QUANTITATIVE DETERMINATION OF THE "BREAK" (AND "FOOTS") IN LINSEED OIL*

By GEORGE S. JAMIESON and WALTER F. BAUGHMAN

It is believed that one indication of the quality of linseed oil is the quantity of the break—the so-called mucilaginous materials dissolved by the oil during the crushing process—and the quantity of the sediment, which is termed foots. As is well known, linseed oil gradually deposits foots during storage. These foots are a portion of the break which has precipitated. Some of the higher melting glycerides may also separate from the oil with the foots. Much thought and time have been spent by investigators in attempting to develop a satisfactory procedure for the quantitative determination of the break and foots in linseed oil.[1]

The method designated as D-51-18T[2] is still being studied by Sub-Committee V. on Linseed oil A. S. T. M. This method consists in shaking 25 cc. of linseed oil with 25 cc. of acetone and 10 cc. of an acidified saturated calcium chloride solution. The mixture is allowed to stand in a burette for 24 hours, and the volume of the precipitated break and foots (if present) is then read. The method to be described has an advantage in that it is a gravimetric procedure which can be completed in about 6 hours. Gravimetric results cannot be compared with those obtained by the D-51-18T volumetric method.

The procedure employed in the present investigation is based upon the Wesson method[3] for the determination of the total quantity of neutral glycerides in crude oils. After some practice, if close attention is paid to following the directions, this method is capable of yielding reasonably accurate results. The method is as follows:

The Method

Weigh accurately 10 grams of the sample in a 50 cc. flask and transfer with the aid of petroleum ether to a 500 cc. pear-shaped separatory funnel, using in all 50 cc. of low boiling petroleum ether (B. P. less than 80° C.). Have the stopcock of the separatory funnel lubricated with water. Agitate the oil and petroleum ether until a homogeneous solution is formed. Add 10 cc. of a 14 per cent potassium hydroxide solution, insert the stopper, and shake vigorously for 3 minutes. Then add 25 cc. of 50 per cent alcohol and shake for 15 or 20 seconds. Allow to stand until the mixture separates into 2 layers. If the alcohol-alkali solution is allowed to remain

* Presented before the Paint and Varnish Section, A. C. S., at the Philadelphia meeting, September, 1926.

[1] Glenn H. Pickard, J. Oil and Fat Ind., **2**, 60 (1925).

[2] Proc. Amer. Soc. Test. Mat. **20**, 678 (1920).

[3] G. S. Jamieson & W. F. Baughman, The Cotton Oil Press, **6**, (No. 4) 33 (1922).

in contact with the petroleum ether solution too long there is danger of saponifying some of the neutral oil. A contact of one-half hour will not cause a perceptible error and this time is more than ample to effect a good separation of the layers. Draw off the lower layer and the precipitate into a 200 cc. separatory funnel, and rinse the inside of the outlet tube of the 500 cc. separatory funnel with a little petroleum ether. Add 20 cc. of petroleum ether to the contents of the 200 cc. separatory funnel, shake, and allow the layers to separate. Draw off the lower layer and the precipitate into a 250 cc. beaker. Rinse the outlet tube of the separatory funnel with petroleum ether into the beaker. Add the upper layer to the main petrolum ether solution in the large separatory funnel. Pour the alcohol-alkali solution back into the 200 cc. separatory funnel and extract with another 20 cc. portion of petroleum ether. Repeat this treatment a third time to insure the complete recovery of neutral oil. Save the alcohol-alkali solution for the determination of the fatty acids. Wash the petroleum ether solution of the oil three times with 15 cc. portions of 50 per cent alcohol and add the washings to the alcohol-alkali solution in the 250 cc. beaker. Transfer the solution of the oil to a weighed 300 cc. Erlenmeyer flask and rinse the separatory funnel with several small portions of petroleum ether. Distill off as much as possible of the solvent by placing the flask in a water bath. Heat the flask in an oven at 120° or 125°, using an atmosphere of carbon dioxide to prevent oxidation of the oil, until a constant weight is obtained. In most cases 2 hours' heating is sufficient. Calculate the percentage of neutral oil.

Place the beaker containing the alcohol-alkali solution on the steam bath and evaporate the alcohol. Then add about 75 cc. of water and, when the soap is dissolved, acidify the solution with hydrochloric acid. Cover the beaker and heat on the steam bath until the fatty acids have collected on top of the solution. Cool until the fatty acids become solid, filter, and wash with water until the fatty acids are free from chlorides. Place the funnel containing the filter paper with the fatty acids in the 250 cc. beaker and heat on the steam bath until beaker and filter are dry. Dissolve the fatty acids with small portions of petroleum ether. If the solution of the fatty acids is turbid, refilter it through the original filter. Collect the filtrate and washings in a weighed 200 cc. Erlenmeyer flask. Remove the solvent as described for the determination of neutral oil, and weigh. Calculate the percentage of fatty acids. To obtain the per cent of break or break and foots, subtract the percentages of neutral oil and fatty acids from 100.

The results obtained are given in Table I on the page following:

Table 1

ANALYSES OF RAW LINSEED OILS

Sample	Neutral Oil %	Fatty Acids %	Break %	Acid Value of Oil	Acidity as Oleic Acid %	Iodine Number (Hanus)
A. S. T. M. No. 60* ..	98.32	1.26	0.42	2.23	1.12	179.5
" " " ..	98.35	1.22	0.43			
A. S. T. M. No. 61* ..	98.49	1.23	0.28	2.23	1.12	184.8
" " " ..	98.45	1.30	0.25			
A. S. T. M. No. 62* ..	97.92	1.43	0.65	2.28	1.14	190.5
" " " ..	97.93	1.45	0.62			
" " " ..	97.95	1.38	0.67			
No. 1 (1924)	98.36	1.15	0.49	1.89	0.95	178.5
"	98.38	1.19	0.43			
"	98.39	1.20	0.41			
No. 2	98.77	0.98	0.25	1.67	0.84	188.9
"	98.69	0.98	0.33			
No. 3	98.54	1.19	0.27	2.17	1.09	181.3
No. 4	98.97	0.77	0.26	1.26	.63	186.3
"	98.96	0.75	0.29			
No. 5	98.18	1.38	0.44	2.35	1.18	184.0
"	98.16	1.37	0.47			

* Figures given under "Break" include also the foots. Each sample was thoroughly mixed before analysis. These oils were kindly furnished by R. D. Bonney, Chairman of A. S. T. M. Sub-Committee V on Linseed Oil.

Oils 1, 2 and 3 were hot pressed and oils 4 and 5 were cold pressed.
Oils 1 and 2 were expressed from Argentine seed while 3, 4 and 5 were obtained from American seed.

Occasionally, after the withdrawal of the alcohol-alkali solution, a small quantity of a finely-divided precipitate gradually separates from the petroleum ether solution of the neutral oil. During the washing with 50 per cent alcohol, this precipitate settles between the layers and it is usually safer not to withdraw it with the wash solution as there is danger of losing some neutral oil. In the few cases observed it has been found possible to decant the petroleum ether from this slight precipitate. However, if necessary, the precipitate should be removed by filtration. Then the greatest care must be taken to recover all of the neutral oil from the filter with petroleum ether.

From the results given, it will be observed that there is apparently no relation between the quantity of break in an oil and its iodine value. The one sample with the highest iodine number also contains more of the break than any of the other samples given in the table.

It is hoped that this method will be given a thorough test by those interested in the quantitative determination of break or foots in linseed oil.

OIL, FAT AND WAX LABORATORY
Bureau of Chemistry
U. S. Dept. of Agriculture,
Washington, D. C.