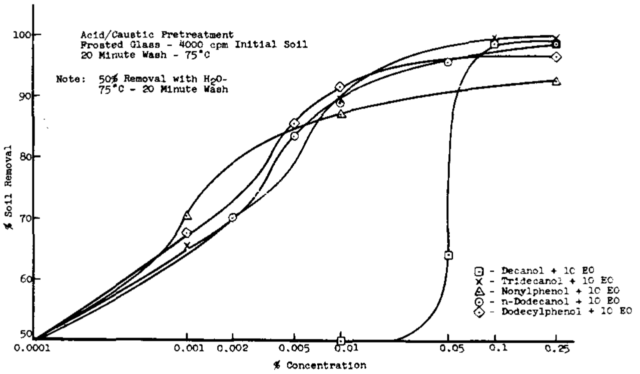

FIG. 9. Stearic acid carbon-14 soil: nonionic surfactant.

tion is sodium lauryl sulfate, which was ineffective with tristearin; but with stearic acid soil was as effective as the alkylbenzene sulfonates. Another difference is in level of removal, which is generally lower for tristearin soil.

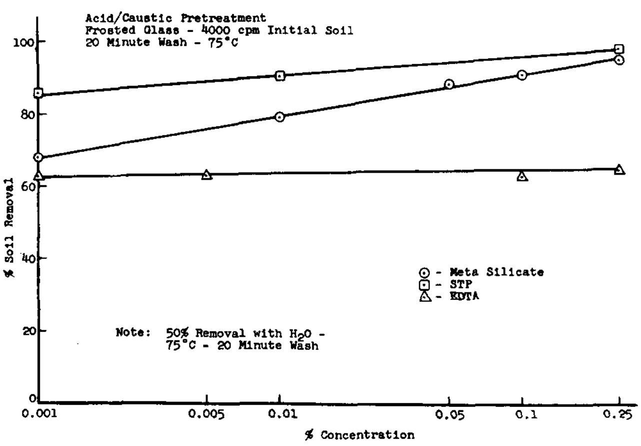

FIG. 10. Stearic acid carbon-14 soil: removal by builders.

Increase in soil removal level of anionics for protein and stearic acid soils may be at least partially ascribed to an ion-exchange mechanism.

Similarities also exist between the two soils when washed with nonionic surfactants. Though higher solution concentrations are required for tristearin removal, the shapes of the decanol-10-EO, nonylphenol-10-EO, and tridecanol-10-EO product curves are rather similar. The decanol product exhibits a similar sharp increase in effectiveness over a narrow, but higher concentration range.

Removal by builders, Figure 10, shows ethylenediamine sodium tetraacetate as relatively ineffective; and, at sufficiently high concentration, sodium metasilicate approached STP effectiveness. The shape of the EDTA and STP curves suggests that sequestration is not the controlling factor in stearic acid soil removal. STP has an additional unspecified quality.

Surfactant-STP built compositions, in general, were superior to the pure surfactant, and high removal levels were achieved at lower solution concentrations. Synergism was particularly notable at low solution concentration levels (Figure 11).

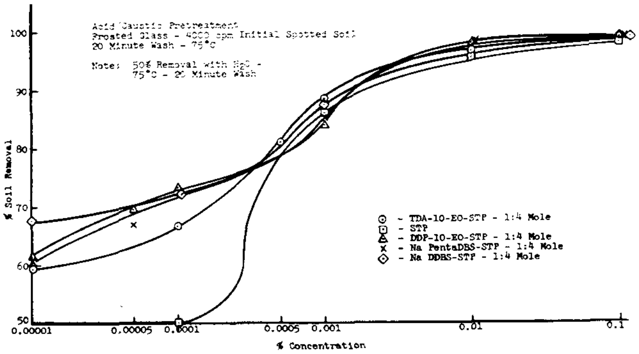

FIG. 11. Stearic acid carbon-14 soil: STP built compositions.

Effect of nonionic use at cloud-point temperatures closely duplicated the findings with triolein soil (3). Optimum removal for a given surfactant occurred at its cloud-point temperature, and, as before, only certain nonionics could be used most satisfactorily over a broad temperature range.

Decrease in deflection of the sigmoid portion of the stearic acid soil removal curves, as compared with tristearin, may be attributed to the influence of an ion-exchange mechanism.

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Determining Refining Loss by the Sodium Balance Method[1]

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The Sodium Balance Method is a rapid and reliable procedure for determining plant refining loss. By sodium analysis of each stream flow, treated crude, refined oil, and soap, the refining loss is calculated through substitution of sodium values for each component in an equation. The accuracy of this Sodium Balance Method for refining loss equals that of conventionally accepted methods, such as weight and total fat loss.

REFINING LOSS is a measure of the efficiency of a refining operation. To the refiner this value is important for determining how effectively his plant is operating and for compliance with negotiated contract agreements under the accepted trading rules.

In either a batch- or continuous-refining operation the loss occurs in the soap phase. As a result of the chemical reaction and processing procedure the soap

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phase contains saponified free fatty acids, the impurities present in original crude such as meal and phosphatides, and entrained or saponified neutral oil. Since the revolutionizing of the vegetable oil industry with the introduction of the first continuous refinery a quarter-century ago (1), there have been steady improvements in processing techniques to minimize refining loss. In order to appraise the increased oil yields with these new methods of processing, various analytical procedures have been developed.

Current Refining Loss Methods

Determination of refining loss by conventional methods was well presented by James at the A.O.C.S. Short Course in 1955 (2). Herein were described the Official A.O.C.S. Refining Method, used as a yardstick in trading rules, and the theoretical loss methods (Wesson, Chromatographic, and Acetone insolubles), which give the absolute glyceride content of any crude vegetable oil. These methods are used for comparison with actual refinery loss data to calculate oil savings over cup loss or percentage of refining efficiency.

This presentation covers the refiner's methods of determining the yield of refined oil from a particular type of crude, processed under a given set of conditions. This type of information is important, for losses on any crude oil may vary considerably, depending upon operational procedures. Such factors as the type and quantity of reagent, reaction time, temperature, kind and degree of mixing, conditions of centrifugation, all affect the yield and quality of product. Generally the plant loss is appraised by the weight of feed and products recovered, or by the chemical analyses of feed and each product, from which loss values are determined by calculation.

Direct weight is the simplest of these methods and is readily applicable where large volumes of the same oil are handled on a daily basis with no change in processing conditions. However this method is not always practical when processing a number of different oils or even the same oil of different fatty acid content, or when varying refining procedure or studying refinery parameters. In these cases accurate loss values are best established by spot-checking refined oil and soap rates for a given period of time, collecting samples of feed, soap, and refined oil at the same interval, and chemically evaluating the collected samples.

Two analytical procedures, at present widely used in this chemical evaluation, are total fat method and water balance method. In the former, from analysis of the soapstock for total fat content, it is possible to calculate the over-all refining loss. If the soapstock is analyzed for fatty acids and neutral oil and if the nonglyceride components of the original crude are known, it is possible by calculation to note where in the process any additional oil loss in soapstock over theoretical quantity is occurring, for example, the quantity of neutral oil saponified. That fraction, which may be entrained, can be noted. In the water balance method, by analyzing each stream component for moisture, plant refining loss may be calculated (3).

A study of the foregoing analytical methods for plant refining loss emphasizes the importance of both accurate weight samples and experienced chemists, together with the need for sufficient time and adequate laboratory facilities. These conditions mean slow answers for the plant operator eager to establish the correct processing procedure in the refinery. Quite possibly uneconomical operation will also occur until ideal refining conditions are established.

The Sodium Balance Method

By contrast the Sodium Balance Method is potentially a quick, accurate measurement of refining loss. Only one 4-oz. sample each of the feed extraction mixture, refined oil, and a soapstock is required. There is no necessity for flow-rate data. Thus, in a single day, a number of variables may be appraised in a refinery. As soon as constant conditions are established, small average samples may be easily collected and quickly analyzed.

In the Sodium Balance Method the refining loss is calculated by substituting known analytical values in the formula appearing in Figure 1.

$$\%\ \text{Refining Loss} = \frac{\%\ \text{Treat}\,(\%\ \text{Na r} - \%\ \text{Na s}) - 100\,(\%\ \text{Na o})}{\%\ \text{Na s} - \%\ \text{Na o}}$$

Where % Treat = % reagent used per weight of crude oil
% Na r = % sodium in reagent
% Na s = % sodium in soapstock
% Na o = % sodium in refined oil

FIG. 1. Refining loss equation for Sodium Balance Method.

The equation was derived, as indicated in Figure 2, from the proposition:

Pounds Na in original feed = pounds Na in soap + pounds Na in refined oil.

It should be noted that this formula can be used to evaluate both caustic and soda ash refining processes.

For calculating loss by the Sodium Balance Method the only required values are: percentage of treat, percentage of sodium in reagent (% Na r), percentage of sodium in soap (% Na s), and percentage of sodium in refined oil (% Na o).

The percentage of treat can readily be determined by the simple, rapid method, as presented by Mattikow to the American Oil Chemists' Society in 1956 (4). For example, by direct potentiometric titration with 0.5N sulfuric acid to pH 4, the total alkali in a sample mixture of 50 g. of crude oil plus reagent, diluted with four parts of water, is determinable in an 8–10-min. period.

The percentage of sodium in the reagent (% Na r) is calculable from laboratory titration of percentage of caustic or soda ash (5), analyzed routinely each time the reagent is prepared.

The method for total sodium present in soapstock (% Na s) closely parallels the method for percentage of treat but with a few variations. The procedure for percentage of sodium in soapstock requires an accurately weighed, 8–10-g. sample of thoroughly mixed soapstock in a tared 250-ml. beaker. Add 100 ml. of hot distilled water. Agitate mixture well until there is a uniform soap solution. Unusually viscous soapstock may be well dispersed with the water in a Waring Blendor. Titrate with 0.5N sulfuric acid to pH 4, using a pH meter with glass electrode-calomel electrode assembly. As the pH approaches 5, the sulfuric acid addition should be by 0.2 ml. or less increments to assure accurate measurements at pH 4. The pH reading should be constant at 4 for one full

STEP 1:

Pounds Na in feed = pounds Na in soap + pounds Na in refined oil

As equivalents in 100 pounds crude oil basis:

Pounds Na in feed

$$= \frac{\%\ \text{treat}\ (\%\ \text{Na r})}{100}$$

Pounds Na in soap

$$= \frac{\%\ \text{Na in soap (weight of soap)}}{100}$$

$$= \frac{\%\ \text{Na s}\ (\%\ \text{treat} + \%\ \text{loss})}{100}$$

Pounds Na in refined oil

$$= \frac{\%\ \text{Na in refined oil (weight of refined oil)}}{100}$$

Yet weight refined oil

= 100 pounds crude − % loss

Thus

Pounds Na in refined oil

$$= \frac{\%\ \text{Na o}\ (100 - \%\ \text{loss})}{100}$$

STEP 2:

Substituting in original formula, Step 1, the equation reads:

$$\frac{\%\ \text{treat}\ (\%\ \text{Na r})}{100} = \frac{\%\ \text{Na s}\ (\%\ \text{treat} + \%\ \text{loss})}{100} + \frac{\%\ \text{Na o}\ (100 - \%\ \text{loss})}{100}$$

STEP 3:

Solving for % loss, the final equation becomes:

$$\%\ \text{Loss} = \frac{\%\ \text{treat}\ (\%\text{Na r} - \%\ \text{Na s}) - 100\ (\%\ \text{Na o})}{\%\ \text{Na s} - \%\text{Na o}}$$

FIG. 2. Derivation of refining loss equation for Sodium Balance Method.

minute before noting final value. Throughout the titration the soap solution is agitated and the temperature is compensated in pH readings. The percentage of sodium in soapstock is calculated:

% Na s = ml. acid × acid N × the factor 2.3/ weight of sample.

The sodium content of the refined oil (% Na o) is determined by calculation from its soap content:

% Soap in refined oil × factor 0.08 = % sodium in refined oil (% Na o).

A number of methods for analyzing the soap content of refined oils have been presented by Rodeghier (6) and Braae and associates (7). The most rapid, extensively used in this country, is the conductivity method. This method of water extraction of the soap from the refined oil in a tetra-ethyl lead extractor and the measuring of the sodium ion by conductivity bridge and cell is well described by Goff and Blachly (8).

Comparison of Methods

During the past three years the Sodium Balance Method has been compared with the conventional total fat and weight method to appraise its accuracy.

For this comparative study the samples were all collected from a continuous vegetable oil refinery, while operating at certain established conditions. A number of crude oils of varying free fatty acid content were alkali-refined. Accurate weight data of crude, soap, and refined oil flows were obtained. The samples were analyzed for total fat loss and by the Sodium Balance Method. The complete set of samples for each loss evaluation by the Sodium Balance Method was analyzed by a single chemist in 2 hrs. However the complete total fat laboratory evaluation and calculations took more than a day.

The results of the comparative refining loss data on various types of crude oils are summarized in Table I.

TABLE I
Comparative Refining Loss Data

Type of crude oil	% FFA (as oleic)	% Refining Loss		Deviation
		Total fat weight method	Sodium balance method	
Coconut	2.5	2.7	2.7	0
Coconut	4.1	5.7	5.9	+0.2
Coconut	6.8	8.3	8.5	+0.2
Cottonseed	4.1	5.0	4.9	—0.1
Soybean	0.6	2.9	2.9	0
Soybean	0.8	4.1	4.2	+0.1
Degummed soybean	0.4	1.7	1.6	—0.1
Linseed	0.7	3.0	2.9	—0.1
Linseed	1.5	3.8	3.8	0

It should be noted that the percentage of refining loss by the proposed Sodium Balance Method is the same as or very closely approximate to, within ± 0.1 to 0.2%, the loss by the longer, more tedious, time-consuming, conventional methods.

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