The following table shows the calorific value of various California oils. The determinations were made in a Mahler bomb, with oxygen at 25 atmospheres pressure, in the usual manner.

CALORIFIC VALUE OF CALIFORNIA PETROLEUMS.

Number.	Specific gravity.	°Bé.	Calorific value. T. U. (calories.)	B. T. U.
103	0.9589	16.3	10,380	18,684
111	0.9760	13.5	10,190	18,342
112	0.9651	15.2	10,471	18,847.8
113	0.9518	17.5	10,350	18,630
115	0.9397	19.5	10,827	19,488.6
129	0.8861	28.6	10,800	19,440
134	0.9458	18.5	10,375	18,675
135	0.9628	15.6	10,317	18,570.6
...	0.9276	21.1	10,531	18,956
159	0.8515	34.4	11,192	20,145.6
145	0.9700	14.5	10,360	18,648
115	0.9397	19.3	10,725	19,305
156	0.9572	16.5	10,359	18,646.2
110	0.9760	13.5	10,263	18,473.4
157	0.9533	17.2	10,443	18,797.4
103	0.9589	18.0	10,380	18,684

Many more results of determinations might be given, but the foregoing serve to give an idea of some of the characteristics of California crude petroleum, and indicate the great diversity in physical properties. Chemically, they resemble each other much more closely, as will be shown in a subsequent paper.

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BERKELEY, CALIFORNIA, January 9, 1903.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 83].

THE INFLUENCE OF ATMOSPHERIC OXIDATION UPON THE COMPOSITION AND ANALYTICAL CONSTANTS OF FATTY OILS.

BY H. C. SHERMAN AND M. J. FALK.

Received May 6, 1903.

IT is well known that the so-called non-drying and semi-drying as well as the drying oils may absorb oxygen from the air at ordinary temperatures and that the analytical constants are more or less changed by such oxidation. This subject was studied by Ballantyne[1] who found that olive, rape, cottonseed, arachis and linseed oils after exposure to sunlight in uncorked bottles showed

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[1] *J. Soc. Chem. Ind.*, 10, 29 (1891).

lower iodine figures, higher specific gravities and higher temperature reactions with sulphuric acid. These changes took place without alteration of the volume of the oil and independently of the appearance of rancidity or free acid. In fact, there was no increase in acidity in olive, rape and arachis and only a very slight increase in the cottonseed and linseed oils.

Having found that such oxidation is less dependent upon sunlight and occurs more often in stored samples than is commonly supposed, we undertook a comparison of the changes produced in some of the constants to ascertain whether any quantitative relations could be traced which would enable one to judge the original nature of the oil from the results obtained upon a sample thus altered by exposure.

Samples of oils of about 200 grams each were allowed to stand for several months, with occasional shaking, in uncorked bottles, loosely covered to exclude dust, on a shelf in the laboratory which was frequently exposed to direct sunlight. No special effort was made to give the different samples the same amount of exposure and shaking since it seems impossible to control all the conditions which affect the rate of oxidation. These "exposed" samples were then compared with duplicate samples from the same packages which had been kept in well-filled, air-tight bottles or cans in a dark closet. Many of the oils had been analyzed when first received and in all such cases the agreement between the results first obtained and those found on the carefully protected samples was sufficiently close to show that no appreciable change had taken place in the latter.

The table which follows shows the changes which had taken place in the samples exposed to the air.

In each case there is a decrease in the Hübl figure (percentage of iodine absorbed) and an increase in specific gravity and temperature reaction with sulphuric acid. There is also, in each case, a slight increase in acidity and in the proportion of volatile acids present, but these changes are irregular and much too small to account for the changes in the other figures. These results show that the rise in temperature with sulphuric acid is not necessarily parallel with the Hübl figure and should not be used instead of the latter, but rather in connection with it. For instance, a sample of pure olive oil which had taken up oxygen from the air would, if judged by the high specific gravity and high temperature reaction.

be condemned as adulterated, whereas these results considered in connection with the low Hübl figure would at once indicate the true nature of the sample.

CHANGES PRODUCED IN ANALYTICAL "CONSTANTS" BY EXPOSURE TO LIGHT AND AIR.

Description of oil.	Specific gravity 15.5°/15.5°	Hübl figure.[1]	Temp. reaction.		Free acid as oleic.	Reichert-Meissl figure.
			Maumené.[2]	Mitchell.[3]		
Olive oil (2058) fresh	0.917	83.8	100	16.9	2.65	0.43
" " " after exposure	0.923	77.4	127	20.3	3.27	0.75
Lard oil (2057) fresh	0.917	73.3	106	16.7	0.90	0.56
" " " after exposure	0.927	66.7	116	18.4	1.92	1.59
Cottonseed oil (2053) fresh	0.920	102.8	161	21.4	0.14	0.16
" " " after exposure	0.934	92.0	215	27.0	1.27	1.96
Cottonseed oil (2055) fresh	0.923	105.2	171	20.3	0.07	...
" " " after exposure	0.937	92.9	217	27.2	1.29	...
Maize oil (2056) fresh	0.924	117.2	174	...	2.78	0.60
" " " after exposure	0.935	107.0	216	...	4.59	1.40
Poppyseed oil (2069) fresh	0.923	125.3	202	25.2	2.75	...
" " " after exposure	0.931	117.1	214	27.7	3.63	...
Seal oil (2103) fresh	0.926	145.3	...	...	0.69	1.00
" " " after exposure	0.947	120.3	...	...	3.39	2.40
Linseed oil (2070) fresh	0.938	177.1	...	30.5	1.26	...
" " " after exposure	0.954	148.1	...	34.3	2.05	...
Linseed oil (2052) fresh	0.934	178.0	...	31.3	1.33	0.49
" " " exposed 4 months	0.942	165.8	...	...	2.23	1.10
" " " " 8 "	0.966	139.4	...	32.8	4.45	2.64

In the case of the linseed oil (No. 2025), where the greatest amount of oxidation had taken place, it seemed desirable to determine the effect upon the elementary composition to find if possible whether oxygen or hydroxyl had been added. In addition to the unchanged oil and the portion which had been exposed in a bottle for eight months, another portion which had been exposed in a thin layer until semi-solid was analyzed. The results were as follows:

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[1] Determinations of the Hübl figure were carried out as previously described (this Journal, **23**, 168), using only the purest obtainable reagents and allowing always an excess of iodine about equal to the amount absorbed.

[2] Specific temperature reaction (referred to that of water as 100) on mixing 10 cc. of concentrated sulphuric acid with 50 grams of the sample.

[3] The figures in this column show the actual rise of temperature (in degrees centigrade) on mixing 10 cc. of concentrated sulphuric acid with a solution of 10 grams of the sample in 50 cc. of carbon tetrachloride.

	Carbon.	Hydrogen.	Oxygen.	Ratio C:H.
Linseed oil, unchanged	75.46	10.92	13.62	1:0.145
" exposed eight months	73.23	10.46	16.31	1:0.143
" " till semi-solid	69.03	10.06	20.91	1:0.146

In this case, therefore, the net result of the exposure was an increase in oxygen without any appreciable change in the ratio of carbon to hydrogen. This is practically in agreement with the experience of Bauer and Hazura in an experiment[1] in which a thin film of linseed oil was allowed to dry quite completely in the air.

It has already been shown[2] that atmospheric oxidation decreases the heat of combustion of fatty oils to an extent nearly proportional to, but slightly greater than, the increase in the specific gravity. This relation may now be explained somewhat more fully. The linseed oil (No. 2052) on exposure in bulk for eight months increased in specific gravity from 0.934 to 0.966 or 3.43 per cent., calculated on the original weight. The analyses show that it took up oxygen to the extent of 3.16 per cent. of its original weight. The greater increase in specific gravity is probably due to a slight contraction in volume. The original heat of combustion was 9364 calories per gram. Correcting for the increase in weight we have $9364 \div 1.0343 = 9053$ calories, but since the sample took up 3.16 per cent. of its weight of oxygen the "available hydrogen" must have been diminished by 0.395 per cent. of the original or 0.38 per cent. of the increased weight, requiring a further reduction of 131 calories. This gives an estimated heat of combustion for the exposed sample of 8922 calories per gram. Taking the increase in specific gravity as a direct measure of the oxygen absorbed, this calculated value would be 8910 calories. The value as determined by combustion in the bomb-calorimeter was 8899 calories per gram. These figures agree within the limits of experimental error and confirm the suggestion made in a previous paper that the heat of combustion taken in connection with the specific gravity may prove a useful factor in the study of the fatty oils.

With glycerides other than those having strong drying properties, it may be considered as practically established by the work of Hazura that the oxidation consists essentially in the addition of hydroxyl to the unsaturated fatty acids, oleic being converted into dioxystearic, and linolic into sativic acid. If, as stated by Ballan-

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[1] *Monatsh. Chem.*, **9**, 459 (1888).

[2] This Journal, **23**, 164; **24**, 348.

tyne,[1] the oxidation takes place without change in volume, the increase in specific gravity due to the introduction of hydroxyl should be directly proportional to the decrease in iodine-absorbing power due to the saturation of the double bonds. The quantitative relation would then be:

Percentage increase in specific gravity : Decrease in Hübl figure : : OH : I, or as 17.008 : 126.85, or as 1 : 7.46.

Thus the sample of olive oil shown in the table above had increased in density from 0.917 to 0.923 or 0.65 per cent. The Hübl figure of the exposed sample was 77.4. Adding to this 7.46 × 0.65 = 4.9, we obtain as a corrected value 83.3 as against 83.8, the Hübl figure of the unchanged sample.

Correcting, according to the same proportion, the Hübl figures of all the "exposed" oils in the table we obtain the "recalculated" values given in Column III.

	Hübl figure.		
Sample.	I. In fresh condition.	II. After exposure.	III. Recalculated.
Olive oil (2058)	83.8	77.4	83.3
Lard oil (2057)	73.3	66.7	74.8
Cottonseed oil (2053)	102.8	92.0	103.3
Cottonseed oil (2055)	105.2	92.9	104.2
Maize oil (2056)	117.2	107.0	115.9
Poppyseed oil (2069)	125.3	117.1	123.6
Seal oil (2103)	145.3	120.3	137.2
Linseed oil (2070)	177.1	148.1	161.0
Linseed oil (2052) after 4 months	178.0	165.8	172.2
" (2052) " 8 "	178.0	139.4	165.0

In the first five samples, representing non-drying and semi-drying oils, the difference between the original and the recalculated Hübl figure is in no case greater than 1.5, while the difference for the average of the five samples is only 0.2 per cent. Poppyseed oil which is usually classed as a drying oil, but which is also edible, shows a discrepancy of 1.7 per cent. It appears, then, that with such oils the results obtained on an exposed sample may be recalculated according to the proportion above given, if either the original specific gravity or the original Hübl figure is known.

When neither of these is known, assume as the original specific gravity the average figure for the variety of oil under examination, calculate the apparent increase in specific gravity (in percentage of the original) and then recalculate the Hübl figure as above. If

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[1] *Loc. cit.*

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.