

"BLOWN" OILS.

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THE published analytical data of any value in the chemical examination of "blown" oils are very few, and indeed extend only to two or three isolated facts. About six years ago Messrs. Fox and Baynes showed that the percentage of insoluble fatty acids in rape oil was reduced to 85.5 per cent., and those in cotton-seed oil to 84.7 per cent., when these oils were oxidised by blowing air through them, at a temperature of 70° to 75° C., until they reached a specific gravity near that of castor oil. Allen, in his second volume on "Commercial Organic Analysis," showed that the alkali-neutralising power of blown rape oil was considerably higher than that of the original unoxidised oils. Taken in conjunction with their high specific gravity, these are the main facts known, or at least published with regard to blown oils. In the following paper we have endeavoured to throw a little more light on the composition of these oils, in order that their detection and differentiation may be effected with somewhat more certainty than has been before possible. As our time has been limited we have confined our observations to blown rape, cotton-seed, and sperm oils; and the results of the experiments are embodied in the accompanying table.

The first three columns contain the results of experiments on rape oil at different stages of oxidation. After analysing the pure rape oil about 50 cc. of it were placed in a tall narrow glass provided with a cork, through which passed two glass tubes, one above the level of the liquid and the other reaching to the bottom of the glass. The latter had a few minute perforations at the lower end to allow the passage of air in a finely divided form through the oil. The shorter glass tube was now connected with a suction pump, by means of which a rapid stream of air was drawn through the oil. During the passage of the air the vessel containing the oil was immersed in a large beaker of water maintained at a temperature of 72° to 76°. After five hours treatment the product, as shown in the second column, had increased in specific gravity and alkali-neutralising power, and decreased markedly in iodine absorption. After "blowing" for 20 hours the specific gravity of the oil had risen from 914.1 to 961.5, which is about the average gravity of castor oil. It is interesting to observe that the free acidity had at the same time increased about 2 per cent., and the potash-neutralising power more than 2 per cent.; while the iodine absorption had fallen more than 37 per cent. This loss of power to

absorb iodine appears to be directly due to the absorption of oxygen during the "blowing" with air, and the further the oxidation is carried the lower will the iodine absorption become. The increase in free fatty acid points to the fact of decomposition of the oil, but that it is no true measure of the extent of decomposition will be seen by a reference to the partial analysis of the oil next given in the table. While the pure rape oil contained 94.76 per cent. of insoluble fatty acids, the "blown" product contained only 85.94 per cent. of insoluble acids, with an additional 9.2 per cent. of soluble non-volatile acids, and 0.82 of soluble volatile acids. These results were arrived at by saponifying the oil with alcoholic potash, evaporating off the alcohol, dissolving in water, and liberating the insoluble acids with sulphuric acid. These were collected, washed with hot water, dried, weighed in the usual way, dissolved in alcohol, and their molecular weight determined by titration with standard alcoholic potash, using phenolphthalein as indicator. The filtrate was then distilled to dryness, the distillate neutralised with standard barium hydrate, the solution evaporated to dryness, the barium salt weighed, then converted into barium sulphate, and from these data the molecular weight and proportion of the soluble volatile acids were calculated. The soluble non-volatile acids were extracted by ether from the dry residue left after distilling off the volatile acids, weighed after expelling the ether, and their molecular weight determined by standard alcoholic potash.

With these facts before us it is scarcely necessary to point out how they can be utilised in the detection and estimation of blown rape oil in other oils. With regard to the molecular weight of the insoluble acids it may be mentioned that Messrs. Fox and Baynes state it to be 186, while our result shows 327. The first figure seems to us to be quite inconsistent with the alkali-neutralising power of the oil as given by Allen, and determined by ourselves.

In the fourth column of the table are given the results of an analysis of a commercial sample of blown rape oil, which confirm those just described. This sample, however, contains a somewhat large proportion of unsaponifiable matter, probably derived from some fish oil adulterant in the original rape oil.

The fifth column of the table contains the results of an analysis of commercial blown cotton-seed oil, and a similar change in constitution is observable by blowing with air as in rape oil. It will be noticed, however, that the molecular weight of the soluble volatile acids contained in blown cotton-seed oil is much higher than that of the product from rape oil. The true means of distinguishing them is

TABLE SHOWING RESULTS OF ANALYSIS OF OILS.

	No. 1. Pure Rape Oil.	No. 2. Partially Blown Rape Oil prepared from No. 1.	No. 3. Blown Rape Oil prepared from No. 1.	No. 4. Blown Rape Oil, Commercial Sample.	No. 5. Blown Cotton-seed Oil, Commercial Sample.	No. 6. Pure Sperm Oil.	No. 7. Blown Sperm Oil prepared from No. 6.
Sp. gr. at 15.5° C. (water at 15.5° = 1000).....	914.1	927.5	961.5	967.2	971.0	879.0	898.0
Free (oleic) acid..... Per cent.	5.10	5.01	7.09	4.93	3.88	1.97	3.27
Unsaponifiable matter..... "	0.65	..	0.76	2.80	1.00	36.32	31.65
KOH neutralised..... "	17.39	18.30	19.40	19.77	21.32	13.04	14.23
Iodine absorption..... "	100.5	88.4	63.2	63.4	66.4	82.1	67.1
Specific temperature reaction.....	135	251	227
Insoluble acids..... Per cent.	94.76	..	85.94	82.40	84.97
Soluble non-volatile acids..... "	0.52	..	9.20	11.16	9.00
Soluble volatile acids..... "		..	0.82	1.90	1.94
Iodine absorption of insoluble acids.....	66.5	70.2	62.7
Molecular weight of " ".....	327	317	293
" " soluble non-volatile acids.....	241
" " soluble volatile acids.....	72	76	104

to be found in the large difference in alkali-neutralising power, as all the other data approach too close to each other to provide any means of determining which oil is being tested. In making these comparisons it is apparent that the oils must have reached the same state of oxidation before correct deductions can be made. Thus, a blown rape oil of a specific gravity of about 960 ought to be compared with a blown cotton-seed oil of about 968.

The only other point to which special reference may be made is the largely increased power of developing heat when mixed with sulphuric acid, possessed by the blown over the unblown rape and cotton-seed oils. This is expressed as the specific temperature reaction, for the definition of which term, and method of determination, see our paper in this Journal for 1891, page 233. The increase in specific temperature reaction by oxidation of oils exposed to air and light has already been shown by one of ourselves (see "The Effect of Exposure under certain Conditions upon some Constants of Oils," by H. Ballantyne, in this Journal for 1891, page 29).

In the sixth and seventh columns of the table are recorded results obtained in the analysis of pure sperm oil, and the same oil after treatment for 25 hours with air in the same apparatus as was used in blowing the rape oil. Of course blown sperm oil is not an article of commerce, but it occurred to us that it might be at least interesting to observe the effect of oxidation on an oil having a totally different chemical constitution to that of rape or cotton-seed oil. It will be observed that the increase in specific gravity is not nearly so great with sperm as with rape oil, for while 25 hours treatment raised the specific gravity of the sperm oil 19 units, a treatment extending only to 20 hours sufficed to raise the specific gravity of the rape oil 47.4 units. This plainly shows that rape oil is more easily oxidised than sperm oil, a fact which almost goes without saying when their comparative qualities as lubricants are taken into account. These observations are corroborated by the iodine absorptions, which were reduced 15 per cent. only in the case of sperm oil, and 37.3 per cent. in that of rape oil. Thus, although these oils differ so entirely as regards their source and chemical constitution, yet their specific gravity and power of absorbing iodine rises and falls in almost exactly the same ratio during oxidation by air-blowing. If we assume that the change is regular from one extreme to the other, the fact is established that a unit of rise in specific gravity is equal to a decrease of 0.787 per cent. of iodine absorption in the case of sperm, and of 0.789 in that of rape oil. Another noticeable fact is the increase in free fatty acids, in which sperm agrees with rape oil, and which may be regarded as an invariable accompaniment of the prolonged oxidation of oils. Lastly, there is a fall in the proportion of unsaponifiable matters to the extent of 1.67 per cent., a circumstance which is not at all surprising, as these alcohols may be in part oxidised to acids during the blowing, and thus be lost in the subsequent saponification.

DISCUSSION.

The CHAIRMAN said that Mr. Thomson had gone into the subject with quite his usual minuteness. The experiment on sperm oil seemed to him to be remarkable.

Dr. CLARK said that Mr. Thomson had referred to the fact that experiments with oil blown on the large scale differed from those made on oil blown in the laboratory. Would this not be due to the fact that on the large scale a higher temperature was maintained while blowing the oil?

Mr. PATTISON asked if Mr. Thomson noticed any increase in the weight, or if there was any product driven off during blowing.

Mr. THOMSON, in reply to Dr. Clark, said, the only difference referred to was the difference in the unsaponifiable matter. With regard to the increase in weight mentioned by Mr. Pattison, they had that point in mind, but had not had time to investigate it. There was no doubt that gases were given off during blowing.

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I.—GENERAL PLANT, APPARATUS, AND MACHINERY.

Iron Vessels for Molten Substances. Fahr. Chem. Zeit. 16, 503 and 532—533.

See under X., page 526.

PATENTS.

Improvements in the Process of and Apparatus for Evaporating or Drying. F. M. Robertson, London. Eng. Pat. 20,166, December 10, 1890.

THROUGH a horizontal cylindrical chamber, filled partly with the material to be dried, passes a shaft which carries a screw of about the same diameter as the vessel, which on rotating pushes the material towards the forward end. Openings near both ends of the chamber, on a level with its lowest point, are connected to large outside tubes which run parallel with it, and lead the materials back to the starting point, where they come again under the influence of the screw. A current of hot or cold air is maintained through the upper parts of the chamber, taking up the moisture from the materials and from the exposed surfaces of the screw.—B.

Improvements in Filters. R. W. Barker, London. From H. Goodacre, Lexington, U.S.A. Eng. Pat. 4817, March 12, 1891.

THE improved filter consists of an upright cylinder, with double walls packed with a non-conducting substance. It

* Any of these specifications may be obtained by post by remitting 8d.—the price now fixed for all specifications, postage included—to Sir Henry Rander Luck, Comptroller of the Patent Office, Southampton Buildings, Chancery Lane, London, W.C.