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Composition
of Acid from
Thomson Apparatus
Macdonald

London Section.

Meeting held at Burlington House on Monday, February 20th, 1911.

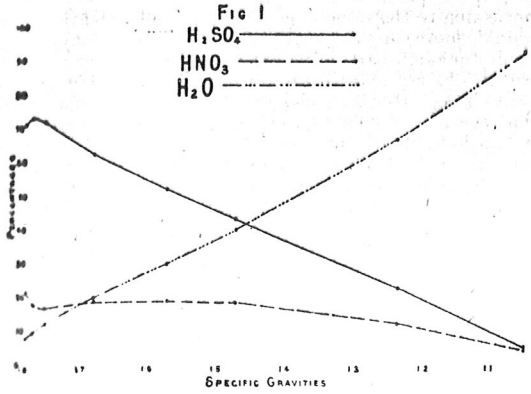
MR. E. GRANT HOOPER IN THE CHAIR.

THE COMPOSITION OF THE ACID FLOWING FROM THE THOMSON DISPLACEMENT APPARATUS FOR THE MANUFACTURE OF GUNCOTTON.

BY GEORGE W. MACDONALD, M.SC.

The details and method of working the Thomson apparatus for the manufacture of guncotton have been fully dealt with by Colonel Sir Frederic L. Nathan in a paper read before the Society (see this J., 1909, 177). For the purpose of following the results to be quoted it is, consequently, only necessary to state briefly, that the cotton waste is immersed in the mixture of sulphuric acid and nitric acid contained in shallow earthenware pans provided

FIG 1



with a stop-cock at the lowest point. When nitration is complete, at the end of 2½ hours, this cock is opened, and, as the acid slowly runs away, the water runs in on top at an equivalent rate, and the acid is thus completely displaced from the guncotton. At the Dartford Guncotton Works of Messrs. Curtis's & Harvey, Ltd., the course of the displacement has been followed by analysing samples of acid which were drawn, at fairly frequent intervals, as displacement proceeded. The results are given in the following table :—

Time from commencement of displacement. (Mins.)	Temperature °C.	Specific gravity.
5	12·5	1·782
15	14·0	1·781
30	16·0	1·780
45	17·0	1·778
60	17·5	1·777
75	19·0	1·776
90	20·0	1·775
105	20·5	1·774
120	21·0	1·774
135	22·0	1·774
150	23·0	1·760
155	24·0	1·74
160	25·7	1·688
165	26·5	1·542
170	26·5	1·300
173	26·5	1·100

From the detailed results we have the following data per set of 4 pans :—Seventy-eight per cent. of the acid collected to be dealt with in the factory was revivified. The ratio of nitrating acid to cotton waste was 34·37 to 1. The rate

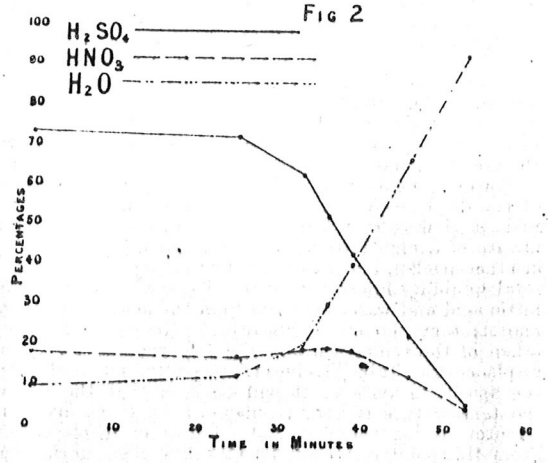
Details.	Time occupied in collecting acid. (Mins.)	Weight of acid.	Collected between sp. grs.	Specific gravity.	Sulphuric acid.	Nitric acid.	Nitrous acid.	Water.
Original acid as used for nitrating	—	2750 lb. (collected)	—	1·79	70·84	21·26	0·53	7·37
Acid collected for revivification..	145	2033 lb.	— to 1·76	1·778	72·93	17·57	0·56	8·94
	25	324 ,,	1·76 to 1·7	1·757	71·55	16·46	0·56	11·43
Acid to be denitrated and concentrated.....	8	86 ,,	1·7 to 1·6	1·68	61·93	18·26	0·45	19·36
	3	35 ,,	1·6 to 1·5	1·57	51·56	18·86	0·31	29·27
	3	33 ,,	1·5 to 1·4	1·47	42·22	17·99	0·24	39·55
	7	83 ,,	1·4 to 1·1	1·236	21·94	11·83	0·16	66·07
	7	71 ,,	1·1 to 1·0	1·050	4·24	3·61	0·15	92·0
Acid running to waste to drain.	45	589 ,,	until free from acid.	1·005	0·48	0·44	0·10	98·98

In Figure 1 the percentage amounts of sulphuric acid, nitric acid, and water, are plotted against the specific gravities of the samples of acid, commencing with the nitrating acid itself. In Figure 2 they are plotted against time, in minutes, beginning from the point where the acid was shut off from the storage tank for acid to be revivified, and allowed to flow to the storage tank holding the acid which is to be denitrated and concentrated. The interesting point is brought out that sulphuric acid is displaced at a relatively much more rapid rate than nitric acid, and that, for a short time during displacement, the percentage of nitric acid actually rises in the mixed acid. As an explanation it may perhaps be suggested that the guncotton fibre has a selective adsorption for nitric acid, or that a labile nitrate has gradually broken up. The nitrating acid in use at the time that the experiments were carried out had a composition suitable for the preparation of guncotton intended for the manufacture of cordite. Quite similar results, as regards the course of the displacement, have also been obtained where the acids used were intended for the manufacture of cellulose nitrate of a high nitrogen content, and a high solubility in ether-alcohol, and further, a low nitrogen content and total solubility in ether-alcohol. These acids have higher nitric acid and water contents than the acid used for the manufacture of cordite guncotton. Readings were also taken of the temperature of the acid running off during displacement. Table II. gives these results, and, in addition, the specific gravities. It will be seen that the rise of the temperature is very regular—about 1° C. every 15 minutes during the first 150 minutes of displacement. From this point a rise of 3·5 C. takes place during the next 15 minutes, after which the temperature remains constant.

The amount of flow of the acid to be revivified was about 14 lb. per minute. The loss consisted of, approximately, 6 lb. of sulphuric acid and 5 lb. of nitric acid, (0·4 per cent. of the acid originally used), or only about 0·08 lb. total loss of both acids per lb. of guncotton produced. The amount of acid to be denitrated and concentrated

was 4·12 lb. per lb. of guncotton produced. The amount of water consumed during the whole of the displacement

FIG 2



was about half a gallon per lb. of guncotton produced. My thanks are due to the Directors of Messrs. Curtis's & Harvey, Ltd., for permission to publish these results.

Discussion.

Dr. Robt. Robertson said that on account of the importance of the quantity of acid in the first boiling of guncotton, any information such has had been brought forward regarding the mechanism of the Thomson displacement process was of interest.

As regards the significance of the phenomenon, it seemed that the table might contain the data for deciding if hydrolysis of a higher nitrate of cellulose had taken place, for Benl and Klaye (Zeit. f. d. g. Sch.-u. Spreng, 2, 403) had found that, when they transferred highly nitrated cellulose to an acid bath capable of producing a nitrocellulose of a lower degree of nitration only, a denitration of the former resulted.

He had not found that nitric or sulphuric acids of decinormal strength were markedly adsorbed by nitrocellulose, although alkali of this strength could be adsorbed. Häussermann (Zeit. f. d. g. Sch.-u. Spreng., 3, 121) had shown that with stronger nitric acid, the first stage in the nitration of cellulose was most probably the formation of an adsorption compound. As guncotton was not fully nitrated, there existed the possibility of its adsorption of nitric acid, and the matter might be settled by determining the affect of the addition of guncotton on the composition of mixed acids of the various strengths given in the table.

Mr. Jas. M. Thomson said the author stated that 0·08 lb. of acid per lb. of guncotton ran to waste; and that agreed very well with the results they found at Waltham Abbey, though they allowed 0·12 lb. of acid lost per lb. of guncotton. Objectors to the process found that the nitric acid rose when the displacement reached a point close to where the water joined the acid. They came to the conclusion that the guncotton was highly nitrated at the beginning, and that when the water layer mixed to some extent with the strong acids the guncotton became de-nitrified. That statement became current; but all experiments led to the conclusion that the displacement process gave a better stability than the ordinary process. That had been shown very definitely by Dr. Robertson; and they had found the same thing at Waltham Abbey in doing some experiments. The nitric acid did rise there too, but as many seemed to be afraid of the stability they concluded naturally to draw very little attention to it. At the first he was almost afraid to displace the older process altogether and adopt the new one but, being assured that the stability of the product was excellent, they adopted the displacement process and it had turned out quite satisfactorily. With regard to adsorption of nitric acid by guncotton, that was quite a new theory to him; but it was quite possible that both conjectures might be correct. At any rate it was quite certain that there was a de-nitrification of the guncotton when the acids became reduced in strength. As Dr. Robertson had pointd out, if highly nitrified guncotton was immersed in weaker acid the nitrogen content was reduced, this would to some extent explain the increase of nitric acid at a certain level in the waste acid which came away.

Dr. W. R. E. Hodgkinson said, with regard to adsorption, that something of the kind undoubtedly took place between guncotton and benzenoid (partially nitrated or not) substances when nitrated together. The figures obtained on analysis and general behaviour of the products pointed to it very distinctly.

Mr. E. Hatschek said as far as the adsorption theory went, if there was adsorption it was absolutely abnormal adsorption phenomenon. All normal adsorption proceeded according to the same exponential formula, and the curves would more or less approach an equilateral hyperbola. Unless a small part only of the curve was drawn to a scale which did not shew its nature there was nothing of that sort here. He had also used, not indeed guncotton, but acetic acid collodion gel in adsorption experiments to a considerable extent, and had found that the adsorption always proceeded normally and that the descending curves, which were here straight lines, were invariably in the shape of an equilateral hyperbola.

Mr. G. W. Macdonald in reply, said Dr. Robertson had already referred to the question of the work of Häussermann. Both Knecht and Häussermann had shown the existence of labile nitrates of cellulose under the following conditions:—On immersing cellulose in dilute nitric acid, removing the adherent acid first by pressure and finally by exposing *in vacuo* over freshly burnt lime, a cellulose nitrate of about 7 per cent. nitrogen was produced. On immersion in water, nitric acid was liberated, thus pointing to the breaking up of a labile nitrate and the production of a stable nitrate containing a lower percentage of nitrogen. The symmetrical nature of the curves for water and sulphuric acid appeared to show, conclusively, that there was no adsorption of sulphuric acid by the guncotton fibre. There was probably a considerable breaking up of the cellulose nitrate which caused an increase of nitric acid in the mixed acids. He had had considerable experience with nitrating centrifugals before Messrs. Curtis's & Harvey introduced the Thomson system. A brief comparison of some of the points of the two systems might be of interest. When using nitrating centrifugals the ratio of mixed acids to cellulose was at least 50 to 1, and if a circulating system was employed a very constant composition of the nitrating acid was thus obtained. The total time of contact of the cellulose and acid was less than one hour, and the nitrogen content of the cordite guncotton produced, when using an acid of the same composition as in the displacement process, was from 13·1 to 13·2 per cent., and was thus quite appreciately higher than the nitrogen content of displacement cotton, which averaged practically 13 per cent. Every pound of guncotton from the nitrating centrifugal carried away with it, at least, one pound of adherent acid, which was lost by drowning the guncotton in a very large volume of water. This loss of acid was equivalent—taking the market price of sulphuric and nitric acid—to about £6 per ton of guncotton produced. Consequently, in the question of economy the process introduced by Messrs. Thomson offered a very considerable advantage, since it brought down this loss to about one-tenth of the above amount. One point advanced against the system was the considerable amount of dilute acid which had to be dealt with by denitration and concentration, but this expense was more than counterbalanced by the other economies introduced.