factory neutralized)	None	3	4
	0.02% BHA	4	8
Soybean oil (factory neutralized, 0.005% citric acid added in deodorization)	None	1–2	3
	0.02% BHA	2	5
Rapeseed oil (laboratory neutralized)	0.02% BHA	2	8
Palm kernel oil (factory neutralized)	None	3 ½	8
	0.01% BHA	4	10
Hardened peanut oil, m.p. 33C (prehardened treatment with activated earth)	None	4 ½	14

TABLE II
Use of Once-Revivified Alumina Columns

Oil	Keeping Time (weeks)		
	Earth bleached	Fresh column	Revivified column
Peanut oil (mean of 8 determinations)	4 ½	9	7 ½
Soybean oil (mean of 4 determinations)	1 ½	3 ½	5

In all cases 0.02% BHA was added to the refined oil.

power of such a column proved to be very poor and led to no improvement in oil quality.

Variations on the Standard Process. It is obvious that in order to operate alumina treatment as a realistic means of oil refining, certain variations from the standard process have to be investigated. Numerous studies have been made with peanut oil. It is naturally of advantage to use as much oil as possible in relation to the quantity of alumina necessary for adsorption, and in this connection it has been found that the quantity of peanut oil used can be as much as four times the weight of the alumina, but probably not much more than this. Correspondingly, a reduction can be made in the quantity of solvent necessary, but the minimum amounts required have not yet been defined. It has been established that a column is necessary; merely stirring the solution of oil with the appropriate weight of alumina, followed by filtration and evaporation of the solvent, produces an oil distinctly inferior to that obtained by the standard process, although it still shows an improvement over the normal bleaching process. Moreover it is essential that a solvent be used; oil passed through an alumina column in the absence of solvent had only a poor keeping time.

The boiling point of the petroleum ether used in the treatment on alumina may influence the quality of the resulting oil. P.E. boiling between 40C and 60C has normally been used in the present work, but the use of P.E. boiling between 60C and 80C led to oils of poorer quality.

The next point that will concern the technologist is the extent to which the column, having been used for one batch of oil, can be re-utilized for refining further batches and, equally important, the overall oil yields for the process.

Revivification of the Alumina Column. As alumina is a costly material it was important to find out how many times a column could be used, before discarding it or regenerating the alumina in its original activated form. By a solvent stripping procedure it has been found that a column can be revivified and re-used a number of times, using the following process.

A stripping solution of 10% of methanol in light

petroleum was allowed to percolate through the alumina column after use, three volumes of this solvent being used per unit weight of alumina. The solvent removes colored impurities and the greater part of the residual oil. After solvent treatment, the alumina column was heated for several hours by means of a steam jacket, either under partial vacuum or preferably with the passage of air or inert gas through the alumina. It has been demonstrated that the efficiency of drying is the main factor in determining the effectiveness of the revivified column. Thus in the laboratory, removal of the alumina from the column followed by drying in vacuo at 110C was the most effective method, but this is not likely to be economic on the larger scale.

After revivification, the column was effective for further refining although it was usually slightly less active. Table II shows results obtained on once-revivified columns for peanut and soybean oils.

It is evident that adsorbed impurities still remain on the column after revivification, as was shown by re-activating the alumina following the treatment of a number of batches of oil, by heating it at 400C when charring occurred. During each treatment of oil on a column of alumina a small proportion of the impurities present are adsorbed and not removed by the revivification procedure. The gradual build-up of these impurities eventually affects the quality of the oil treated on the column, and therefore places a limit on the number of times a column can be revivified.

After it has no longer become profitable to revivify the column by solvent stripping, the alumina can be removed and re-activated by heating at 400C for 7 hr. but this process, being expensive, would in practice only be employed after revivification had been carried as far as possible.

Yields of Refined Oil. An improvement of quality of oils treated on alumina compared with those treated on bleaching earth has been demonstrated. However it is important for a commercial process that the oil yield from the alumina treatment should be high and, if possible, comparable with that from conventional bleaching. The oil retention on fresh alumina is ca. 14%, and on revivified alumina ca. 8–10%. The yield of top-quality alumina treated oil is therefore 86–92%, the remainder of the oil being obtained as a by-product during solvent revivification. When sufficient of this latter material has accumulated it may be treated on alumina to yield an oil of quality as good, or slightly better, than a normally bleached oil. The overall yield of the two grades of oil should be higher than 99% which compares favorably with typical losses on bleaching earth.

The Effect of Pretreatment on the Quality of Alumina Treated Oils. The alumina column does not effectively replace conventional desliming and refining processes. Fatty acids would normally be removed by alkali neutralization prior to treatment on alumina; for although free fatty acids can be removed, for example, from crude soybean oil by adsorption on the column, the oil obtained after deodorization is not of edible quality. However it was shown that desliming with phosphoric acid, followed by removal of free fatty acids as part of the alumina treatment process, produced a soybean oil of good keeping quality. Experience shows that, particularly for soybean and rapeseed oils, desliming with reagents such as phosphoric acid may be particularly important i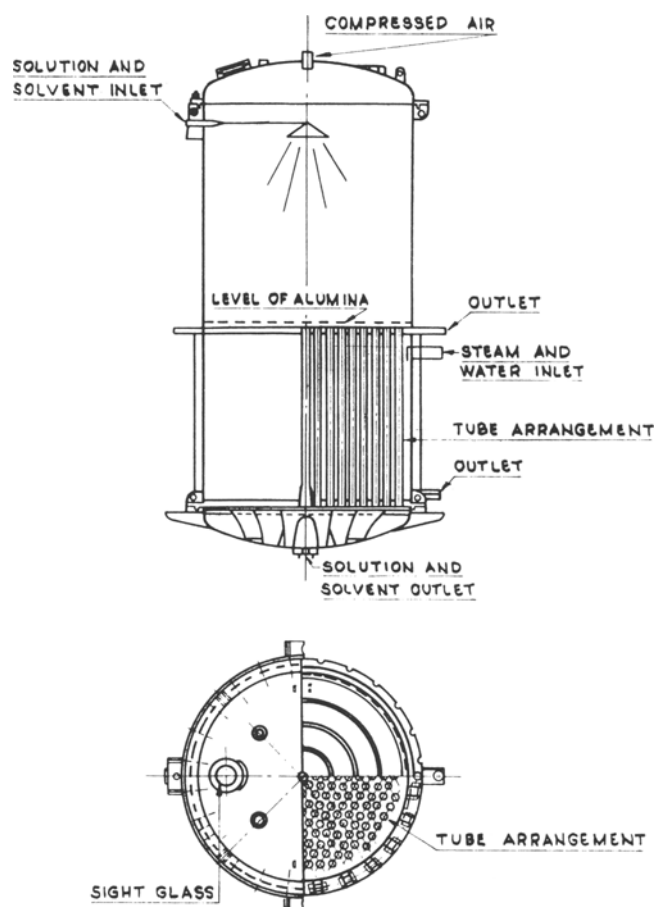n the pretreatment. Moreover the addition of citric acid during deodorization is as desirable with alumina refined oils as it is with bleached oils.

The alumina treatment process would be particularly attractive if it were combined with neutralization in solvent, e.g., by the de Smet process (2). In this way the solvent used for extraction of the oilseeds could be used throughout the refining operation, including alumina treatment. Investigations on these lines have, however, been too limited for definite conclusions to be made.

Operations on a Larger Scale. In pilot plant experiments the treatment with alumina was made in a mild steel "calandria" in which were grouped 37 parallel tubes, 18 in. in length, containing the charge of 50 lb. of alumina. This is illustrated in Figure 1. Refined oils obtained when operating on this scale were generally equal in quality to those obtained by laboratory processing from the same raw material.

FIG. 1. Calandria for alumina treatment of oils.

Mechanism of the Process

The nature of materials removed in conventional bleaching with diatomaceous earth, and the chemical changes involved, are incompletely known. It is not, therefore, easy to determine the reason for the improvement in quality of oils when treated on alumina. However it seems probable that precursors of off-flavor present in the neutral oil are removed, or chemically modified on the alumina, whereas they remain unaffected during bleaching. Alternatively a metallic autoxidation catalyst such as an iron or copper salt may be removed on the alumina. It is known that the amounts of trienes present in an oil are slightly increased by bleaching earth due to decomposition of

oxygenated compounds, whereas no such increase occurs by treatment with alumina (3). We have confirmed this finding with oils refined by the two processes, but do not believe that the small amounts of triene present in the bleached oils can account for their inferior quality. An investigation has been made of the nature of the materials removed from the alumina columns after treatment of an oil in an effort to determine the mechanism of the improvement in quality. This work will be published at a later date.

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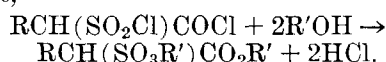# Diesters and Diamides of *a*-Sulfopalmitic and *a*-Sulfostearic Acids [1]

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a-Methylsulfopalmitic acid and dimethyl, diethyl, dibutyl, and isomeric methyl butyl esters of a-sulfopalmitic and stearic acids were prepared and characterized. Reaction of a silver salt with an alkyl iodide was preferred to the acid chloride method found to involve competing side reactions. Diamides of a-sulfopalmitic and stearic acids were prepared from ammonia, ethanolamine, and isopropanolamine by an acid chloride method. Infrared spectra of representative compounds are discussed.

THE DIESTERS of short chain a-sulfo fatty acids have been made in the past either by reaction of an appropriate silver salt with an alkyl iodide,

$$RCH(SO_3Ag)CO_2Ag + 2R'I \rightarrow$$
$$RCH(SO_3R')CO_2R' + 2AgI$$
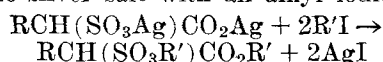
or by reaction of the acid chloride with an alcohol or alkoxide,

$$RCH(SO_2Cl)COCl + 2R'OH \rightarrow$$
$$RCH(SO_3R')CO_2R' + 2HCl.$$

Diethyl sulfoacetate has been prepared from the silver salt and ethyl iodide by Franchimont (1) and Manzelius (3) who found this diester to resemble diethyl malonate in alkylation reactions. Dimethyl sulfoisobutyrate (4) has also been prepared from the silver salt; and dimethyl, diethyl, and dipropyl sulfoacetates from the acid chloride (6). Both methods should be versatile in the synthesis of either simple or mixed diesters.

We have found the silver salt method for diesters to be easier to carry out without complicating side reactions. Diesters of a single alcohol were conveniently prepared by the reaction shown above. Esters of the sulfonic acid group only can be prepared from the mono-silver salt $RCH(SO_3Ag)CO_2H$ and an alkyl iodide. Mixed diesters of a-sulfostearic acid, $C_{16}H_{33}CH(SO_3R'')CO_2R'$, were formed from an alkyl iodide $R''I$ and the silver salt of the monoester $C_{16}H_{33}CH(SO_3Ag)CO_2R'$, prepared by direct esterification of a-sulfostearic acid and conversion to the silver salt.

The acid chloride method for diesters or diamides is less easily adapted to higher fatty acids. Vieillefosse (6) succeeded in the preparation of $CH_2(SO_2Cl)COCl$ as a colorless liquid bp 90C/8 mm by heating sulfoacetic acid with excess of thionyl chloride in a sealed tube at 120C; and found the sulfonyl chloride group to be less reactive than the carboxylic acid chloride. Moll van Charante (4) has reported that when one attempts to prepare the diacid chloride of a-sulfoisobutyric acid at lower temperatures the anhydride

$$[(CH_3)_2CSO_2]_2O$$
$$|$$
$$COCl$$
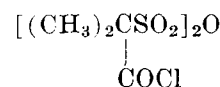
is the principal product. The sulfonic acid anhydride is considered to be more reactive than the sulfonyl chloride.

Thus it would seem that conversion to the diacid chloride requires higher temperatures than are usual for conversion of carboxylic acids, yet excessive heat must be avoided to prevent the type of decomposition reported by Hemilian (2):
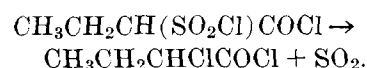
$$CH_3CH_2CH(SO_2Cl)COCl \rightarrow$$
$$CH_3CH_2CHClCOCl + SO_2.$$

TABLE I
Diesters of a-Sulfo Acids

	Melting point	n_D^{70}	Saponification equivalent[a]		% S	
			Found	Theo.	Found	Theo.
Palmitic acid						

C₁₄H₂₉CHCO₂H[b]
  |
  SO₃CH₃
	69.5°	1.4450	179	175	9.76	9.15

C₁₄H₂₉CHCO₂CH₃
  |
  SO₃CH₃
	60°	1.4376	183	182	8.77	8.80

C₁₄H₂₉CHCO₂C₂H₅
  |
  SO₃C₂H₅
	14°	1.4340	199	196	8.07	8.17

Stearic acid						

C₁₆H₃₃CHCO₂CH₃
  |
  SO₃CH₃
	65°	1.4389	201	196	8.05	8.17

C₁₆H₃₃CHCO₂C₂H₅
  |
  SO₃C₂H₅
	31°	1.4353	211	210	7.64	7.62

C₁₆H₃₃CHCO₂C₄H₉[c]
  |
  SO₃C₄H₉
	27°	1.4372	249	238	6.97	6.73

C₁₆H₃₃CHCO₂CH₃[d]
  |
  SO₃C₄H₉
	30.5°	1.4379	216	217	7.16	7.38

C₁₆H₃₃CHCO₂C₄H₉[e]
  |
  SO₃CH₃
	29°	1.4380	217	217	7.54	7.38

[a] The reflux time was increased in order to approach complete hydrolysis of the carboxylic ester (5). A 0.3 g sample was refluxed 3 hr with excess of 0.2 N alcoholic KOH.

[b,c,d,e] Systematic names are as follows: 2-sulfohexadecanoic acid, 2-methyl ester; dibutyl 2-sulfooctadecanoate; methyl 2-sulfooctadecanoate, 2-butyl ester; butyl 2-sulfooctadecanoate, 2-methyl ester.