

ON OXIDIZED OILS.

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IN my last paper, read before this Society at a meeting, November 1, 1899,* I pointed out that the examination of the "oxidized acids" occurring in blown oils and solid linseed oil had been taken in hand by me.

This investigation has made very slow progress, and I should not have published the following incomplete results had not a paper appeared by Em. Lecocq and

* ANALYST, 1899, p. 319.

TABLE I.—*Blown Oils.*

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.
Acid Value.	Sap. Value.	II.-I.	Iodine Value.	Total Soluble Acids.	Specific Gravity.	Unsaponifiable.	Oxidized Acids.	Hehner Value.	Acetyl Value.	Ap- parent.	Sap. Value of Acetyl- ated Oil.	True Acetyl Value x 0.55.	Hehner Value after Acetyla- tion.	XII.- II.
Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per Cent.	Mgrms. KOH.		Per Cent.	Per Cent.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.			
Ravison rape...	10.47	198.31	187.84	72.66	0.9685	1.23	21.22	83.52	88.37	52.93	243.2	29.11	—	44.9
East India rape	13.25	215.57	202.32	61.92	0.9623	0.93	20.74	82.18	102.87	46.61	253.33	25.63	—	37.76
Cottonseed ...	9.41	224.59	215.18	65.74	0.9785	1.37	29.39	82.59	110.73	64.29	273.30	35.36	83.85	48.71
Solid linseed oil (linoleum mass)	*	287.47	—	52.2	—	1.33	53.01	53.92	—	—	367.75	—	—	—
Maize ...	7.33	208.63	201.30	90.7	0.9806	2.28	31.93	82.34	113.16	63.37	268.75	34.85	—	60.1

* Acid value was difficult to take. Experiments made by adding excess of alkalies and titrating back led to the impossible value 369.9 (?).

TABLE II.—*Total Fatty Acids.*

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
Acid Value.	Sap. Value.	II.-I.	Iodine Value.	Total Soluble Acids.	Hehner Value.	Acetyl Value.		Sap. Value of Acetyl-ated Acids.	IX.-II.	Hehner Value of the Acetyl-ated Acids.
						Ap- parent.	True.			
Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per Cent.	Mgrms. KOH.		Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.		Per Cent.
Blown Ravison rape oil	175.14	191.7	73.31	7.26	—	50.0	42.75	227.4	35.7	—
Blown East India rape oil	171.93	190.0	60.80	10.71	—	66.2	55.5	237.8	47.8	—
Blown cottonseed oil	194.79	210.46	72.43	12.94	93.76	67.35	55.67	254.8	44.4	92.11
Solid linseed oil (linoleum mass)	209.63	248.74	39.11	60.27	81.32	115.01	55.04	304.24	55.5	84.4
Blown maize oil	192.8	209.93	17.13	88.08	86.4	88.97	59.52	267.3	57.37	—

TABLE III.—Oxidized Acids.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
	Acid Value.	Sap. Value.	II.-I.	Iodine Value.	Total Soluble Acids.	Hehner Value.	Acetyl Value.	Sap. Value of Acetyl-ated Acids.	IX.-II.		True Acetyl Value \times 0.55.	Hehner Value of Acetyl-ated Acids.
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per Cent.	Mgrms. KOH.		Ap- parent.	Mgrms. KOH.	Mgrms. KOH.			
Blown Ravison rape oil	...	171.5	208.0	36.5	49.14	22.56	102.5	80.0	307.5	99.5	44.0	—
Blown East India rape oil	...	173.3	211.3	38.0	39.79	22.35	128.0	105.65	315.9	104.6	58.1	—
Blown cottonseed oil	...	174.7	220.71	46.01	48.6	36.12	154.4	118.28	322.69	101.98	55.02	83.85
Solid linseed oil (linoleum mass)	...	—	—	—	46.49	59.68	164.67	104.99	341.43	86.29	57.74	76.38
Blown maize oil	...	171.94	215.74	43.60	70.87	48.0	173.58	126.68	326.45	111.11	69.67	—

TABLE IV.—Fatty Acids freed from Oxidized Acids.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
	Acid Value.	Sap. Value.	II.-I.	Iodine Value.	Total Soluble Acids.	Hehner Value.	Soluble Acids.	Acetyl Value.	Sap. Value of Acetyl-ated Acids.	X.-II.	True Acetyl Value \times 0.55.	Hehner Value of Acetyl-ated Acids.	
	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	Per Cent.	Mgrms. KOH.	Per Cent.	Mgrms. KOH.	Ap- parent.	True.	Mgrms. KOH.	Mgrms. KOH.	Mgrms. KOH.	
Blown Ravison rape oil	...	176.8	188.6	11.8	61.88	6.97	6.75	42.5	35.53	220.3	31.7	19.54	—
Blown East India rape oil	...	166.6	176.8	10.2	55.93	10.09	8.85	47.13	37.54	219.2	42.95	20.64	—
Blown cottonseed oil	...	188.0	196.15	8.15	56.02	11.0	7.27	33.69	22.69	232.0	33.6	12.49	96.17
Solid linseed oil (linoleum mass)	...	179.97	187.58	7.61	61.31	18.89	—	50.25	31.36	246.11	58.53	17.24	96.05
Blown maize oil	...	172.37	177.68	5.31	85.52	6.14	7.54	43.8	36.7	228.76	50.52	20.18	—

H. Dandervoort (*Chem. Revue*, 1902, 13), which partly covers the same subject, although it refers to blown colza oil only.

The oils I chose for examination were: Commercial blown Ravison oil, commercial blown East India rape oil, commercial blown cottonseed oil, solid linseed oil (so-called "scrim" oil), and blown maize oil.

All the values that have been determined in these oils are set out in Table No. I., headed "Blown Oils" (see p. 140).

For the preparation of the oxidized acids, 100 grammes were saponified in the usual manner, the total fatty acids separated, and the separation of the oxidized acids from the other acids effected by means of petroleum ether.

The total fatty acids as well as their components—viz., the oxidized acids and the acids freed from oxidized acids—were examined, and the values so obtained are set out in Tables II., III., and IV. (see p. 141).

On acetylating the *original oils*, it was found that emulsions were formed in the washing-out process in the case of blown Ravison oil, rape, cottonseed oil, and maize oil. This has been pointed out already by Archbutt, but the separation caused little trouble. The blown Ravison oil formed the strongest emulsion; the scrim oil caused more trouble, the acetylated product separating as a sticky mass denser than water.

In contradistinction to the behaviour of the oils, the total fatty acids, which were also acetylated, did not give emulsions, as has also been pointed out by Archbutt.

Oxidized Acids.—The values obtained on examination are set out in Table No. III. The acetyl values were determined by the filtration method. As found before in the case of the oxidized acids from solid linseed oil, all the oxidized acids showed considerably higher saponification values than acid values. The surmise that these acids would be saturated acids is not borne out by experiment, for the iodine values are comparatively high. A difficulty arose in the determination of the iodine values, inasmuch as the oxidized acids were found to be practically insoluble in carbon tetrachloride, hence strong alcohol was used as a solvent. The error, if any, introduced thereby cannot have been a considerable one, for while a blank test with carbon tetrachloride required 50.6 c.c. of thiosulphate, the alcoholic solution took 50.00 c.c.

To obtain the true acetyl value the total soluble acids had to be determined. Naturally one would have expected to find no soluble acids, as they should all have been washed away or dissolved out in the treatment with petroleum spirit. However, considerable quantities were found in each case. The explanation suggested itself that these soluble acids were formed on treatment with the alcoholic potash by the action of the latter on the oxidized acids, for the soluble acids were determined after the original substance had been boiled with excess of alcoholic potash for the determination of the saponification value.

If this explanation be the true one, then a check experiment with the oxidized fatty acids as they were obtained originally should give no soluble acids on washing, but the actual experiment gave considerable amounts of soluble acids, in some cases almost approaching those obtained after treatment with alcoholic potash. This is shown in the following table:

SOLUBLE ACIDS IN OXIDIZED ACIDS.

Oil.				After boiling with Alcoholic KOH.	By washing with Water.
Blown	Ravison rape	22.56	21.38
„	East India rape	22.35	9.5
„	cottonseed I.	36.12	16.36
„	„ II.	26.30	21.39
Solid	linseed	59.68	24.11
Blown	maize	46.90	19.20

No such differences were observed in the cases of the total fatty acids and the fatty acids freed from oxidized acids, as will be seen from the following table :

SOLUBLE ACIDS IN

Oil.				TOTAL FATTY ACIDS.		FATTY ACIDS FREED FROM OXIDIZED ACIDS.	
				After boiling with Alcoholic KOH.	By washing with Water.	After boiling with Alcoholic KOH.	By washing with Water.
Blown	Ravison rape	7.26	7.09	6.97	6.75
„	East India rape	10.71	9.84	10.09	8.85
„	cottonseed	12.94	12.99	11.0	7.27
„	maize	29.4	24.8	6.08	7.54

Unfortunately, the soluble acids in the solidified linseed oil oxidized acids have not been determined, as it was taken for granted at the time that they were free from soluble acids, which now appears to be very doubtful.

The values obtained by multiplying the true acetyl values by 0.55 are again remarkably low, as they should have been, of course, 100 per cent. This proves that the molecular weight of 300 is not to be taken without further evidence.

The differences between the saponification and acid values point to the presence of lactones. Further investigation is in hand, but so far it appears pretty certain that the oxidized acids are not insoluble in water, and it is not unlikely that they split off volatile fatty acids when treated in a current of steam.

Acids freed from Oxidized Acids.—It was to be expected that these acids would have no acetyl value. If such a one were obtained, it would perhaps point to the presence of hydroxy-acids, which are soluble in petroleum ether. The considerable acetyl values found and set out in Table IV. may be due to oxidation having taken place after isolation, although free access of air had been guarded against. The acids still possessed considerable iodine values, and the differences between saponification and acid values again point to the presence of lactones, although their proportion can be only very small, not amounting to more than 4 to 6 per cent. Even these acids contain small amounts of soluble acid, as shown in the table.

Further examination must show whether, under the conditions I worked with, the oxidized acids are completely insoluble in petroleum ether, for small experiments

seem to show that the petroleum spirit solution of the fatty acids does dissolve some oxidized fatty acids.

The further examination of the oxidized acids is in hand, and experiments must show whether the preparation of their esters or of salts will give an insight into their nature.

As evidenced by the figures given in the table headed "Oxidized Acids," they must contain lactonic substances, since otherwise the differences between the acid and saponification values would not be explicable. If that difference be due to lactones, then it should be possible to separate them in the usual manner—viz., by neutralizing the acids with aqueous potash and extracting the solution with ether. The supposed lactones so obtained were very thick, viscous liquids, soluble in alcohol, with the exception of those lactones that were obtained from solidified linseed oil.

The saponification values of these lactones are given in the following table, Column I. The soap solution was decomposed by mineral acid, and the acid values of the recovered fatty matter determined. No lactone had been reformed, because on boiling with alcoholic potash no further amount of alkali was absorbed :

Lactones from :	Saponification Value. I.	Acid Value of Fatty Acids recovered from the Saponified Lactones. II.
Blown Ravison rape	117.8	125.3
„ East India rape	42.72	80.25
„ cottonseed	72.116	86.6
Solid linseed	35.51	57.44
Blown maize	101.1	106.9

The aqueous soap solution of the oxidized acids after the removal of the lactones was treated with mineral acid under ether, so that the separating fatty acids were immediately dissolved.

The following table shows that in the fatty matter so obtained some lactonic substances had been formed again, as evidenced by Columns I. and II.:

OXIDIZED ACIDS FREED FROM LACTONES.

	Acid Value. I.	Saponification Value. II.	Fatty Matter recovered from Soap Solution, obtained sub. II.		
			Acid Value. III.	Saponification Value. IV.	Difference. V.
Blown Ravison rape	172.2—175.6	220.6—221.5	184.8	223.7	38.9
„ East India rape	194.0—195.4	237.7—247.6	198.5	234.1	35.6
„ cottonseed	177.9—204.5	215.1—222.9	190.2	221.7	31.5
Solid linseed	190.8—194.5	255.5	212.9	249.8	37.9
Blown maize	182.2—284.3	216.0—217.7	185.8	218.8	33.0

The solutions were very dark, so that it was very difficult to titrate accurately, somewhat considerable differences between duplicate determinations.

The solutions containing the completely saponified mass were treated with mineral acid, and the fatty matter so recovered again examined for acid and saponification values, with the results set out in Columns III. and IV. of the last table. Allowing for the errors caused by the very dark solution, the numbers given under Columns III. and IV. may perhaps be looked upon as giving practically the same values as those stated in Columns I. and II., with the exception of solid linseed oil. The practically constant differences in Column V. are notable.

The process of re-extracting the lactonic substances, etc., was repeated once or twice, but lactonic substances were always formed again.

My thanks are due to Messrs. C. D. Robertshaw and George Warburton for the numerous analyses made in the preparation of this paper.

DISCUSSION.

Mr. JENKINS said that in dealing with blown cotton oil of about 0.975 specific gravity he had found that the fatty acids from such oil were distinctly more soluble in methylated ether than in petroleum spirit, which appeared to confirm the author's experience. It was a rather peculiar fact that the blowing of these oils decreased their miscibility with petroleum compounds. The blown oil could be mixed or blended only to a slight extent with American petroleum; it mixed, however, a little more freely with Scotch petroleum, and comparatively easily with Russian petroleum. Another peculiarity, probably due to the oxidized condition of the fatty acids, was that the sulphuric acid reaction increased out of proportion to the iodine value, whereas in the case of most oils a certain ratio existed between these two factors. The bromine thermal rise also did not bear a normal relationship to the iodine value; there was generally a low Hehner value and a low flash-point. The flash-point might be 100° lower than that of the original oil.

Mr. ALLEN said that although the author had stated that at present the exact bearing of all these figures could not be definitely laid down, nevertheless, the accumulation of data of this kind was extremely valuable, and would probably be followed by the removal of the difficulties which at present existed, and by a consequent better understanding of the chemistry of blown oils. These oils were of an extremely complex nature, and any method by which a proximate analysis of their constituents could be made was of great value.

Mr. HORATIO BALLANTYNE said that he was pleased to see that in their general aspect these figures accorded with the results obtained by Mr. R. T. Thomson and himself some ten years previously. One most interesting point was the very high percentage of soluble fatty acids which blown oils contained. In testing for the presence of blown oil in castor oils of doubtful purity, the percentage of soluble fatty acids—determined just as in the case of butter analysis—was probably the very best criterion by which to judge.

Dr. LEWKOWITSCH said that the miscibility of blown oils with petroleum distillates showed that, after all, in some sense the surmise was correct that these oxidized acids were hydroxy acids, because in that respect these oils approached castor oil, and, in fact, were known, when first brought into the market, as "soluble

castor oil." In regard to solubility, they evidently took an intermediate position between castor oil and the other fatty oils. That Russian petroleum behaved somewhat differently from American petroleum could only be due to a difference in composition. Whilst the American petroleum distillates consisted chiefly of hydrocarbons of the paraffin series, the hydrocarbons of Russian petroleum largely belonged to the naphthene series, and must therefore exhibit a different solubility. He was afraid that he had not a very favourable opinion of the usefulness of the Maumene test and the bromine thermal test. It seemed to him much better to determine the iodine value itself. The low flash-point of blown oil was due to the considerable amount of volatile acids. Of course, the acetyl value, which might be indicative of the presence of castor oil, would break down in these cases. No doubt the determination of the percentage of volatile acids was a very good test indeed. It was somewhat puzzling to find such a large amount of volatile or soluble fatty acids in a product which from its treatment would hardly be expected to contain any volatile fatty acids at all.
