from 12 to 45%, depending largely on the amount of liquid used to rehydrate. The ratio of neutral oil to fatty acids varies from about 1:4 to 1:12, with some of the common ones around 1:6. In view of the absence of loss due to saponification of neutral oil, the avoidable loss is virtually the free oil in the soapstock, plus the small losses incurred in the caustic wash and water wash steps.

Where the per cent of total fatty acids in the soapstock is low, acidulation becomes a preferred procedure in disposing of the soapstock. The excess soda ash in the soapstock consumes additional sulphuric acid, but the value of the acid is but a fraction of the increased value of the neutral oil saved. Acidulation proceeds readily when proper care is taken to add the acid slowly in increments, allowing it to decompose the excess sodium carbonate and permitting the evolution of carbon dioxide to be complete before adding more acid.

Performance

The new Clayton process has given consistent, uniform low refining losses close to the Wesson Loss. The closeness of approach to the Wesson Loss is primarily roughly proportional to the amount of gums in the crude and to the color of the crude. With low-gum, light colored crudes we have come within several tenths of one per cent of the Wesson Loss. With high-gum crudes the difference between the Clayton Refining loss and the Wesson Loss is higher. Crude cottonseed oil from the Valley, characterized by low cup losses, low free fatty acids, but high ratio of gums to F.F.A., have responded particularly well to the treatment of the new process. Crude corn oil has been refined to give low refining loss. In one instance recently, a low-gum, dry-milled, crude corn oil, refined through a new process unit, gave a loss of 2.5% as against a Wesson Loss of 2.34% of which 1.1% was gums. The cup loss of the crude was 4.9%. Peanut oil, tallow and other oils have been processed through a new process unit with encouraging results. Peanut oil, in particular, has yielded losses very close to the theoretical.

The efficiency of the process is illustrated in the table below in which the results of the refining of several different crude oils are given. The plant losses were determined from the weights of crude oil pumped into the system and the washed dried refined oil recovered. From 1 to 4 tank cars of crude oil were used in each instance.

TABLE I

Performance of the Clayton Soda Ash Oil Refining Process

Crude oil	F.F.A.	Wesson loss	Plant loss Clayton soda ash process	Official cup loss
Crude Cottonseed Oil—Mississippi Valley	0.6%	2.33%	2.72%	4.25%
Crude Cottonseed Oil—				
Southeastern	1.1%	3.17%	3.58%	6.45%
Southeastern	1.8%	3.80%	4.41%	7.35%
Crude Corn Oil—dry milled	1.24%	2.34%	2.5%	4.9%
Crude Peanut Oil	0.7%	1.80%	2.17%	4.75%

The soda ash soapstock discharged from the primary centrifuge possesses unique properties. The oil-soluble nature of some of the gums becomes manifest when the "free oil" is determined in the accepted manner of extracting a dispersion of the soapstock in 50% aqueous alcohol with petroleum ether. A considerable portion of the gums goes into the petroleum ether layer. A simple method of extracting oil, relatively free from gums, was devised. The soapstock was first dried in an oven at 100°C. The dried residue was then extracted with acetone. The extracts, filtered, were collected in a weighed flask and the solvent evaporated. The solvent-free residue was an oil. When the soapstock, dispersed in 50% aqueous alcohol, was extracted with petroleum ether, the extract, rid of the solvent, was a semi-solid mass.

I do not wish to give the impression that the new process gives theoretical, absolute losses, but what I do want to stress is that the performance is so good that the existing standards become obsolete, and some more exacting standard such as the Wesson Loss is within reach.

BIBLIOGRAPHY

1. U. S. Pat. 2,190,593; 2,190,594, and others.
2. U. S. Pat. 2,000,274, and others.
3. "Le Raffinge des Corps Gras," p. 60, G. Porchez-Dunod, Paris, 1938.
4. "Vegetable Fats and Oils," G. S. Jamieson; pp. 400-02, Chemical Catalogue Co., New York, 1932.

The Determination of Small Amounts of Free Sulphur in Bleaching Earth

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Sulphur is one of the impurities found in bleaching earths which are used in treating edible oils. In bleaching earth this element exists in the combined and free states. The combined sulphur usually exists as a complex iron sulphide, a sulphate, and sometimes, although rather infrequently, as free sulphuric acid.

This paper is primarily concerned with the detection and determination of free sulphur in bleaching earths since it is in this form that sulphur easily unites with cottonseed, corn, soya bean oils, and the like, especially at the temperatures normally used in bleaching operations. Since the bleaching operation is carried out after the refining operation, any sulphur that finds its way into the refined oil usually remains in it during storage.

When an oil containing sulphur is hydrogenated the sulphur interferes with the activity and selectivity of the catalyst, causing longer hydrogen absorption time which in turn lowers plant output and also requires the use of more catalyst. As a result hydrogenation costs are increased. Since the amount of free sulphur in a bleaching earth is quite small, being well under 0.05 per cent, it often escapes notice. We propose a test that can detect between 0.001 to 0.0005 per cent free sulphur in a bleaching earth.

There are several methods used to determine free sulphur. One of these is the use of acetone to extract the free sulphur, oxidation with bromine water and finally estimation as barium sulphate. If there is no combined sulphur present, the free sulphur can be determined by alkaline oxidation fusion followed by precipitation from acid solution and weighing as barium sulphate. However, since it is unusual to find a bleaching earth that does not contain some combined sulphur this method is only of limited application. A serious difficulty in the determination of free sulphur in a bleaching earth is the presence of varying amounts of iron and large amounts of silica which makes it difficult to precipitate pure barium sulphate.

Another method is that proposed by Bolotnikov and Gurova (1). This method consists in boiling the sample under examination, in a sodium sulphite solution which unites with any free sulphur present to form sodium thiosulphate. Then under specific conditions the sodium thiosulphate that is formed is titrated with iodine solution. A blank is run at the same time. From the figures obtained the free sulphur is calculated (1 c.c. of tenth normal iodine solution corresponds to 0.003206 gms. of free sulphur). This method gives good results but introduces the problems of thoroughly washing and filtering the earth, and strict adherence to the procedure and besides, it is time-consuming. A test for free sulphur that would be more rapid and accurate between 0.01 to 0.001 per cent or better would be highly desirable.

Thornton and Latta (12) proposed a modification of the Halphen test for the detection and determination of free sulphur in petroleum distillates. However, with the use of carbon bisulphide as a solvent the free sulphur in a bleaching earth can be extracted and in turn can then be determined by using the Halphen reagents.

Some forty years ago Halphen (2) proposed the use of a solution of sulphur in carbon bisulphide and amyl alcohol which when added to a sample of oil would turn red upon heating if cottonseed oil were present. We propose to use a modification of this test in which all of the ingredients, except the sulphur, are combined and then under known conditions to test for the free sulphur. Before doing this it will be in order to review briefly the history of the Halphen test bearing in mind that we are primarily interested in the determination of free sulphur.

Shortly after Halphen's test was published considerable work was done by various investigators to show that reagents other than amyl alcohol or carbon bisulphide would give the red color of the Halphen test. One of these reports was that by Rosenthaler (3) who stated that amyl alcohol was not necessary for the Halphen reaction but that several other alcohols, ketones, glycerine, etc., could be substituted if the heating was carried out in a sealed glass tube.

Utz (4) claimed that the use of pentachlorethane as a solvent for sulphur was as satisfactory as carbon bisulphide. Little mention was made of the kind of color obtained by these investigators. Gastaldi, in a series of papers (5, 6, 7, 8), refuted the claims of Rosenthaler, Utz and others by proving that one of the impurities in amyl alcohol, namely pyridine, was responsible for the characteristic wine-red color of the Halphen test. If the carbon bisulphide is left out, an orange-red coloration is obtained. This is not the characteristic wine-red color of the Halphen test and has caused no end of differences of opinion in reporting positive Halphen tests by different investigators. Attempts to substitute organic sulphides for the sulphur or carbon bisulphide in the Halphen tests were not successful (3).

Gastaldi recommended the following procedure for the Halphen test:

> Five c.c. of oil are mixed with 4 c.c. of a 1 per cent solution of sulphur in carbon bisulphide and one drop of pyridine and heated in a boiling water bath for one-half hour. The sensitivity of the test was given as one-fourth of 1 per cent cottonseed oil.

Other oils such as kapoc and baobob also give a positive Halphen reaction (9, 10). Kapoc oil has been shown to be ten times more sensitive to the Halphen reaction than cottonseed oil (11). According to Gastaldi pure amyl alcohol will not give a positive Halphen reaction (5). The use of one or two drops of pyridine, as he proposed, instead of amyl alcohol, allows the use of the temperature of boiling water which is more easily maintained than a brine bath, and is much cleaner. It has been our experience that more consistent results are obtained with pyridine than with amyl alcohol.

Since the Halphen test requires the use of sulphur, carbon bisulphide, pyridine, and cottonseed (kapoc or baobob) oil, under controlled conditions a mixture of carbon bisulphide, pyridine, and cottonseed oil can be used to detect sulphur, using the wine-red coloration produced upon heating as a means of comparison against solutions containing known amounts of sulphur that have been tested in the same manner. A blank is used to check the purity of the reagents.

The method we propose for the determination of free sulphur is as follows:

> Twenty-five gms. of bleaching earth are extracted with 50 c.c. of carbon bisulphide for one hour using a Smalley or Butt extraction tube, a paper extraction thimble and a reflux condenser. Rubber stoppers must not be used. A rapid reflux is maintained during extraction. Care must be exercised to prevent the earth from getting into the extract for if this occurs the color that is developed later in the test is adsorbed by the earth.
>
> After extraction, the carbon bisulphide extract is transferred to a long Pyrex test tube (25 x 300 m.m.) and carefully evaporated to approximately 2 c.c. Since carbon bisulphide is extremely inflammable, due precaution should be observed.
>
> Ten c.c. of cottonseed oil and 2 drops of pyridine are added, mixed by swirling the tube and placing in a steam bath containing cold water. It is heated slowly to boiling so as to avoid bumping and then boiled for exactly one hour.
>
> If no wine-red color develops, free sulphur is absent. If a wine-red color develops, the solution is diluted to 50 c.c. in a Nessler tube with carbon tetrachloride. The color developed is then compared against the color of solutions containing known amounts of free sulphur that have been treated in the same manner.
>
> It is desirable to match the color of the unknown against the color actually developed in the

control sample rather than by diluting the color of the unknown to match the color of the control sample.

The preparation of tubes containing the color developed by known amounts of free sulphur in cottonseed oil (control samples) is relatively simple and can be carried out along with the sample being tested. Usually this is done by dissolving a known amount of sulphur in cottonseed oil to approximately the free sulphur concentration in the earth, using 10 c.c. of this solution, adding 2 c.c. carbon bisulphide and 2 drops of pyridine in the 25 x 300 m.m. tube and heating in the water bath.

After heating, the solutions are made up to 50 c.c. in Nessler tubes with carbon tetrachloride for the color comparison. A blank is run on the reagents using the same procedure as on the sample under test but eliminating the earth. Since the color developed in this test is affected by light and heat it is advisable to make up known color standards at the time the sample is being tested and also to avoid exposure to sunlight. This test will detect 0.001 to 0.0005 per cent free sulphur in a bleaching earth. A similar procedure may be used in determining the amount of free sulphur in bleaching carbons.

In carrying out this test it is necessary to prevent loss of material during evaporation or boiling. Should a tube ignite during the manipulation the test must be rejected because carbon bisulphide forms sulphur on ignition in the air. The extracted earth or carbon containing carbon bisulphide can spontaneously ignite in coming in contact with the air. Due care should be exercised in the disposal of these residues. It is not advisable to boil for over one hour in the steam bath. Prolonged heating has a tendency to break down the carbon bisulphide and give positive tests.

TABLE I

Some Typical Results Obtained on the Free Sulphur Content of Several Bleaching Earths and Carbons

Description	Coloration
1. Control sample	Straw
2. Standard containing 5 parts per million of free sulphur	Slight wine-red
3. Standard containing 10 parts per million of free sulphur	Wine-red
4. Standard containing 20 parts per million of free sulphur	Increasing in intensity to a strong wine-red color.
5. Standard containing 50 parts per million of free sulphur	
6. Standard containing 80 parts per million of free sulphur	
7. Standard containing 100 parts per million of free sulphur	
8. A.O.C.S. standard bleaching earth (Official Fullers Earth 1940-41)	Straw (less than 5 parts per million of free sulphur)
9. Domestic bleaching earth "A"	Straw (less than 5 parts per million of free sulphur)
10. Domestic bleaching earth "B"	Very strong wine—red (200 parts per million of free sulphur)
11. Domestic bleaching carbon "A"	Straw (less than 5 parts per million of free sulphur)
12. Domestic bleaching carbon "B"	Very strong wine—red (400 parts per million of free sulphur)

BIBLIOGRAPHY

1. V. Bolotnikov and V. Gurova. Journal of the Rubber Industry of the U.S.S.R., *10*, 61-2 (1933). (Chem. Abs. 28: 4934). Also J. Applied Chem. U. S. S. R., *7*, 409-14 (1934), (Chem. Abs. 29: 2026).

2. Halphen. J. Pharm. Chim., *6* (9), 390 (1897), (Allen's Commercial Organic Analysis, Vol. *2*, 177, 1924).

3. L. Rosenthaler. Z. Nahr. genussm., *20*, 453-4 (1911), (Chem. Abs. 5: 388).

4. Utz. Munich Chem. Rev. Fett-Harz Ind., *20*, 291-5 (1913), (Chem. Abs. 8: 587).

5. R. Gastaldi. Chem. Ztg. *35*, 688 (1912), (Chem. Abs. 6: 3135).

6. E. Gastaldi. Bologna. Giorn. farm. chim., *61*, 289-97 (1912), (Chem. Abs. 6: 3474).

7. R. Gastaldi. Seifen Ztg. *40*, 747 (1913), (Chem. Abs. 7: 3245).

8. E. Gastaldi. Torino. Ann. chim. applicata., *2*, 203-7 (1914), (Chem. Abs. 9: 389).

9. M. Millian. Matieres Grasses, *2*, 1545 (1909), (Chem. Abs. 4: 969).

10. T. Millian. Bol. chim. farm., *51*, 187 (1912), (Chem. Abs. 6: 2858).

11. H. P. Trevithick and W. H. Dickhart. Oil and Fat Industries, *8*, 305 and 317 (1931).

12. M. K. Thornton, Jr. and J. E. Latta. Ind. Eng. Chem. Anal. Ed., Oct. 15, 1932, 441.

Report of the Cooperative Work of the International Fat Commission, 1938-1939—Part II*

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SOAP ANALYSIS

(Part B of the work program)

I. Determination of Rosin Acids

The method of the *French Delegation* whose procedure follows was to be tested:

Necessary reagents: 98-99% methyl alcohol, containing about 10 g. per 1000 cc. of sulfuric acid of 66° Be′.

$\frac{N}{5}$ alcoholic potash.

Procedure: For the investigation about 2 g. (designated as "p") of fatty acid, containing rosin acids is accurately weighed into a 150 cc. ground joint flask. Exactly 20 cc. of the methyl alcohol solution of sulfuric acid is added and the solution refluxed for about 30 minutes. The solution is allowed to cool and the free acid titrated with standard $\frac{N}{5}$ alcoholic potash in the presence of phenolphthalein. Let "N" be the volume of potash used. As a blank, also accurately determined, exactly 20 cc. of the methyl alcohol solution of sulfuric acid is heated as in the test.

Let "N′" be the volume of potash used in the blank. The per cent of rosin is given by:

$$\frac{(N - N') \times 6.6}{p} - 1.6$$

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* This is the second section of this report, the first part of which was published in OIL & SOAP, February, 1942. In Part II, the names of the investigators and their comments have been omitted, except for the remarks on the Determination of Free Alkali, as adding little or no value to the article.