of the sewage (Sheets & Malaney—*Sewage & Ind. Wastes 28,* 10). The same type of work on detergent builders showed that 100 p.p.m. of Versene and sodium carboxymethylcellulose increase five-day B.O.D. by 35 and 70%, respectively; salt, bicarbonate, sodium tripolyphosphate were inactive; and other phosphates, carbonate, and silicates diminish B.O.D. in sewage (Malaney & Sheets—*Ohio State Univ. News in Eng. 28,* 30).

Addition of nonionic synthetic detergent to wool scouring waste and flocculation with aluminum compounds permit disposal of the waste without pollution of the stream (Crowely—*U. S. 2,762,681*).

The interaction of proteins with surface-active agents was studied mainly to elaborate certain structures in protein. With gelatin sodium dodecyl sulfate is bound in acid solution, whereas dodecylamine binds at pH values greater than the isoelectric point (Tamaki & Tamamushi—*Bull. Chem. Soc. Japan 28,* 555). The maximum values of detergent binding at each pH were said to correspond to the acid- and base-combining power of the gelatin at that pH. Reaction products of egg albumin and sodium dodecyl sulfate at above the isoelectric point where no precipitate is formed give rise, depending on concentration, of electrophoretic patterns which may be divided into three groups (Aoki—*Bull. Chem. Soc. Japan 29,* 369). The changes occurring with changes in pH are interpreted to indicate that the detergent reacts as a single ion and not only as a micellar former. Electrophoretic studies show that sodium dodecyl sulfate combines with α-keratose in amounts far in excess of that required for stoichiometric binding of the positive groups on the protein (O'Donnell & Woods—*Proc. Int. Wool Text. Res. Conf. Australia B, 1955,* 71). An amount equivalent to the number of positive sites is more firmly bound than the remainder. The observation that sodium dodecyl sulfate bound to legumin was removed by dialysis was interpreted to indicate that detergent ion pairs rather than paraffin chain ion alone were largely bound (Brand & Johnson—*Trans. Faraday Soc. 52,* 438). A small amount was considered adsorbed without major change. Ovalbumin, bovine serum albumin, and serum globulin are precipitated by lower concentration of cationic detergent when treated with carbon monoxide or hydrogen cyanide (Stary & Tekman—*Bull. fac. med. Istanbul 19,* 39).

The hemolysis by hexadecyl shows a definite phase of latency; the activity of the solutions decrease on standing; short boiling and quick cooling double the activity of fresh solutions and increase that of old ones; and the activity is independent of concentration beyond certain critical concentrations (Jung *et al.*—*Naunyn-Schmiedebergs Arch. exptl. Pathol. Pharmakol. 229, 281,* 293).

It was impossible to detect the presence of alkoloids when nonionic detergents were present, except with the reagent silicotungstic acid, because other agents and alkaloid are precipitated together (Gallo & Casadio—*Bull. Galenica 16,* 98).

The minimum percentage of soap required in water for complete wetting, in insecticide uses, has been worked out for different kinds of leaves (Srivastava & Srivastava—*J. Econ. Entomol. 49,* 266). In general soap in excess of 0.5% is superfluous for use as a spreader. The influence of natural fleece on the interfacial activity of surface active agents has been determined as basic knowledge for application of insecticide emulsions to sheep fleece (Addison & Furmidge—*J. Sci. Food Agr. 7,* 552, 556).

In tests on influence of 10 detergents on ascarid development: Duponol 80 and Nacconol NR were most effective; more eggs were destroyed by detergents at 38 than at 31°; and the eggs of various species differ in their resistance to the detergent (Jaskoski—*Am. Midland Naturalist 52,* 142).

The surface areas of carbon blacks were determined by soap adsorption (Maron—*J. Colloid Sci. 11,* 21).

The chief requirements for the use of detergents to produce foam in the manufacture of light concrete has been recorded (Pfanner—*Silikattech. 6,* 396).

In a discussion on removal of scale from automotive cooling systems, it was suggested that surface active agents appear to be the best prospects for development of compounds for inhibiting or the removal of the scale (Singer—*Soap & Chem. Specialties 32,* No. 9, 43).

Nonionic detergents decompose rapidly in soil; cationics decompose after an initial lag period; while anionics resist decomposition (Ivarson & Pramer—*Soil Sci. Soc. Am. Proc. 20,* 371). The cationics reduce the total number of microörganisms in soil and inhibit nitrification and anionics are more determinal.

Feeding detergents may have value in cockerel raising (McDonald—*Agr. N. S. Wales 67,* 39, 375). The detergent sodium tetrapropylenebenzene sulfonate stimulated growth of chickens up to 12 weeks of age, particularly when procaine penicillin was also used to improve growth.

Some Problems Involved in the Water Wash of Neutralized Vegetable Oils

BEN BRAAE, ULLA BRIMBERG, and MARIANNE NYMAN, Chemical Laboratory,
AB Separator, Stockholm, Sweden

CONVENTIONAL ALKALI-REFINING of vegetable oils involves the neutralizing of the free fatty acids by caustic soda and separating of the soapstock from the neutral oil. Whether this separation is carried out by gravity settling or by centrifugal separation, the neutral oil still contains a certain amount of soap. According to Boekenoogen (3), a dry neutralized peanut oil dissolves 0.10% of sodium or potassium soap at 75°C. and 0.025% at 20°C. Although this solubility is rather low, small amounts of water or fatty acids in the neutralized oil may increase the solubility of the soap to a considerable degree. The soap also may be colloidally dissolved in the oil. Thus Newby (15) found 0.03–0.7% of soap in continuously neutralized soybean and cottonseed oils.

A high soap content of the neutralized oil may impair the refining operations to follow. Especially when activated earth is used for bleaching, it has been found (16) that the FFA rises when the soap content is high and that the amount of earth necessary to obtain a desired color is increased. Soap is also a catalyst poison for the hardening process. Furthermore soap may interfere with deodorization of the oil or lead to an increase in the FFA, especially with oils containing fatty acids of high molecular weight such as rapeseed oil.

Although the soap content of neutralized oils may be reduced by prolonging the settling time or by drying and filtering the oil, these operations are time-consuming and difficult to carry out as the filter cloths are easily clogged by the soap. It is therefore customary to remove the soap by washing the oil with water, usually at 70–90°C. Because the sodium soaps are easily soluble in water, the partition coefficient is favorable for an extensive reduction of the soap content of the oil. Despite this fact the refiner knows that the washing of neutralized vegetable oils often is a tedious procedure; several successive washings may be necessary to obtain complete removal of the soap (1, 11). Some producers (5, 6) of continuous centrifugal refining plants recommend a double water-wash to reduce sufficiently the soap content of the neutral oil.

Unfortunately a generally accepted method for the determination of soap in oil is lacking. The effectiveness of the water wash is therefore usually judged by the alkalinity of the wash water even though this does not furnish information about the soap content of the oil. In this connection it should be remembered that calcium and magnesium soaps are much more soluble than sodium soaps in oil and cannot be removed by washing with water. It seems highly probable that crude oils contain calcium, magnesium and other cations which may form oil-soluble soaps. In addition, the oil may be contaminated with these cations if hard water is used for the water wash or for preparation of the neutralizing lye. Therefore the amount of soap found in neutralized oils will depend to a large degree on the analytical method used, that is, whether the oil or the wash water is analyzed and whether sodium or calcium soaps or both are determined. Consequently any statement of soap content in refined oils is of little value when the method of analysis is not stated.

In view of the increasing use of continuous refining processes, where the contact time between the oil and the water is considerably shorter than in the older kettle refining system and where changes in operating conditions or repeated treatments are impractical, the effective removal of soap from neutralized oils becomes increasingly important. In the present work a number of factors influencing soap removal and several methods for the determination of soap were investigated.

Experimental Methods

A number of crude vegetable oils from European refineries were refined on a laboratory scale by one or more of the following treatments.

REFINING TREATMENTS

For all mixing operations a high-speed laboratory mixer of the Turmix type was used. The mixer has a cylindrical glass container with a diameter of 10 cm. and a total capacity of one liter. The propeller, which is placed at the bottom of the container and driven by a 275-watt motor through a stuffing box, has six blades and rotates at 10,000 r.p.m. About 300 g. of oil were used in each experiment.

Pretreatment. In some cases a pretreating agent was added to the oil prior to neutralization. In these cases the oil was heated to 85°C. and placed in the mixer, and the mixing was started. A suitable amount of reagent was then added, and the mixing was continued for 60 seconds. Neutralization was carried out immediately after the pretreatment.

Neutralization. Oil preheated to 85°C. was placed in the mixer, the mixing was started, and the proper amount of lye of 20°Bé added from a burette. Next 20% excess of lye over the stoichiometrically calculated amount was used. Mixing was continued for 60 seconds. Soapstock was immediately separated by spinning the mixture in a heated laboratory centrifuge for 5 min. In a number of cases various kinds of additive refining agents were dissolved in the lye used for neutralization.

Re-refining. The neutralized oil was heated to 85°C. and agitated in the mixer for 60 seconds with 2% lye of 12°Bé. In this lye 10% of Na_2CO_3 was usually dissolved. The mixture was centrifuged hot for 5 min.

Washing. The neutralized or re-refined oil was washed in the mixer for 1 min. with 10% of water at 85°C. and centrifuged hot for 10 min.

The effectiveness of these treatments was judged by the determination of soap contents according to one or more of the following methods. For comparison, soap determinations were also made on industrially refined oils, especially oils which had been continuously refined. The treatment of such oils has been described by Braae (4).

METHODS FOR THE DETERMINATION OF SOAP

Ashing Method. One of the oldest methods consists in converting the soaps in the oil to carbonates by ashing the sample, dissolving the ash in water, and determining the carbonates by titration (14). The present writers have found the method tedious and time-consuming as well as extremely difficult to reproduce, especially when the soap content is low. Calcium and magnesium soaps are converted to insoluble carbonates and phosphates not determinable by titration. Consequently this method was abandoned at an early stage of the investigation.

Extraction Method. Several methods for the determination of soap in vegetable oils are based on extraction with water, alcoholic solutions, and/or dilute acids. In the extract the soap may be determined by several methods. According to Durst (9) and Stillman (17), the oil is mixed successively with 0.05 N ammonia, concentrated hydrochloric acid, and water. By this treatment the soaps are converted to the corresponding chlorides. After evaporation of the water from the combined extract, the residue is heated strongly to drive off the ammonium chloride. The ash is then dissolved in water. The solution is filtered, and the chloride ion is titrated according to Mohr. In a number of cases the authors also determined the calcium contents of the filtrate and the water-insoluble part of the ash by means of the method described below.

Boekenoogen (3) used the same extraction method as Durst and Stillman but determined the sodium content of the water-soluble part of the ash by precipitation with Kahane's reagent.

Direct Titration Method. Wolff (20) has described a very simple method for determination of soap by direct titration of the oil. The modified procedure used in the present study was as follows.

The hydrochloric acid solution was prepared by diluting 10 ml. of aqueous 1 N HCl solution with acetone to 1 liter. The acetone must be pure and must not react with hydrochloric acid to any large extent. Nonetheless the strength of the freshly prepared 0.01 N hydrochloric acid may change relatively quickly, and it should consequently be standardized once or twice a week. When the strength of the acid has fallen below 0.007 N, it should be discarded. For the standardization 50 ml. are pipetted into a flask and 25–50 ml. of water and one or two drops of a 1% alcoholic solution of phenol red are added. The hydrochloric acid is titrated with 0.1 N NaOH from a microburette.

The indicator solution for the soap determination is prepared by dissolving 0.1 g. bromphenol blue in 20 ml. of water and diluting with 1 liter of acetone. The acidity of this solution is adjusted by first adding 0.1 N NaOH to green. Immediately before use the solution is titrated with 0.01 N HCl in acetone until the green color just turns yellow. Because of the sensitivity of the test, the flasks used for the soap determinations must be perfectly clean. This is conveniently checked by rinsing the flasks with the indicator solution before use.

For the soap determination 5–10 g. of an unwashed oil or 40 g. of a washed oil are weighed or pipetted into a clean Erlenmeyer flask and 25 or 50 ml., respectively, of the bromphenol blue indicator solution are added. The mixture is titrated with the 0.01 N HCl reagent while shaking vigorously until a constant yellow change in the acetone phase is obtained. For unwashed oils with high soap contents warming the solution a little during the titration is advisable.

This method was found to give good accuracy for known amounts of soap dissolved in refined vegetable oil. FFA contents lower than 0.3% had no effect on the results. For small soap content this method was easier to reproduce than any other method investigated.

For all methods of soap determination the experimental results have been expressed as parts per million of sodium oleate, regardless of the fact that calcium soaps or other alkaline-reacting materials were often involved.

METHODS FOR DETERMINATION OF SOME INORGANIC ELEMENTS IN THE OILS

Calcium and Magnesium. McGuire *et al.* (10) found that nitrogenous substances in vegetable oils could be completely transferred to a water solution by boiling the sample with concentrated hydrochloric acid. Results of the present investigation showed that the same procedure could be used for the conversion of calcium and magnesium salts in the oil to water-soluble compounds. The reaction was complete after only one hour of boiling.

In a few cases the oil or other samples were ashed, and the ash was dissolved in concentrated hydrochloric acid. The solutions thus obtained were neutralized against phenolphthalein, and the calcium ions were determined by titration with a solution of EDTA (disodium ethylene-diaminetetraacetic acid), using murexide (ammonium purpurate) as an indicator (2). The sum of calcium and magnesium was determined by the same procedure except that the indicator was eriochrome black T (8, 18).

Phosphorous. The oil samples (5–10 g. depending on the phosphorous content) were ashed after having been mixed with magnesium oxide. The residue was then dissolved in 2 N sulphuric acid, and the solution was neutralized with ammonia and filtered. In the filtrate the molybdenum blue color was developed according to Kitson and Mellon (13) by the addition of ammonium molybdate, hydroquinone, and sodium sulphite. The extinction was measured at 720 mμ.

Because the blank values with commercially available magnesium oxide were high, the magnesium oxide used for the ashing was prepared by adding ammonia stepwise to magnesium chloride (A. C. S. grade), discarding the first precipitates and heating the pure magnesium hydroxide to 950°C.

Soap Removal by Water Wash of Various Neutralized Vegetable Oils

Experience with a number of neutralized oils from many sources has shown that several of the washed oils showed a considerable soap content as determined by the method of Wolff but that various oils exhibit great differences in this respect.

These observations are rather astonishing in view of the fact that sodium salts are easily soluble in water. A possible explanation is that two different groups of substances which are both determined as soap by the method of Wolff may be present in the neutralized oil.

One type of soap is easily removed by a single water-wash, provided that proper temperature, amount of water, and degree of mixing are chosen and that the phases are effectively separated either by gravity settling or centrifugal separation. The second type, on the contrary, is only slightly soluble in water and cannot therefore be removed even by repeated washings with water.

It follows that the introduction of several washing steps in continuous refining is justified only if the mixing or the separation of the phases in the first step is incomplete.

The soaps, formed during the neutralization of cocoanut, palm, and olive oil, belong to the first group. According to the experience of the present authors, the soap content of these oils is easily reduced to a very low level by a single water-wash even if the soap content of the neutralized oil is high. Other oils, such as rapeseed and linseed, occasionally also peanut, cottonseed, and soybean, form both types of soap.

In the following the first type of oil is designated as washable and the second type as unwashable.

Comparative Soap Determinations on Washable and Unwashable Oils

It seemed reasonable to assume that the difference in washability of different vegetable oils was connected with the presence of calcium and magnesium soaps in the oils. On this assumption, different methods for the determination of soap would be expected to give incompatible results.

By cold treatment with strong hydrochloric acid the sodium soaps and at least part of the calcium and magnesium soaps are converted to the corresponding chlorides. The Durst-Stillman method, which determines the total chlorides thus formed, will consequently include part of the calcium and magnesium soaps; on the other hand, the method of Boekenoogen which uses the specific Kahane reagent determines only the sodium soaps.

Finally the method of Wolff may be assumed to determine all kinds of soaps in the oil as well as any other substance with an alkaline reaction. Free alkali, such as sodium hydroxide or sodium carbonate remaining after the neutralization, will, of course, be determined as soap by all three methods.

In Table I the soap contents of a number of neutralized oils as determined according to the methods of Boekenoogen, Durst-Stillman and Wolff are compared. For three of the oils, which may be classified as washable, the different methods of analysis gave practically the same result, indicating that only sodium soaps were present in appreciable amounts. For unwashable oils, on the contrary, considerable disagreement is found. As would be expected, the method of Wolff gave the highest values, and the method of Boekenoogen the lowest. From the table it is also seen that the filtrate used for the Durst-Stillman determination contained considerable amounts of calcium. If the calcium content of the filtrate is calculated as soap and subtracted from the soap content according to Durst-Stillman, the difference may be regarded as sodium soaps, corresponding with reasonable accuracy to the value obtained by the method of Boekenoogen.

For a number of oils it was found that part of the ash obtained by evaporation of the extract was in-

TABLE I

Comparative Soap Determinations on Washable and Non-washable Oils

Oil	Treatment [a]	Soap content (p.p.m.)			Calcium content (as p.p.m. Na-soap)		
		Wolff's method	Boekenoogen's method	Durst-*Stillman's* method	In filtrate *from* Durst-Stillman	Difference between soap according to Durst-Stillman and calcium in *filtrate*	Calcium *in ash from* Durst-Stillman
Washable							
Peanut	Neutralized	760	730	600	0	600	0
Cottonseed	Neutralized	450	390	380	0	380	400
Rapeseed	*Neutralized and re-refined*	2070	1990	1990	50	1940	200
Non-washable							
Rapeseed	Neutralized	1790	1410	1500	200	1300	1100
Rapeseed	Neutralized and water washed	930	280	530	190	340	1600
Linseed	Neutralized and water washed	2600	1390	2980	1820	1160	7800
Soyabean	Neutralized	2740	*1600*	*2010*	*300*	*1710*	*5000*

[a] For description of neutralization and re-refining procedure see Section A, Refining Treatments.

soluble in water. As is shown in Table I, this residue usually contained considerable amounts of calcium even when the corresponding oils were washable. Apparently part of the calcium present in the crude oil is combined with other inorganic elements, possibly phosphorus, forming compounds which are not converted to calcium soaps but are found in the insoluble part of the ash.

It is of minor importance to the practical refiner that most of the methods commonly used for the determination of soap are not specific for sodium or calcium soaps, or for soap at all. This is because alkali present in the oil after neutralization and washing will usually be transformed to soap during the subsequent refining operations, such as drying and deodorizing, and because the calcium and magnesium soaps produce the same harmful effects as the sodium soaps.

The best method therefore of controlling the efficiency of washing appears to be Wolff's, which is the fastest and the most convenient of the methods investigated and determines all alkaline-reacting impurities in neutralized or washed oils. It has been extensively used throughout this investigation.

Some Factors Influencing the Washability of Neutralized Oils

Pretreatment. According to Colomb (7), the phosphorous in crude linseed oils may be completely removed by treatment with a solution of phosphoric acid. A similar treatment of other vegetable oils prior to neutralization now has been found to improve the washability of all the oils. A relatively concentrated acid should be used; the amount depends on the quality of the crude. For most oils, treatment with 0.05–0.2% by weight of phosphoric acid is adequate; in no case has more than 0.4% been necessary to obtain a completely washable oil after neutralization. At a temperature of 70–90°C. a reaction time of less than one minute is sufficient if adequate mixing is provided. At lower temperatures and with insufficient mixing 10 minutes or more may be necessary to complete the reaction between phosphoric acid and oil. The small amount of phosphoric acid used is usually soluble in the oil, at least at higher temperatures.

The effect of pretreatment with phosphoric acid on the washability of neutralized oils is clearly seen from Table II. Strong mineral acids, such as sulphuric and hydrochloric acid, have a similar effect, but even when greater amounts are used the soap content of the washed oils is higher than for oils treated with phosphoric acid. In addition, the mineral acids have the disadvantage of being strongly corrosive, and sulphuric acid provokes undesirable side reactions, such as sulphonation.

A number of organic acids, such as oxalic, tartaric, and citric acid, may also be used as pretreating agents, but the effect is not so pronounced as that of phosphoric acid, which is also more economical. The same applies to pretreatment with ortho- or metaphosphates and sequestering agents, such as EDTA.

On account of its low price and high efficiency, phosphoric acid is especially suitable for pretreatment in the continuous refining process. A continuous dosing system for small amounts of acid may be installed at low cost, and no corrosion of the bowls of the centrifuges takes place if the acid is neutralized prior to the separation.

Neutralization with Additive Refining Agents. The addition of a number of chemicals to the neutralization lye may also improve the washability of the neutral oil. As may be seen from Table III, the effect of these chemicals is however either incomplete or the necessary concentration of the additive so high that it becomes impractical and uneconomical to

TABLE II

Effect of Pretreatment on Washability of Neutralized Oils

Pretreating Agent			Oil	Soap content (p.p.m.)	
Name	Conc. (%)	Amount (% of oil)		After neutralization	After water wash
None	....	....	Rapeseed	2300	1000
Phosphoric acid	85	0.2	Rapeseed	1300	30
Phosphoric acid	85	0.1	Rapeseed	1200	40
Prim. sodium phosphate	Sat.	5.0	Rapeseed	1200	90
Prim. sodium phosphate	20	5.0	Rapeseed	1000	540
Citric acid	20	0.5	Rapeseed	1900	570
Citric acid	20	1.0	Rapeseed	2100	440
Citric acid	20	2.0	Rapeseed	2000	230
Citric acid	60	1.0	Rapeseed	1700	200
Tartaric acid	40	1.0	Rapeseed	2800	530
Oxalic acid	30	1.0	Rapeseed	....	90
Hydrochloric acid	37	1.0	Rapeseed	1100	100
Sulphuric acid	98	1.0	Rapeseed	1200	110
EDTA	17	2.0	Rapeseed	1900	110
Urea phosphate	*50*	*0.1*	Rapeseed	*1000*	*70*
None	....	....	Linseed	1500	750
Phosphoric acid	85	0.2	Linseed	1000	40
None	....	....	Linseed	3400	2700
Phosphoric acid	85	0.1	Linseed	1000	620
Phosphoric acid	85	0.25	Linseed	500	60
Urea phosphate	50	0.2	Linseed	500	10
Prim. sodium phosphate	15	5.0	Linseed	3100	2700
Prim. sodium phosphate	Sat.	5.0	Linseed	2600	520
Sodium metaphosphate	15	5.0	Linseed	1500	200
None	....	....	Peanut	1100	260
Phosphoric acid	85	0.1	Peanut	480	20
None	....	....	Soyabean	2700	1600
Phosphoric acid	85	0.2	Soyabean	800	60
None	....	....	Sunflower	2200	310
Phosphoric acid	85	0.2	Sunflower	1100	80
None	....	....	Cottonseed	5000	2100
Phosphoric acid	*85*	*0.2*	*Cottonseed*	*1100*	*110*
Citric acid	20	0.5	Cottonseed	3000	800

achieve the desired reduction of the soap content in this way.

It is noteworthy that all chemicals improving the washability of the neutralized oils form either insoluble or complex calcium and magnesium salts.

TABLE III

Effect of Additive Refining Agents on Washability of Neutralized Oils

Additive[a]	Conc. of additive (g./l.)[a]	Oil	Soap content p.p.m.	
			After neutralization	After water wash
None	....	Rapeseed	2300	1000
Sodium carbonate	85	Rapeseed	2500	240
Trisodium phosphate	Sat.	Rapeseed	2400	320
Sodium metaphosphate	Sat.	Rapeseed	2000	380
Sodium pyrophosphate	Sat.	Rapeseed	2100	430
Sodium gluconate	230	Rapeseed	3200	850
Sodium glycerol phosphate	100	Rapeseed	2400	850
EDTA	250	Rapeseed	1100	60
EDTA	85	Rapeseed	1800	120
None	....	Linseed	1700	1100
Sodium carbonate	85	Linseed	1000	140
Trisodium phosphate	Sat.	Linseed	1100	760
Sodium metaphosphate	Sat.	Linseed	1200	330

[a]Additive refining agent dissolved in the lye used for neutralization.

Re-refining with Additive Refining Agents. Repeated alkali treatments do not improve the washability of the oils, but if the re-refining lye contains sodium carbonate, a washed oil with a very low soap content is obtained. As may be seen from Table IV, this treatment is as efficient as the pre-treatment with phosphoric acid.

Treatment of the neutralized oil with sodium carbonate alone does not give the desired result; the combined action of a hydrolytic and a precipitating agent is obviously necessary. Phosphates, oxalates, or other compounds forming insoluble or complex calcium salts may be used instead of carbonate. The strongly alkaline trisodium phosphate may be used without the presence of sodium hydroxide. In continuous processes a re-refining step is often used to improve the color or the organoleptic properties of the oil (4). In such cases a low soap content, even of unwashable oils, is easily obtained by adding sodium carbonate to the re-refining lye. At the same time the presence of sodium carbonate or any other strong electrolyte tends to avoid formation of emulsion and to reduce re-refining losses.

Effect of Water Hardness on Soap Content of Refined Vegetable Oils. The soap content of the washed oil might be expected to increase if hard water is used for preparing the refining lye or as wash water. As is shown in Table V, the soap content of cottonseed, peanut, and rapeseed oil actually was increased when hard water was used as wash water.

TABLE IV

Effect of Re-refining on Washability of Neutralized Oils

Re-refining lye			Oil	Soap content of washed oil (p.p.m.)	
Strength (Bé)	Na_2CO_3 (g./l.)	Amount (% of oil)		Neutralized	Neutralized and re-refined
12°	....	2.5	Rapeseed	980	350
12°	100	2.5	Rapeseed	1000	60
None	200	2.5	Rapeseed	1050	320
12°	....	2.5	Linseed	2700	2800
12°	100	2.5	Linseed	2700	30

It is however difficult to distinguish the effect of calcium originally present in the oil and that contained in the wash water. In order to eliminate this ambiguity, samples of alkali-refined and bleached rapeseed, and linseed oil, to which acid-oil (obtained by sulphuric acid splitting of soapstock from previous neutralizations) had been added, were neutralized with a lye containing equal amounts of sodium and calcium hydroxides. Although the amount of calcium in the refining lye was many times greater than that in the crude oil, the soap content of the washed oil was, in the case of rapeseed oil, lower than that of a natural rapeseed oil neutralized only with sodium hydroxide. This fact seems to indicate that the high soap content of natural rapeseed oil is attributable not only to calcium soaps but also to some other components which are determined to be soaps by the method of Wolff.

In the case of linseed oil the soap content of the oil which had been neutralized with a mixture of sodium and calcium hydroxide was much higher than in the case of rapeseed oil. This probably results from the fact that calcium linoleate and linolenate are much more soluble in oil than are the calcium soaps of other fatty acids.

In all cases washable oils were obtained if the neutralized oil was re-refined with lye containing sodium carbonate, whether the calcium content originated from the crude oil or from the process water.

Presence of Calcium, Magnesium, and Phosphorus in Crude Oils and in Unwashable, Neutralized and Washed Oils

As has already been mentioned, there is reason to believe that the calcium and magnesium content of

TABLE V

Effect of Water Hardness on Soap Content of Washed Oils

Oil	Lye used for neutralization		Hardness of wash water (p.p.m. CaO)	Soap content of washed oil (p.p.m.)
	Base	Water		
Cottonseed	NaOH	Distilled	0	50[b]
Cottonseed	NaOH	Distilled	50[a]	80[b]
Cottonseed	NaOH	Distilled	100[a]	130[b]
Cottonseed	NaOH	Distilled	200[a]	130[b]
Peanut	NaOH	Distilled	0	180[c]
Peanut	NaOH	Distilled	300	380[c]
Rapeseed	NaOH	Soft[d]	Soft[d]	100[b]
Rapeseed	NaOH	Tap	Tap	360[b]
Rapeseed	NaOH	Soft[d]	Soft[d]	950[c]
Refined and bleached rapeseed oil containing acid oil	NaOH	Distilled	0	50[c]
Refined and bleached rapeseed oil containing acid oil	NaOH and $Ca(OH)_2$	Distilled	0	250[c]
Refined and bleached linseed oil containing acid oil	NaOH	Distilled	0	60[c]
Refined and bleached linseed oil containing acid oil	NaOH and $Ca(OH)_2$	Distilled	0	4800[c]
Refined and bleached linseed oil containing acid oil	NaOH and $Ca(OH)_2$	Distilled	0	80[b]

[a] $CaCl_2$ added to distilled water. [b] Re-refining with lye of 12°Bé containing 100 g. Na_2CO_3 per liter before washing. [c] No re-refining. [d] Permutite.

TABLE VI

Relationship of Certain Inorganic Elements in Crude Oil to Soap Contents of the Neutralized and Washed Oils

Crude oil	Analysis of crude oil						Soap[b] in neutralized and washed oil (p.p.m.)
	Calcium + magnesium[a] (p.p.m.)	Calcium (p.p.m.)	Magnesium (p.p.m.)	Phosphorous (p.p.m.)	Molar ratio $\frac{Ca+Mg}{P}$	Soap[b] (p.p.m.)	
Rapeseed	270	180	50	210	1.02	370	910
Linseed	100	78	14	91	0.86	570	120
Linseed	110	....	....	63	1.25	200	30
Linseed	110	....	....	110	0.80	260	30
Linseed	130	....	....	110	0.95	400	110
Linseed	770	370	240	510	1.17	600	2700
Peanut	8	....	....	0	......	50	30
Soyabean	100	....	....	140	0.56	240	180
Soyabean	260	140	50	220	0.92	150	150
Cottonseed	290	120	100	390	0.57	750	90
Cottonseed	150	....	....	430	0.28	910	2100

[a] Calculated as calcium. [b] Soap as determined by method of Wolff (20).

the crude is related to the washability of the neutralized oil. This is illustrated by the data in Table VI. If the neutralized oil was not washable, a considerable amount of calcium and/or magnesium was always found in the corresponding crude oil. However the opposite conclusion is not justified. Thus most crude cottonseed oils contain appreciable amounts of calcium and magnesium (12), but the neutralized oils are usually completely washable. Evidently the washability of the neutral oil depends on the way in which the calcium and magnesium are combined with other elements in the oil. A high calcium and magnesium content of the crude usually goes with a high phosphorous content. It seems probable therefore that the calcium and magnesium are combined with lecithins, cephalins, inositol-phosphoric acid, or other similar compounds which have been detected in vegetable oils (19). Phosphatide-free oils such as coconut, palm kernel, babacu, and palm oil, in the experience of the writers, are always washable.

It is interesting to note (*cf.* Table VI) that crude oils having a high calcium and magnesium content gave a reaction for "soap" according to the method of Wolff. Since it seems improbable that true soaps are present in crude oils, the calcium and magnesium must be combined with other weak acids to form salts having an alkaline reaction.

There is no reason to believe that such salts would be completely converted to true soaps during the neutralization process. On the contrary, it seems probable that to a greater or lesser extent they remain unaltered in the neutralized oil. This expectation is confirmed by the data in Table VII. Although a considerable removal of the inorganic elements took place during the neutralization (compare Table VI), a great part remained in the unwashable oils. The fact that both calcium and phosphorus were still present in appreciable amounts indicates that the conversion to calcium soaps was incomplete. The same conclusion may be drawn from the fact that a simple post-treatment with sodium carbonate did not remove the calcium.

Part of the "soap" determined according to the methods of Durst-Stillman and Wolff is therefore not true soap but salts of phosphatides or other lipids. Probably the same applies to a certain extent to the sodium soaps determined according to Boekenoogen. Thus it is seen from Table I that unwashable oils contain considerable amounts of sodium even after washing with water.

As has already been pointed out, this is of minor practical importance because the presence of all these compounds in the oil is harmful because of their interference with the subsequent refining. The direct titration according to Wolff's method is by far the easiest and most convenient way to detect and determine substances which have not been completely removed by the neutralization and water wash whether or not these substances are soaps in the strict sense of the word. The method of Wolff is therefore of great practical importance.

In analogy to such well-known terms as acid, iodine, and acetyl numbers, hydrochloric-acid-number seems to be a suitable designation for the analytical characteristic of crude or refined oils determined as "soap," according to the procedure indicated by Wolff. A suitable unit for the HCl-number is the volume in cc. 0.01 N HCl per 100-g. oil; 1 cc. corresponds to a sodium oleate content of 30.4 p.p.m.

TABLE VII

Soap, Calcium, and Magnesium in Refined and Washed Oils

Oil	Refining treatment	Analysis of washed oil		
		Calcium+ magnesium[a] (p.p.m.)	Phosphorous (p.p.m.)	Soap (p.p.m.)
Rapeseed	Neutralization	10	23	1200
Rapeseed	Pretreatment with H_3PO_4 and neutralization	Nil	Nil	60
Rapeseed	Neutralization with Na_2CO_3 added to lye	6	6	190
Rapeseed	Neutralization and re-refining with Na_2CO_3 added to lye	Nil	Nil	50
Linseed	Neutralization	2	1	30
Linseed	Pretreatment with H_3PO_4 and neutralization	2	Nil	10
Linseed	Neutralization	15	72	1100
Linseed	Pretreatment with H_3PO_4 and neutralization	2	1	30
Linseed	Neutralization	68	120	2600
Linseed	Pretreatment with H_3PO_4 and neutralization	Nil	Nil	30
Linseed	Neutralization and re-refining with Na_2CO_3 added to lye	....	3	60
Soyabean	Neutralization	....	9	160
Soyabean	Pretreatment with H_3PO_4 and neutralization	....	3	30
Cottonseed	Neutralization	....	75	2100
Cottonseed	Pretreatment with citric acid and neutralization	....	24	800
Cottonseed	Pretreatment with H_3PO_4 and neutralization	....	3	140

[a] Calculated as calcium.

Summary

An investigation of the removal of soap from neutralized vegetable oils by washing with water has shown that some oils are obtained practically soap-free after only one water wash whereas the soap in other oils cannot be removed even by repeated washing. Coconut, palm, and olive oils are easily washed whereas linseed and rapeseed oils are not. Peanut, sunflowerseed, soybean, and cottonseed oils are sometimes washable and sometimes not.

With unwashable oils different methods for soap determination give inconsistent results because calcium and magnesium soaps, or other naturally-occurring compounds of these metals, are not determined to the same extent by these methods. Calcium and magnesium in the crude oils are probably combined with phosphatides or other lipids and remain to some extent in this state after neutralization. Calcium and magnesium present as soaps or as any other compound may be detected easily in crude, neutralized, and washed oils by the titration method of Wolff.

Washability of neutralized oils may be improved in a number of ways; the most efficient is pre-treatment with concentrated phosphoric acid or re-refining with a mixture of sodium hydroxide and sodium carbonate. Either of these treatments can be applied in batch or continuous refining processes. To prevent contamination of washable oils with calcium and magnesium, soft water should be used for washing and in preparation of refining solutions.

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The Destruction of Gossypol in Cottonseed Oil Soapstock by a Heat Treatment[1]

JOSEPH POMINSKI and FRANK C. PACK, Southern Regional Research Laboratory,[2]
New Orleans, Louisiana

THERE IS A NEED to find uses for the excess supplies of oil soapstocks. Approximately 120 million pounds of cottonseed oil soapstock are produced annually in this country (reported as refining loss). The market price of cottonseed oil soapstock, when salable, is often insufficient to cover transportation costs. Some refiners have been forced to discard this material, and even its disposal may prove troublesome at times by reason of conservation laws. Examined for the specific case of cottonseed oil soapstock, many proposed uses aimed at an increased utility for this material would benefit by a reduction in the amount of or the outright destruction of the gossypol contained in soapstock. The gossypol content of cottonseed oil soapstock may vary from 0 to approximately 4%. Samples of alkaline soapstock analyzed in our laboratories exhibit a range from a few tenths of 1% to nearly 4%. Acidulated soapstocks show a range of from substantially 0 to 6%. All of our gossypol analyses employ the *p*-anisidine method.

The efficient preparation of considerable amounts of degossypolized soapstock for evaluation purposes necessitated the designing, construction, and operation of a continuous, pilot-plant scale, degossypolizing apparatus. The apparatus based on previously reported laboratory data (1) and its operation is the subject of this paper.

Apparatus

The pilot-plant apparatus is designed to process approximately 1.88 lbs. or 0.25 gal. of raw alkaline soapstock per hour at temperatures of 212°–215°C. and pressures of 290–300 lbs. p.s.i. Figure 1 is a photograph, and Figure 2 a flow diagram of the apparatus. Alkaline soapstock is forced through the system continuously while being subjected to the heat treatment. The pressures developed are the result of heat-treating temperatures and are not in themselves essential for the destruction of gossypol. The heated,

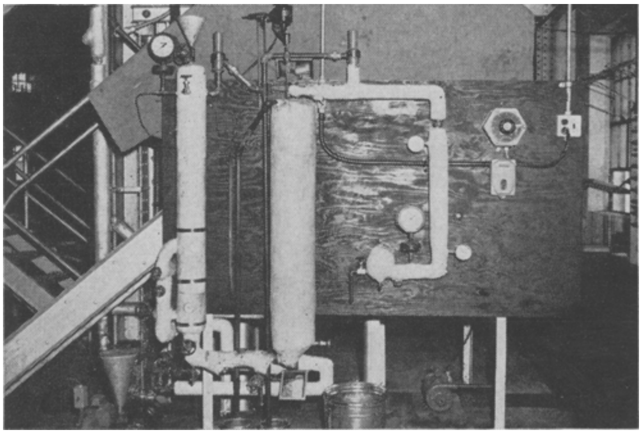

FIG. 1. Apparatus for heat-treating soapstock.

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