the oil is unadulterated, the recalculated Hübl figure should be within the limits of variation of pure fresh samples.

This method cannot be relied upon for oils containing the more highly unsaturated acids (drying oils, fish oils, etc.), since in such oils there is, as shown by analysis, either a direct absorption of oxygen as such or a condensation with elimination of water from the hydroxyl groups first added, probably accompanied by a slight contraction in volume.

As regards the examination of edible oils, however, the results here given may be said (1) to emphasize the importance of determining both the Hübl figure and the specific gravity, whatever other determinations are made, and (2) to show how the mutual relations of these constants enable one to interpret the results obtained upon samples greatly altered by exposure to atmospheric oxidation.

NEW YORK CITY,
May 1, 1903.

COMPOSITION OF THE "BREAK" FROM LINSEED OIL.[1]

BY GUSTAVE W. THOMPSON.

Received May 15, 1903.

FRESHLY pressed linseed oil, or linseed oil that has not been properly settled or prepared for the manufacture of varnish, when heated to, say, 400° Fahrenheit, undergoes a change which the varnish man describes as "breaking". The phenomenon consists in the appearance in the oil of gelatinous masses slightly darker than the oil itself, settling with difficulty and extremely difficult to remove from the oil by filtration. The bulk of the break appears in some instances to be very considerable. The following experiments, however, will show that the percentage, by weight, present is very small.

Twenty-five hundred grams of linseed oil were heated to the breaking-point. The oil was allowed to cool and then filtered. The precipitate clogged the filter considerably, which necessitated its removal to a glass vessel, in which it was washed with petroleum ether, by decantation. Finally, a non-oleaginous residue was obtained, weighing 6.93 grams, equal to 0.277 per cent. of the original oil. On ignition, a portion of this residue was shown to

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[1] Read before the New York Section of the American Chemical Society, May 8, 1903.

contain 47.79 per cent. ash—equal to 0.1177 per cent. of the original oil. The oil, which was filtered from the break, was shown to contain 0.0039 per cent. ash. The following is an analysis of the ash from the break:

CaO	20.96
MgO	18.54
P_2O_5	59.85
SO_3	trace
	99.35

The first thing to note is that the phosphoric anhydride is present in the ash from the break in excess of what would form an orthophosphate when combined with the bases present. It appears, in fact, that the oxygen present in the phosphoric anhydride is to the oxygen in the bases in the ratio of 5 to 2, corresponding closely with that required by a pyrophosphate. The composition of the organic matter in this sample of break was not determined.

Ash determinations were made on a number of samples of oil, the following being a few of the results:

	Ash. Per cent.
No. 1, Fresh double-filtered raw American linseed oil	0.1429
No. 2, " " " " " " "	0.1967
No. 3, Good, well-settled " " "	0.0609
No. 4, Best American linseed varnish oil	trace

The ash from sample No. 1 was analyzed, with the following results:

	Per cent. of the oil.
CaO	0.0235
MgO	0.0221
P_2O_5	0.0705
K_2O	0.0043
SO_3	0.0227
	0.1431

It should be noted that here, also, the phosphoric acid, is in excess of the bases, and is present largely in the pyro form.

Mulder speaks of the presence of calcium sulphate in linseed oil, but, so far as we know, no mention has been made of the presence of phosphates.

In order to locate the origin of the constituents of the linseed oil ash, analyses were made of the ash from American flaxseed, and flaxseed cake made therefrom, which analyses are given here:

	Flaxseed. Per cent.	Oil cake. Per cent.
Ash	3.112	4.899
Composition of ash.		
SiO_2	1.83	1.51
$Fe_2O_3 + Al_2O_3$	1.25	1.59
CaO	9.46	9.24
MgO	18.31	18.52
K_2O	26.18	26.14
Na_2O	1.71	3.59
SO_3	3.96	3.51
P_2O_5	35.44	36.28
	98.14	100.38

These analyses confirm, in the main, analyses already published. If we consider the ratio between the oxygen in the bases and the oxygen in the phosphoric anhydride in an orthophosphate to be as 3 is to 5 we find here that the bases are in excess. It is worthy of notice here that the phosphoric acid, lime and magnesia are dissolved, to some extent, by the oil, while the potash, which is the principal base, is taken up by the oil, only to a very slight extent.

In examining the mucilage from various plants, Schmidt and Kirchner, and Tollens[1] reported the presence of phosphates in the mucilage which they separated from the flaxseed: it seems probable that these phosphates in the seed are largely combined with the mucilage, and that the mucilage and the phosphates combined therewith are dissolved, to some extent, by the oil. This conclusion, however, requires confirmation. Examining a portion of thoroughly extracted break for mucilage, we obtained no reaction. The test made was to heat the break with dilute hydrochloric acid for a few seconds, filter and add alcohol. No precipitate was obtained. It may have been that the mucilage was decomposed at the temperature to which it was subjected. We have not been able, as yet, to pursue our inquiries further along this line.

As to the presence of albuminoids in linseed oil, our experiments have been as follows: The determination of nitrogen in a sample of linseed oil showed less than 0.01 per cent. The same sample of oil showed 0.04 per cent. of phosphorus. This would indicate that, relatively speaking, the phosphates present were considerably greater than the nitrogenous matter. An examination, for nitrogen, of a portion of extracted break indicated that some was present although the amount was less than 1 per cent. of the break. The phosphorus, on the other hand, amounted to 9.60 per

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[1] *Ann. Chem.* (Liebig). **51**, **175** and **215**.

cent. of the break. This, figured to P_2O_5, amounted to 57 per cent. of the ash in the break. It would seem unjustifiable to calculate the phosphorus present in the linseed oil to lecithin, on account of the large percentage of bases present. Inasmuch as albuminoids coagulate at a low temperature as compared with the breaking temperature of linseed oil, we feel that any assumption that albuminoids are present is unjustified. We do, however, feel justified in saying that the principal cause of the break in linseed oil is the phosphates of lime and magnesia present, although their presence in the oil may be due to a combination between them and some organic base or bases.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON A CLASS OF PSEUDOTHIOUREAS DESCRIBED AS NORMAL UREAS.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

Received April 22, 1903.

WHEN thioamides are treated with alkyl halides, compounds are formed having the alkyl group attached to sulphur. In the normal thioureas, for example, it is the sulphur and not the nitrogen that is the point of attack. When a radical is attached to sulphur then further alkylation may take place on the nitrogen.[1] At least this has been found to be true in all cases that have been thoroughly examined.

There are some thioureas, however, that have been represented as yielding nitrogen alkyl derivatives with halides. Wunderlich[2] found that sodium cyanamide unites with mustard oils in alcoholic solution, giving the sodium salts of alkylcyanthioureas RNHCSNHCN, and by treating these salts with alkyl halides the sodium was shown to be replaced by alkyls. The resulting dialkyl compounds were represented by the general formula RNH—CSNR'CN.

Later, Hecht[3] prepared a large number of these compounds. He represents them by the formula above, but he remarks that further work will be necessary to determine their structure and he states that this will be the subject of a later paper. Thirteen years

[1] Bertram : *Ber. d. chem. Ges.*, **25**, 48 (1892).

[2] *Ber. d. chem. Ges.*, **19**, 448 (1886).

[3] *Ber. d. chem. Ges.*, **23**, 1658 (1890).