

Journal of the Society of Chemical Industry.

No. 12, Vol. XXXIV.

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No. 12, Vol. XXXIV.

THE SOCIETY OF CHEMICAL INDUSTRY.

INCOME AND EXPENDITURE ACCOUNT FOR YEAR ENDING 31st DECEMBER, 1914.

EXPENDITURE.				INCOME.			
	£	s.	d.		£	s.	d.
To Journal—Editorial and Sundry expenses—				By Entrance Fees			164 17 0
Editor's Salary	542	16	0	" Life Composition Fees			37 10 0
Do. Expenses	32	11	3	" Annual Subscriptions			4852 15 0
Do. Assistant	156	0	0	" Journal Advertisements	318	4	10
Abstractors	928	8	9	" Sales	885	4	10
Sub-Editor's Salary	150	0	0				1203 9 8
Indexing Journal, &c.	131	6	0	" Collective Index—Subscriptions ..			6 19 0
Foreign Journals, &c.	30	18	4	" Decennial Index—Sales			12 10 0
Sundry Journals	2	14	9	" Dividends and Interest on Invest-			
French and U.S.A. Patents and				ments—			
Specifications	42	1	9	£ s. d.			
Insurance of Stock	6	13	0	4476 9 2 Metropolitan 3%			
				Consolidated	126	0	10
	£1723	14	10	1000 0 0 New Zealand 3%			
Publishing expenses—				(1945)	28	3	9
General	1807	3	6	1277 4 8 New South Wales			
Postage on Copies	741	12	0	3% (1935)	36	0	1
	2548	15	6	1231 0 10 Consols 2½%	28	17	8
				000 0 0 Gas Light and Coke			
" Sectional expenses—				3% Debentures	16	18	3
Boston	10	0	0	1084 13 4 North British 3%			
Birmingham and Midland ..	42	4	2	3% Consolidated ..	30	11	7
Canada	42	3	7	1696 0 0 Midland Rly. 2½%	39	17	8
Liverpool	85	14	3	1509 0 0 Great Eastern Rly.			
London	101	17	3	4% Irredeemable ..	56	15	5
Manchester	83	2	11	073 0 0 South Eastern Rly.			
Newcastle-on-Tyne	0	10	0	4½% Preference ..	28	9	1
New York	100	0	0	1000 0 0 Metropolitan Water			
Nottingham	20	19	4	Board 3% " B "			
Scotland	15	15	0	Debentures	28	3	9
Sydney	16	16	4	200 0 0 Nottingham Joint			
Yorkshire	23	1	4	Station 3%	5	12	11
				1250 0 0 Great Western Rly.			
" Annual Meeting expenses				5% Guaranteed ..	58	15	10
" Working expenses—				800 0 0 Great Northern Rly.			
Secretary's Salary	300	0	0	3% Debentures ..	22	11	6
Assistant to Secretary and				450 0 0 Nottingham and			
Editor	250	0	0	Grantham Canal			
Honorarium to Treasurer's				4½% Consolidated	17	5	5
Assistant and for Clerical				724 8 0 India 3½%	23	16	0
Assistance	77	10	0	834 0 2 India 3%	23	10	1
Rent, Lighting and Cleaning	208	9	1	1400 0 0 Dominion of Canada			
Stationery and Binding	59	10	0	—Canadian Pacific			
Postages, Bank Charges, Tele-				Rly. 3½% Land			
phone and Sundry expenses	167	14	0	Grant Bonds 1938	45	18	9
Medallist Portrait	31	5	6	700 0 0 Canada 4% (1940—			
				1960)	26	6	2
				703 8 5 Western Australian			
				Government 4% ..	13	2	7
				Interest on Deposit	36	3	0
" Excess of Income over Expenditure							693 0 4
							£6971 1 0
	£6971	1	0				

Manchester Section.

Meeting held at the Grand Hotel on Friday, January 8th, 1915.

MR. JULIUS HÜBNER IN THE CHAIR.

AN IMPROVED METHOD FOR THE DETECTION OF COBALT BY MEANS OF α -NITROSO- β -NAPHTHOL.

BY F. W. ATACK, M.Sc. TECH., B.Sc. LOND., A.I.C.

The use of α -nitroso- β -naphthol (β -naphthoquinone- α -oxime) in alcohol or acetic acid solution as a reagent for cobalt was first suggested by Ilinski and Knorre (Ber., 1885, 18, 699). The cobalti-compound so obtained is somewhat soluble in alcohol and in acetic acid, and the test does not appear to be one of great delicacy compared with the reagents for nickel which have been suggested by Tschugaev (Ber., 1905, 38, 2520)

and by Atack (Analyst, 1913, 38, 316). The exact composition of the reagent to be used is not stated by Ilinski and Knorre, but Chapin (J. Amer. Chem. Soc., 1907, 29, 1029) suggests the use of a solution of 8 grms. of α -nitroso- β -naphthol in 300 c.c. of cold glacial acetic acid, to which an equal volume of water is added, and the solution filtered. It is stated that the solution cannot be preserved for more than one month; the present author has found that the nitrosobnaphthol is gradually precipitated from the 50% acetic acid solution. Using this solution it was found impossible to detect with certainty less than 0.1 mgrm. of cobalt in 1 c.c. of water (1:10,000) in presence of several drops of dilute hydrochloric acid. No mention is made by Chapin of the delicacy of the test, but the smallest amount of cobalt detected by Ilinski and Knorre (*loc. cit.*) appears to have been 0.00004 gm. in presence of 0.0105 gm. of nickel in 5 c.c. of water (1 part of cobalt in 100,000 parts of water). In presence of large amounts of nickel, the author has found it impossible to prevent the precipitation of the nickel salt, which masks the cobalt color-

THE SOCIETY OF CHEMICAL INDUSTRY.

BALANCE SHEET, 31st DECEMBER, 1914.

		£	s.	d.	£	s.	d.			£	s.	d.	£	s.	d.
To Sundry Creditors					755	15		By Sundry Debtors (Publishers, &c.) ..					461	18	0
„ Subscriptions received in advance					01	4	0	„ Arrears of Subscriptions (received up to 8th April, 1915)					35	0	0
„ Accumulated Fund—								„ Cash at Bank on Deposit	400	0	0				
Balance 31st December, 1913 .	20,344	4	7					„ Do. do. Current Account	138	4	3				
Add—Excess of Income over Expenditure, 1914	894	15	2					„ Cash in hand (Secretary)	9	17	7				
					21,238	19	9	„ Investments as last year—					548	1	10
								£ s. d.							
								4470	0	2	Metropolitan 3% Consolidated	4163	2	1	
								1000	0	0	New Zealand 3% (1915)	870	0	0	
								1277	4	8	New South Wales 3% (1915)	1122	3	1	
								1231	0	10	Consols 2½%	1031	15	4	
								600	0	0	Gas Light and Coke Co. 3% Debentures	507	0	0	
								1084	13	4	North British 3% Consolidated	900	5	6	
								736	0	0	Midland Rly. 2½% Perpetual	1187	4	0	
								960	0	0	Midland Rly. 2½% Guaranteed Preference	1620	14	5	
								1500	0	0	Great Eastern Rly. 4% Irredeemable	747	0	7	
								673	0	0	South Eastern Rly. 4½% Preference	922	10	0	
								1000	0	0	Metropolitan Water Board 3% "B" Debentures	186	0	0	
								200	0	0	Nottingham Joint Station 3%	1762	10	0	
								1250	0	0	Great Western Rly. 5% Guaranteed	696	0	0	
								800	0	0	Great Northern Rly. 3% Debentures	495	0	0	
								450	0	0	Nottingham and Grantham Canal 4½% Consolidated	700	0	0	
								724	8	0	India 3½%	700	0	0	
								834	9	2	India 3%	700	0	0	
								1400	0	0	Dominion of Canada (Canadian Pacific 3½% Land Grant Bonds 1938)	1372	4	0	
								700	0	0	Canada 4% (1910-1960)	676	8	1	
													19,648	17	1
								Add—Purchased during 1914—							
								703	8	5	West Australian Government 4%	698	3	0	
								700	0	0	War Loan 3½% ..	661	0	2	
													21,008	0	3
					£22,056	0	1						£22,056	0	1
								Market value on Dec. 31st, 1914, £18,003	4	8.					

We have examined the above Balance Sheet, dated 31st December, 1914, and have verified the investments and the balances at the Bank. In our opinion the Balance Sheet shows correctly the position of the Society at 31st December, 1914.

28, Basinghall Street, London, E.C.
28th April, 1915.

(Signed) FEASEY & CO.,
Chartered Accountants.

tion, even by the addition of a considerable amount of hydrochloric acid, which is stated by Chapin to decrease considerably the delicacy of the test. Moreover, the addition of the reagent to water alone produces a heavy yellow to brown precipitate.

It appeared to the author that a more stable solution of this oxime would be obtained in the form of its sodium salt, which, according to Hinski and Knorre (*loc. cit.*), gives on addition to a solution containing cobalt a salt in which the cobalt is only divalent. It has been found that such a solution provides a far more delicate test for cobalt than the acetic acid solution of the reagent. The solution recommended for use is much more dilute, a reagent of a convenient

strength for general use being prepared as follows: 0.1 gm. of α -nitroso- β -naphthol is boiled with 20 c.c. of water to which has been added 1 c.c. of dilute caustic soda, the solution filtered, and diluted to 200 c.c. A sample of the reagent has been preserved for a year, and there does not appear to be any reason to suppose that it cannot be kept indefinitely. In carrying out the test 1 c.c. of ammonium chloride and then 1 c.c. of the reagent are added to the neutral or slightly alkaline solution under examination. The production of an orange to claret coloration, or a red precipitate, unaffected by acidifying with dilute sulphuric acid, is characteristic of the presence of cobalt. 0.001 mgrm. of cobalt in

1 c.c. of water, or 1 part of cobalt in a million parts of water, may be detected readily by the test as now described, this amount giving immediately a claret coloration, and a slight red precipitate on allowing to stand. This method of carrying out the test with the sodium salt is hence far more delicate than the method originally proposed and now in general use; the test may be made even more delicate by using the reagent of one-fifth the concentration recommended above for general use, and comparing the test with a "blank." The colorations obtained with nickel, ferric, etc., salts are all destroyed on acidifying with sulphuric acid. It is immaterial whether the cobalt is present in the solution as nitrate or other salt, provided that it is in the cobaltous condition, whereas Hinski and Knorre (*loc. cit.*) state that it is necessary to have the cobalt present as chloride or sulphate in order that their method shall succeed.

The test is not affected by the presence of zinc or manganese salts in the solution. The presence of large amounts of nickel interferes with the intensity of the coloration, although it does not prevent the detection of the cobalt, a yellow coloration, and eventually a red precipitate, being obtained with a solution of a sample of nickel ammonium sulphate which contained cobalt, whereas solutions of samples of nickel nitrate and nickel chloride, containing the same concentration of nickel but free from cobalt, gave green solutions on acidifying the test solution with sulphuric acid. For the detection of cobalt in presence of large quantities of nickel, it is advisable to reduce the concentration of the nickel by precipitation with an alcoholic solution of dimethylglyoxime (Fschugaev, *loc. cit.*) or *o*-benzildioxime (Atack, *loc. cit.*). As the presence of either of these nickel reagents in excess gives rise to a cobalt salt which will not react with the nitrosomaphthol reagent, it is essential to separate the nickel partially only.

It is to be noted that this interference with the test by large amounts of nickel is an advantage in general analysis, as the amounts of cobalt present in commercially pure nickel salts do not give a precipitate, but only a coloration, with the new reagent at the concentrations usually employed in qualitative analysis, whereas such amounts are sufficient to give the test with the acetic acid solution in such a manner that, as Chapin remarks (*loc. cit.*), students report cobalt as present in every solution of nickel which they analyse.

The test is not affected by the presence of tartaric or citric acid, which may therefore be employed to keep in solution members of Group III. of the analytical classification; in this manner 0.001 mgrm. of cobalt was readily detected in presence of 1 mgrm. of iron (as ferric ammonium citrate).

The quantitative application of the method is under examination.

Meeting held at the Grand Hotel on Friday, April 9th, 1915.

MR. JULIUS HÜBNER IN THE CHAIR.

THE CONSTANTS OF THE FATTY ACIDS FROM SULPHONATED COD OIL.

BY L. G. RADCLIFFE AND C. W. PALMER.

It is well known that all saponifiable oils can be sulphonated with considerable ease and completeness; moreover, the process is largely carried out on the cheaper oils. A sulphonated oil has properties and constants which differ entirely

from the original oil, and it is therefore extremely difficult to identify an oil after it has been sulphonated.

It has been thought useful to sulphonate certain oils and then to hydrolyse the sulphonated product so as to remove completely the sulphonic groups and finally to prepare the fatty acids therefrom and compare their properties with those of the fatty acids from the unsulphonated oil, in the hope that the figures so obtained would prove of use in the analysis and identification of the original oil.

The cod oil used was a brown variety, having a sp. gr. of 0.931 at 15.5° C.; saponification value, 163.3; acid value, 17.6, corresponding to 8.0% of free fatty acid calculated as oleic acid; iodine value, 173.7%.

From this oil the free fatty acids were prepared by saponifying with strong potash and alcohol; the soap was boiled with water to remove the alcohol and the fatty acids precipitated by hydrochloric acid. The clear oil was well washed with water, separated, and heated until free from moisture. The fatty acids had a solidifying point (titer test), 22.8° C.; neutralisation value, 191; mean molecular weight, 280.4; iodine value, 178%; yield of hexabromides, 42%. The sulphonation was performed on 100 grms. of the oil in a suitable vessel cooled with a water-jacket and provided with a thermometer and a mechanical agitator driven by a hot air motor. To the oil 35 grms. of concentrated sulphuric acid was added drop by drop from a tap funnel and the reaction was carefully controlled so that the temperature did not at any time rise above 25° C.; no production of sulphur dioxide was noticed. After two hours stirring no further action was observed, and the darkened and thickened product was washed with a cold saturated solution of sodium sulphate until nearly all the free sulphuric acid was removed. The product dissolved in dilute ammonia to a clear solution. On heating the sulphonated oil in the water-oven a clear oil was obtained, and from this the fatty acids were prepared.

The sulphonated oil was saponified with aqueous caustic potash and alcohol in the same way as was the original oil, and after saponification the fatty acids were liberated as before, well washed, and dried in the water oven. The clear oily fatty acids were tested for sulphur with negative results. These acids were of much harder consistency than the acids from the unsulphonated oil and on examination gave the following data: Solidifying point (titer test), 25.7° C.; neutralisation value, 183; mean molecular weight, 308.6; iodine value, 144.4%; yield of hexabromides, 11.0%. These figures indicate a very extensive alteration in the chemical constitution of the fatty acids regenerated from the sulphonated oil as compared with those of the original cod oil.

The behaviour of other oils is being investigated and the further results will be communicated in a later paper.

DISCUSSION.

Mr. J. ALLAN said that the so-called commercial cod oils were mixtures of oils obtained from all kinds of fish, and usually of a dark brown colour, and in an advanced state of decomposition. Such oils were obtained not only from the liver of the fish but also from the entrails. Hence their characteristics were extremely variable. It was, therefore, difficult to understand how the authors could hope to find any means of establishing the origin of sulphonated oils which were of such diverse origin. The treatment of fatty glycerides with sulphuric acid inevitably resulted in the formation of hydroxy acids or stearylactones; the determination of the acetyl value of the oil before and after sulphonation, thus measuring