Soap in Refined Oil

Fatty acids react readily with alkali to produce soaps, and it is during the refining operation that the the soaps are introduced as a contaminant. Traces of soap in a refined oil are detrimental to the quality of the final product, and their adsorption during hydrogenation accounts for off-quality hardened oils.

A low soap content is best insured by water-washing the neutral oil, followed by a thorough drying before bleaching with an adsorbent. The analysis of the refined oil for soap, which should run not over 5 parts per million, is rather uncertain in this low concentration, and there are several methods for this determination.

Essentially the determination involves the extraction of the soap from the oil, followed by the quantitative determination of the sodium ion. Extraction is made by using alcohol and burning off the alcohol in a platinum crucible followed by ignition. The ash is then dissolved in water and titrated with 0.02N-HCl using methyl orange indicator. Extraction is also done with 1:1-hydrochloric acid, followed by evaporation of the extract. Water is added to the residue, and the mixture is titrated with 0.01N-$AgNO_3$ with potassium chromate indicator added.

Although more time-consuming, the oil may be burned off and ignited in a platinum crucible without extraction. The more modern method of determining trace soaps is by the conductivity method where soap is determined against standard soap solutions.

In conclusion, the methods given herein and their implications to trading rules are of concern to all who process, or buy and sell fats and fatty acid products.

The impurities, except for sterols used in hormone and pharmaceutical preparations, are of no commercial value but may indicate to the refiner how best to refine for the maximum recovery of neutral oil.

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The Determination of Refining Loss

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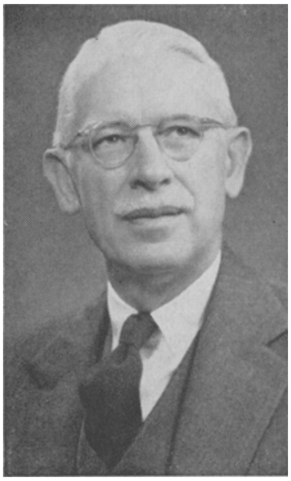
THE ANALYTICAL chemist is required to determine refining losses on crude oils for two distinct purposes: as a basis for settlement of crude oil contracts under the trading rules of the National Cottonseed Producers Association and the National Soybean Processors Association; and as a yardstick for the efficiency of refinery operation.



E. M. James

The standard method of determining refining losses is known as the A.O.C.S. Cup Method. It is described in every detail in the standard methods of the A.O.C.S. and in the manuals of trading rules issued by the two associations mentioned above. Without going into detailed discussion of the cup method, I believe however that you will find of interest the historical background which led up to its development.

Thirty-five years ago the principal oils traded in on the basis of refining loss were cottonseed and peanut oils. Soybean oil, except as imported from Manchuria, was practically unknown in this country. A strong group of mills and refiners, operating under the name of the Interstate Cottonseed Crushers' Association, had formulated a series of specifications for the various grades of crude cottonseed oil, refined oils, and soapstock, and penalties upon the seller were provided for deliveries which were not up to specified quality.

At that time all cottonseed oil was refined in the kettle, and the average loss in the refinery was estimated to be approximately 9.0%. All oil having a loss of 9.0% or less was defined as a prime crude oil. Other requirements were that the oil be sweet in flavor and odor, not musty or sour, and must refine to a color not higher than the combined Lovibond glasses of 35.0 yellow, 7.6 red. Penalties were levied for off-flavor and odor and for colors darker than the specified 7.6. But the principal penalty was for loss and amounted to ¾ of 1% of the purchase price of the oil for every per cent in excess of 9.0%. (With peanut oil, the prime loss was 5.0%.) Limits were also set on the free fatty acid of the crude, which was 2.5% for prime oil. Crude cottonseed oil was sold on "a basis prime" contract, and upper limits were set for the loss (16.0%) and the color of the refined oil (35 yellow, 12 red). No premiums were allowed for losses better than prime.

Now it is obvious that a seller of crude oil could not afford to wait for payment until the refinery had refined his oil and determined whether it met the specifications under which it had been bought. Therefore it became necessary to find a method for refining a small lot of crude oil in the laboratory in a manner which would simulate plant operations to the extent of giving approximate plant lossess and color. A complicating factor was the tendency of some refiners to underrefine oil in the plant, thus obtaining lower losses at the expense of color. So the method adopted had to employ enough caustic solution to give at least a prime color on prime oils.

EVENTUALLY the Chemists' Committee of the Association worked out a method for the laboratory refining of crude cottonseed oil which would give results approximating complete refining in the plant. A set of brief instructions for chemists was included in the manual of trading rules, and a maximum amount of caustic soda, based upon the FFA of the oil, was specified.

Originally laboratory refinings were carried out in makeshift apparatus, using varying types of containers and mechanical agitators. Some time prior to 1921 Worthen Agee, of the Barrow-Agee Laboratories in Memphis, designed a refining machine which would handle 12 refinings at once, and offered to build it for refiners, mills, and commercial laboratories. The advantages of such a piece of standard equipment were obvious, and the machine came into general use. The original machine had four speeds, and was driven by friction between a large metal and a small leather disc running at right angles to one another.

The settlement refining operation differed in various laboratories since several cups of the same oil were often refined, but at least one was treated with a maximum amount of lye. The percentage of dry caustic soda only was fixed, but the strength of the solution used was left to the discretion of the individual refiner. Strengths varied between 12° and 20° Be depending upon the FFA of the oil.

Since the maximum lye was supposed to be enough to give the best possible result on color of the refined oil with a loss which could be expected in the kettle when this color was obtained, the refiner usually made at least two other refinings with lesser amounts of lye to determine whether satisfactory colors and losses could be obtained, and these results were used as a guide for plant operations.

During a number of years when the writer was in charge of refining cottonseed oil at a large refinery, the following procedure was developed.

As the crude oil came in from the various mills, reference was made to the previous season. A lye table was started for each section of the country, the strength of lye used being dependent upon past experience. Percentages were changed for every increment of 0.3% in the FFA of the crude. Three refinings were made, two with the same caustic soda content in the lye, but of different strengths, and one with the maximum amount. The latter was always run with the stronger of the two lyes.

This custom of making two refinings in the cup with the same percentage of caustic soda but different strengths of lye formed the basis for the present system of settlement cup refining.

The refiner, having weighed out his samples of both oil and lye, filled the water bath with cold water of not more than 25°C., placed the cups in the bath, adjusted the paddles, and set the driving discs to drive the paddles at top speed (approximately 250 RPM). He then added the lye in each cup as rapidly as possible and carefully observed the oil for the first sign of a "break."

It was standard practice to run the oil cold for 15 min. before heating the bath, and it was desirable that the "break," or separation of the soapstock in visible flocks, be retarded until heat was applied. It had been observed that if an oil tended to break out while running cold at high speed, instead of agglomerating, the particles of soapstock would break up quickly and settle poorly at the finish. When the refiner encountered such an oil, he would frequently retard the break by slowing down the rate of agitation while the oil was still cold. The medium speeds on the paddle were quite useful in such cases.

After the mixture of oil and lye had run cold for 15 min., the refiner turned steam into the coils in the bath, and when the temperature reached 60°–65°C., he cut off the heat. He continued to observe the break and settle of the oil closely, determining the latter by momentarily depressing the large flat disc with his hand. When he was satisfied that the oil was finished and settled rapidly, he would cut off the agitation from that cup and allow it to settle in the hot bath. Therefore it often happened that, instead of running a full 10 min. at temperature, some oils were shut down and allowed to settle after as little as three minutes at heat, and others ran even longer than the 10-min. standard.

THE RESULT of this method of operation was that the refiner had to know his oils and judge how long to run them to get the best losses, and, of course, no two refiners handled the job in exactly the same way. Also it took a long time to train a man properly to be a good refiner. The oil refinery foreman, whose job it was to specify the lye to be used in the kettle and who based his prescription upon the laboratory results, was thus dependent to a considerable degree upon the laboratory refiner. He himself often followed carefully the behavior of the oil in the refining machine, watching the type of break and time of settle on the various lots of oil being run for settlement.

The results of the settlement refining with the maximum lye were reported to the buying department by the laboratory. If the loss was 9.0% or less, that was the end of the matter. If it was appreciably over 9.0%, then the shipper was notified and settlement eventually made, often after a duplicate sample had been submitted to a referee chemist whose results were accepted as final in the dispute.

During the course of a normal season where the average FFA of the oils was low, it usually happened that the great majority of tank cars received at the refinery showed losses very substantially under 9.0%. The writer has seen many such oils with losses between 4.0% and 6.0%. It became standard practice for a mill manager to have his crude oil analyzed either in his own laboratory or in that of a nearby commercial chemist. If the losses were well under 9.0%, the manager instructed his car loaders to dump 1 or 2% of cottonseed meal into the tank car to raise the loss nearer to the 9.0% limit for prime oil. It paid him to do this for he was thus able to sell some of his meal at oil prices, and so long as he kept the loss at prime or under, he suffered no penalty.

The practice became very widespread, and as more efficient press room technique was developed, more and more meal found its way into crude oil. The refineries were put to considerable trouble and expense in cleaning tank cars, and, since their receipts of low-loss crudes decreased, they had to purchase more oil, which, in turn, increased their costs per 100 lbs. of refined oil produced.

Finally, about 1927, an agreement was reached between the mill men and the refiners that the latter would pay a premium for crude cottonseed oil having a settlement loss under 9.0%. The premium was on the same scale as the existing penalties for excess loss. Thus an incentive was immediately offered to the crude mills to produce a superior grade of oil.

However it was realized that the methods of laboratory refining, which, as we have pointed out, depended to a very great degree upon the judgment and experience of the refiner, were not too well suited to the proposed new trading rules.

Accordingly the Refining Committee of the A.O.C.S., under the chairmanship of the late C. B. Cluff, set out to standardize the laboratory method and prescribed rigid conditions for operation. It was decided that, for oils having a free fatty acid under 1.5%, the maximum percentage of dry caustic was too great. Therefore it was cut to 80% of the maximum, and the strengths set at 12° and 14° Be. Lye tables were prepared, giving the calculated amounts to be used for each 0.1% FFA in the crude. It was decided to set standard running times in both the cold and the hot baths and to standardize on agitation rates of 250 RPM for running cold and 70 RPM for running hot. At the same time Mr. Agee redesigned the refining machine to provide a positive drive through gears instead of discs, which were not altogether satisfactory.

About this time it was recognized that certain mills were producing a crude characterized as "slow breaking," which required a considerably longer running time, both cold and hot, to produce the best loss and color. Also the appearance of expeller oils on the market posed another problem since these crudes not only required cold and hot running times different from both types of hydraulic oils but also needed stronger lyes in greater amounts. So methods were developed for "regular," "slow breaking," and expeller cottonseed oils and were incorporated into the trading rules of the National Cottonseed Products Association, a successor to the old Interstate Cotton Crushers.

THE REFINING Committee has continued to work upon and broaden the standard methods, and they now cover other oils such as solvent-extracted cottonseed and the mixture of prepressed-extracted oils blended in the proportion in which they are removed from the whole seed.

The results of the standardization of laboratory cup refining for settlement purposes have been far-reaching. A refiner no longer needs to be an oil expert; he can learn the required techniques very quickly. Agreement between buyers' and sellers' analyses has become much closer, and the necessity for calling in a referee in disputed cases has been greatly lessened. While the cup test is arbitrary and inexact by modern standards of analytical techniques, it has filled, and continues to fill, a very necessary and important function in cottonseed oil trading.

Beginning in the late 1930's soybean oil appeared on the market in increasing quantities and has now taken the place of cottonseed oil as the major vegetable oil produced in this country.

At first, soybean oil was largely consumed in non-edible fields and was traded in only on the basis of FFA and so-called Gardner break content. This condition prevailed at the time the United States entered World War II, and the OPA froze prices of vegetable oils and fats. The price freeze resulted in a condition which, for the following reasons, the soybean processors felt placed soybean oil at a distinct disadvantage competitively with cottonseed oil.

Premiums for loss under the basis prime 9.0% on cottonseed oil were paid over and above the OPA price. So the soybean millers got together and tried to change the basis of trading to one similar to that used for cottonseed oil. Of course, to do so, it was necessary for the National Soybean Processors Association to obtain the consent of the OPA since their proposal amounted to a price increase. The refiners vigorously opposed change in the trading rules, and the OPA refused to allow it.

It was not until after the war and the removal of price controls that trading in soybean oil for edible purposes was placed upon a basis comparable to cottonseed oil. An important difference was that "prime" loss was set at 7.0%, and penalties for color were applied to the bleached, rather than the refined, oil.

The Refining Committee of the A.O.C.S., under the chairmanship of H. S. Mitchell, had, some considerable time prior to the change in trading rules, undertaken an extensive program to develop standard methods for the laboratory refining of soybean oil.

There were on the market three main types of crude soybean oil: hydraulic, expeller, and solvent-extracted. Methods were worked out for each of these types and have been formally adopted as standard both by the Society and the trade associations. Degummed soybean oil, mostly of the solvent type, for a time posed a problem, but a special method was worked out for this oil also.

Again, we do not propose to go into a detailed discussion of the individual tests, which are all set forth in the A.O.C.S. book of Standard Methods with which you are familiar. Suffice it to say that, as a basis for trading in both cottonseed and soybean oils, the cup refining method, despite its empirical nature, has worked very successfully and, in our opinion, will continue to be relied upon in this field for a long time to come.

Important as is the determination of laboratory refining loss to trading, the other field where it is equally important is of particular interest to the analytical and control chemist. That field is the determination of the efficiency of refining operations in the plant.

One fact that should always be remembered is that the manufacturer of edible oils, shortening, or margarine makes a goodly proportion of his profits in the refinery. To elaborate on this point, the oil buyer provides the refinery superintendent with a certain amount of crude, based upon the best estimate available of the sales of finished products expected in a given period. It is up to the superintendent to get the largest possible yield of refined oil from his supply of crude. If his operation is inefficient and his losses in refining are unnecessarily high, there is no way by which such losses can be made up in the processing steps subsequent to refining. Therefore it is extremely important that there be available a yardstick by which the superintendent may judge the efficiency of his operation. For many years the cup test provided such a yardstick and, in many refineries, still does.

The sampling of a tank car on track is not an easy matter, especially when the contents are not uniform. The standard technique in use today is fully effective only if the oil in the car is clear and free from settlings. The only way in which a truly representative sample of a crude oil can be obtained is by pumping the oil into a tank equipped with a good agitator and stirring it thoroughly, then withdrawing the sample. However the trading rules provide that settlement be based upon the analysis of a sample drawn from the tank car before unloading.

Hence, in many refineries, the sample for cup refining upon which plant efficiency is based is drawn either from a refining kettle or the feed tank for a continuous refining unit. In the days before the development of continuous refining it was standard practice in one large refinery with which the writer was familiar to draw a sample from the refining kettle after the crude oil had been thoroughly mixed and brought to refining temperature. This sample was then taken to the laboratory along with a 4-oz. sample of the batch of lye made up for that particular kettle. The laboratory refiner made a standard refining, using the same percentage of lye that had been used in the kettle, and determined the cup loss. He also made a bleach test by the standard A.O.C.S. bleaching method, using the standard prescribed percentage of bleach earth. The results of these two tests were then compared with those obtained in the plant. (The bleach color of the plant oil was determined by bleaching a sample of the refined oil from the kettle with standard earth by the A.O.C.S. method.)

The results of plant and laboratory were then compared. A good plant refiner was expected to obtain losses and bleach colors not more than 10% in excess of the laboratory results on the kettle samples. Of course, he strove to equal or better them, and in many cases did so. If the plant losses and bleach colors were outside the tolerances, the refinery superintendent immediately took steps to correct the operation.

A similar method of control has been applied to continuous operations. Continuous refining was originally justified on the basis that the losses would be lower than by the standard kettle method. During test periods this was demonstrated by split refinings: *i.e.,* two lots of crude were thoroughly blended, and one-half was refined by the continuous method and the other half in the kettle. At the same time the effectiveness of the split was determined by making a cup refining on a sample from each half of the blended oil.

Once the continuous method of refining had proved its economy, control was achieved by comparing the results with a cup refining on each lot of oil refined in the plant with the results of continuous operation. The latter was expected to have a loss lower than the former by 25%–35%, depending upon whether the oil had been refined for loss or for the best bleach color. At first, the comparison was made on the cup refining of the kettle sample, but, in order to cut down on the laboratory work required, it became common practice to compare the lowest cup loss on the samples drawn for settlement purposes with the result in the plant. When, as is usually the case, a large number of tank cars is run successively, the weighted average of the cup losses and bleach colors is used for comparison with the over-all plant loss and bleach color. This method is followed in the majority of refineries today. That it does not give a true estimate of the actual efficiency of plant operations will be shown in the discussions below.

FOR MANY years thoughtful people in the industry have been convinced that the cup refining method did not give a really accurate determination of the value of a crude oil. It was known that, in addition to the free fatty acid, the oil as received from the crude mills contained a number of minor constituents which should be removed in the refining step before the oil was suitable for processing into finished salad oil or shortening. These minor constituents include coloring matter, material whose composition has not been fully determined but which are loosely classified under the term "gums" or "phosphatids," "gossypol" (in cottonseed oil), a small amount of moisture and volatile material, and, in some cases, more or less of gross impurities such as meal and (or) linters. There is also a certain proportion of unsaponifiable matter (sterols, and in some cases hydrocarbons), which is soluble to a considerable degree in the glycerides themselves and tends to be distributed between the neutral refined oil and the foots. Some of the sterols remain in the oil throughout the whole of the bleaching, hardening, and post-bleaching steps and are only incompletely removed in the deodorizer. (A common source of tocopherols is deodorizer blowover from soybean oil, either hydrogenated or salad oil.) The minor constituents, excluding free fatty acid, of a crude cottonseed or soybean oil may add up to as much as 2.5%–3.0%. Some cottonseed oils have been found to contain as much as 0.8% gossypol, depending upon the source of the seed and the method of extraction. The coloring matter in cottonseed oil is largely a mixture of carotenoids, and in soybean oil of both carotenoids and chlorophyll. The actual percentage is extremely low. Generally speaking, the so-called gums or phosphatides form the bulk of the minor constituents. They include glucosides, inositol phosphatides, lecithin, and cephalin (in the case of soybean oil), and other complex substances. Gross impurities are present in cottonseed oil and peanut oils to a small degree but are practically absent from soybean oil due to the universal practice of filtering the extracted oil either as coming from the expellers or as miscella in the case of solvent oils.

It should be noted that the minor constituents of crude oils, with the exception of the unsaponifiables, are either acidic in nature or are capable of coagulation and absorption in caustic soda solutions.

There are at present three methods of determining so-called absolute glyceride contents of vegetable oils. The oldest and best known is that devised by David Wesson, of the Southern Cotton Oil Company, and described by him in 1922 (The Cotton Oil Press, Vol. VI, No. 4), and again in 1926 (Journal of the Oil and Fat Industry, Vol. III). The Wesson method was substantially modified by Jamieson and described by him in the second edition of "Vegetable Oils and Fats," Reinhold, New York, 1943.

Another method is the so-called "acetone insoluble," which depends upon the determination of the material in a crude oil which is insoluble cold acetone, the moisture and volatile determination, and the free fatty acids. The results of these three determinations are added, and the total glycerides and unsaponifiables are determined by difference.

Still a third method, described by Handschumaker and Linteris in the Journal of the A.O.C.S., Vol. 27, 1950, and known as the Chromatographic Method, has been employed successfully. It is based upon the International Chemical Union's technique for the quantitative separation of neutral oil and unsaponifiable matter from free fatty acids by adsorption of the latter upon activated aluminum.

These three methods offer a means of determining the efficiency of refining by showing the refiner how much neutral oil is present in any given lot of crude since a comparison of the actual yield of neutral oil with that determined by analysis will show him how much theoretically recoverable oil has been lost to soapstock either by saponification or entrainment. We shall now briefly discuss the three aforementioned methods and evaluate them as controls for commercial refining. For complete details the students should go to the original references.

The Wesson Method. As originally developed by Dr. Wesson, the method was designed to determine the alkali absorption of the crude vegetable oil and later was shown to be a means for estimating accurately the available neutral oil in any given sample.

Ten grams of the oil to be analyzed are weighed into a 4-oz. sample bottle. The sample is weighed to the nearest 0.1 milligram. Fifty cc. of petroleum ether are then added, the bottle is stoppered with a sound cork, and the oil is thoroughly dissolved. Ten grams of a 14% caustic potash solution are added to the ether-oil mixture, and the latter is extracted by shaking thoroughly for 3 min. Twenty-five cc. of 50% ethyl alcohol are then added to wash any soap out of the neutral-oil-ether solution. This first wash must be handled carefully to avoid the formation of a tight emulsion between the ether layer and the alkali-soap-alcohol layer. When the refined oil solution has settled cleanly, it is carefully transferred to a second 4-oz. bottle by means of a small glass siphon where it is washed again with 35 cc. of 50% alcohol.

After settling once more, the oil-petroleum-ether solution is transferred to a Soxhlet flask. Two more extractions with petroleum ether are made from the first bottle, each extract being washed in the second bottle, and the whole is finally accumulated in the Soxhlet flask.

The latter is transferred to a steam bath, and the ether is carefully evaporated. Finally, the flask is placed in an oven at 105°C. and heated to constant weight. The absolute refining loss is then calculated from the difference in weight between the neutral oil recovered and the weight of the crude; or conversely, the percentage of neutral oil in the original sample is determined.

This method is not easy and requires a skilled analyst to carry it out successfully and obtain checks on duplicate samples. Extreme care to avoid any oil loss while transferring the solution must be taken, and there is danger of loss in the oven through spattering.

The Jamieson modification uses separatory funnels instead of 4-oz. bottles, and is even more complicated. Jamieson went farther than Wesson and determined the percentage of actual triglyceride in the crude by running an unsaponifiable on the extracted neutral oil and deducting this from the weight of the extract.

In recent years a modification of the original Wesson Method has been devised by Morris Mattikow. The principal difference lies in the fact that four, instead of three, extractions are employed, and a fifth portion of petroleum-ether is used to extract the washing alcohol. Dr. Mattikow has also designed a special extraction bottle having a wide lip at the top and a ground glass stopper.

The Wesson Method suffers from the disadvantage of being quite time-consuming in addition to its requirement of considerable skill on the part of the operator. Its accuracy is claimed to be 0.10% on duplicate determinations. However the same sample recently analyzed by seven laboratories as part of an investigation undertaken by the Fat Analysis Committee of the A.O.C.S. showed a spread of 0.953% between the highest and lowest loss reported. This spread is unquestionably due to lack of practice in the method on the part of certain of the collaborators.

The Acetone Insoluble Method. In this method the moisture and volatile matter of the crude are first determined by standard A.O.C.S. test. The phosphatids are then estimated from the acetone insoluble portion of the oil. Five grams of a well-mixed sample are weighed to the nearest milligram into two 50-cc. centrifuge tubes for a Servall Angle Centrifuge, which have been previously tared with stirring rods (nearest 0.10 milligram). Twenty-five cc. of acetone at 0–5°C. are added to each tube, and the oil-acetone mixture is well stirred. The tubes are then placed in the Servall Centrifuge and centrifuged for at least 10 min. at 2,500 RPM. The acetone-oil solution is then decanted from the residue. A further 25 cc. of cold acetone is pipetted into each tube, thoroughly mixed with the residue, and again centrifuged for 10 min. The supernatant liquid is decanted, and the precipitate is again washed with 25 cc. of cold acetone, centrifuging as before.

Most of the acetone is evaporated by placing the tubes under a stream of air, and the precipitate is dried in an oven at 105°C. for 30 min. The tubes are cooled to room temperature and weighed. To make sure that a constant weight has been obtained the tubes are placed in the oven again for 30 min. and reweighed.

The percentage of acetone insoluble is calculated as the weight of the precipitate x 100 over the weight of the sample. Duplicate analyses should check within 0.10%.

Before atempting to calculate the absolute loss of the sample, a further analysis must be carried out. It is known that the FFA determination on a crude oil is, in reality, the sum of the true FFA plus the caustic absorbed by the phosphatids or gums. Therefore the acetone must be carefully evaporated from the acetone-soluble portion of the sample and the free fatty acid determined. Then the sum of the true percentage of FFA, the percentage of acetone-insoluble, and the percentage of moisture and volatile deducted from 100 will give the percentage of neutral oil in the sample.

When the above procedure was applied to crude soybean oils, the calculated values were in fair agreement with the Wesson loss. However, with cottonseed oil, it was a different story. The neutral oil calculated was always considerably higher than that determined by the Wesson Method. But finally it was found that, if the acetone were saturated with potassium iodide before being used for the extraction of the crude, the calculated values were closer to the Wesson but still did not correlate so closely as those determined on soybean oil.

The Acetone-Insoluble Method, like the Wesson, is time-consuming. It is also quite touchy and requires a skilled and experienced analyst to make it reproducible. Great care must be taken to be sure that the acetone used is dry and that the tubes and contents do not rise substantially in temperature during centrifuging since this will result in re-solution of some of the precipitate. In practical experience it was found that the most reproducible results were obtained when centrifuging was carried out in a cold room maintained at 50°F. Further, in order to determine the percentage of neutral oil in any crude, it is necessary to carry out three analyses, with the possibility of accumulating errors. And, finally, the result sought is determined by difference rather than by actually weighing the refined oil.

The method has its supporters, but we believe it to be too cumbersome, and the chances of error too great to make it a practical day-to-day control on refinery operations.

The Chromatographic Method. This method is covered in detail in the reference already given. However, since the original date of publication, there have been some changes in technique which should be described. Briefly, the procedure is as follows. A sample of 1.0–3.0 g. of the well-mixed crude oil is weighed to the nearest 0.1 milligram. The size of the sample depends upon the FFA of the crude. The higher the latter, the smaller the sample. The weighed oil is taken up with diethyl ether and transferred quantitatively to a column of activated alumina. The solution passes through the adsorbent which removes the FFA, the moisture and volatile matter, and the gums or phosphatids. The ether solution of neutral oil is caught in a tared Soxhlet flask, and the column is washed thoroughly with several portions of ether, the washings also being collected in the Soxhlet.

The ether is evaporated from the recovered oil either on a steam bath or in a glass distillation apparatus. When the solvent is all gone, the flask is placed in a vacuum oven at 105°C. and heated to constant weight. The weight of the refined oil x 100, divided by the weight of the crude, will give the neutral oil content of the sample.

In the method as originally published, the reagents given were F-20 activated alumina, 80-200 mesh, and USP diethyl ether. USP ether may contain up to 3.5% ethyl alcohol and still meet specifications. The lot of USP ether used for the original work gave reproducible results, but a second lot was found unsatisfactory.

An investigation was undertaken, and it was found that the Wesson loss was most closely approximated when analytical ether containing 2.0% ethyl-alcohol was used. Absolute ether gave losses considerably in excess of the Wesson, and ether containing percentages of ethyl-alcohol substantially in excess of 2.0% also gave losses higher than the Wesson. Therefore the analytical grade has been chosen as the standard.

The tube holding the alumina described in the Handschumaker and Linteris paper was made in the laboratory, and the bottom was closed with a piece of oil-free absorbent cotton. It has been found that the standard chromatographic tube containing the sintered glass plate, such as is supplied by the Arthur H. Thomas Company, Central Scientific Company, and others is very satisfactory. The method should give checks of 0.10% or less on duplicate determinations. In the one sample tested by the Fat Analysis Committee the maximum spread between the high and low results reported by the seven collaborators was 0.78%. In our opinion this spread would have been greatly narrowed had the analysts been more familiar with the technique.

The advantage of the chromatographic neutral oil determination over either the Wesson or the Acetone-Insoluble method lies in its simplicity and the rapidity with which results can be obtained. A series of two or more tubes can be set up, and a number of samples run in succession. It has been found that a charge of 20 g. of alumina will absorb at least 0.6 g. of fatty acid, phosphatids, etc., and, in practice, three 3-g. lots of normal oil can be safely run through one charge of alumina.

The work of the Fat Analysis Committee indicated that the reproducibility of the Chromatographic Method, both inter- and intra-laboratory, was higher than that of the Wesson. However, in the collaborative work, the percentage of neutral oil was consistently lower in the former by 0.2%–0.3% than by the latter. Attempts to correlate the Chromatographic Method with the standard A.O.C.S. cup loss were unsatisfactory, and so far it must be assumed that there is no correlation.

The Chromatographic Method has been used for the last five years by one of the large manufacturers of vegetable shortening as a check on the efficiency of his refining operations. It has been found that, when the refining efficiencies (neutral oil yield x 100 divided by theoretical neutral oil) of two plants, one in the East and the other in the Chicago area, are compared, both plants being equipped with continuous refining installations, in normal operation on crude cottonseed and soybean oils there is seldom a spread of as much as 0.2% in efficiency even though there may be rather wide variations in both plant and cup losses and the crudes being handled may vary considerably in quality. Minimum standards of refining efficiency have been set up, and, if these are exceeded, the plant superintendents are called to account and the necessary corrections in refinery practice made to bring the losses down to the accepted level.

For a number of years there has been a strong desire on the part of certain refiners to use the neutral oil content, rather than the cup loss of crude oils as a basis for trading. These gentlemen argue approximately as follows.

> Let crude oil be sold as 100% neutral oil, setting the base price accordingly. Instead of the standard cup refining method, use either the Wesson or the Chromatographic Method to determine the amount of neutral oil in the shipment. Then apply the same discount for excess loss which obtains at the present time. The crude mills would not suffer since the base price would be raised, and there would be an added incentive to produce the best quality crudes and thus hold the discount to a minimum. So far however the idea has been received by the crushers with a noticeable lack of enthusiasm.

What the proponents of this method of trading overlook is the fact that none of the methods for determining neutral oil content provides any index into the quality of the refined oil which can be produced from a given crude as measured by the color and bleach test of the refined oil. The cup test does this, and in our opinion it will continue as the basis for trading in cottonseed, peanut and soybean oils for a long time, pending development of a method of determining color accurately on the refined oil produced either by the Wesson or the Chromatographic Method and the assurance that such a color determination will accurately reflect the color and bleach to be expected in plant operations.

To return to the observation that the neutral oil determined by the Chromatographic Method is always less than that found by the Wesson, the writer has had access to a number of comparative determinations recently carried out in the same laboratory by both methods on both cottonseed and soybean oil.

The Wesson Method was as modified by Dr. Mattikow, and the Chromatographic Method was carried out by the latest technique available. These results are included in Table 1. For comparison the cup losses on the oils analyzed are given. In all cases the chromatographic yields are the average of duplicate samples, and the same is true of the majority of the Wesson results.

A careful study of the table shows that the chromatographic loss, at least in one laboratory, although usually slightly higher than the Wesson, is not so in all cases. Over-all the agreement is remarkably close. The table also illustrates the complete lack of correlation between the Wesson or Chromatographic and the cup loss.

Determinations of the percentage of neutral oil on commercial refined, washed, and dried oils have shown practically quantitative recoveries of neutral oil by both the Wesson and the Chromatographic methods. So far therefore the reason for the slightly higher chromatographic losses remains obscure. We firmly believe however that either method should prove valuable as a control for refinery operation.

TABLE I

Oil	% FFA.	% Wesson	% Chromato.	% Cup.
Cotton Oil, Slow Break........	1.40	4.63	4.35	6.20
Cotton Oil, Slow Break........	1.10	2.56	2.73	5.83
Cotton Oil, Slow Break........	0.90	2.52	2.30	6.62
Cotton Oil, Slow Break........	1.20	3.45	3.61	6.76
Cotton Oil, Slow Break........	1.10	3.20	3.49	5.54
Cotton Oil, South American.	13.82	16.71	16.55	......
Cotton Oil, Expeller.............	2.30	6.58	6.69	10.30
Cotton Oil, Expeller.............	1.70	3.56	3.80	......
Soybean Oil, XT, Non DeG...	0.70	4.18	4.31	5.52
Soybean Oil, XT, Non DeG...	0.80	2.54	2.56	5.00
Soybean Oil, XT, Non DeG...	0.52	2.58	2.73	5.00
Soybean Oil, XT, DeG..........	0.28	0.69	0.44	1.86
Linseed Oil, Raw..................	1.30	2.24	2.22	......

Bleach and Color Methods

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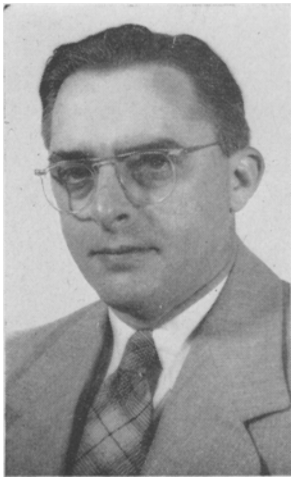
COLOR AND BLEACH METHODS are those used to determine the amount of color in an oil, how easy it is and how much it costs to remove that color, and how much color remains in the oil after bleaching. Why do we wish to know these things? Most of the oils with which we are concerned go into edible shortenings, margarine, winter oil, etc. Consumer studies reveal that the customer likes light fat for edible purposes, and the wise producer gives the customer what she wants. Hence most oils must be bleached to a very light color for use in edible products.


R. C. Stillman

In general, crude oils are sold on the basis of refining loss, refined or bleached oil colors, and flavor. The rules for trading are set up by the National Cottonseed Producers Association and the National Soybean Processors Association. These two oil trading associations accept the methods of the American Oil Chemists' Society as the basis for trading. Hence the methods of the Society must be right and must be up to date.

Most oils are yellowish-red or amber liquids. The color is due to the presence of carotenoid pigments and/or chlorophyll pigments, the latter imparting a greenish cast to the oil. The better the type of seed processed in the making of the oil, the better the color of the resultant oil. Soybeans or cottonseeds which have been left in the field after maturity or which have been heat-damaged in storage will give very dark red oils while frost damaged or immature seed will give greenish oils. The best oils are light in color, low in free fatty acid, and of excellent flavor. Such oils demand and get premium prices.

Color is hard to define and hard to measure. Few people will agree on how the color should be measured or how it should affect the price placed on a particular oil. The fact that the price of crude oils is so closely tied to its color has tended to restrict changes in the color reading methods. Hence today trading is based chiefly on Lovibond red values which, as we shall see later, are inadequate for the purpose. The Wesson method using Lovibond glasses is an abbreviated version of a method originally developed in England for measuring the color of beer. This shortened procedure has been used with questionable success for many years. It is still the official procedure of both the N.S.P.A. and N.C.P.A.

Bleaching and color reading are important laboratory methods for the control of oil processing. These laboratory methods are utilized in the trading of oils, the evaluation of bleaching earths, and the selection of earths to be used for specific purposes. The American Oil Chemists' Society has had committees working on these methods for many years. At the present time the joint effort of the Bleaching and Color Committees is aimed at an adequate solution of the color situation, which is still in an uneasy state. A whole new series of problems have arisen in the past year with the advent of color shortenings, colored synthetic granules, and other color products. These problems will open up new fields for committee study and for industrial laboratory investigations. As a direct consequence the present Color Committee is extending its work to include methods of measuring surface colors. It is with the problems of bleaching and color reading of oils only that we shall concern ourselves today.

Bleaching Methods

There are two methods of bleaching oils in general use: chemical methods and adsorption methods. Both of these methods are designed to reduce the total amount of coloring material in an oil or to remove undesirable pigments, depending upon the end-product of the process. The first method while used in