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Researches on Guncotton

On the Manufacture & Composition of Guncotton

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XIV. *Researches on Gun-cotton.—On the Manufacture and Composition of Gun-cotton.*

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THE general designations of pyroxylin and gun-cotton have been applied, up to the present time, to the several products obtained by the action of nitric acid, either alone, or in admixture with sulphuric acid, upon cotton-wool. In the earlier papers on gun-cotton, published within a short period of the announcement (in 1846) of SCHÖNBEIN'S discovery of a substitute for gunpowder, the action of nitric acid upon cellulose was assumed by the several investigators to furnish one single definite product, to which different formulæ were assigned, based in some instances upon analytical results, in others upon the increase in weight sustained by the cotton on its treatment with nitric acid, or a mixture of nitric and sulphuric acids. PÉLOUZE, who was the first to produce (in 1838) an explosive substance by the action of nitric acid on cellulose, originally believed this product to be identical with that which BRACONNOT obtained from starch by its solution in cold nitric acid and precipitation by water. But in November 1846 that chemist published the results of experiments establishing decided differences between the two bodies. The conclusion which PÉLOUZE then arrived at, regarding the composition of pyroxylin, was founded upon the tolerably constant increase in weight (between 68 and 70 per cent.) of dry cotton-wool and paper, when submitted to the action of monohydrated nitric acid, either employed alone or mixed with an equal volume of concentrated sulphuric acid. He considered that nitric cellulose was the sole product of the reaction, and that it consisted of one equivalent of cellulose *minus* one equivalent of water, combined with two equivalents of monohydrated nitric acid, its formula being

$$C_{12}H_{11}O_{21}N_2(C_{12}H_{22}O_{21}N_4).$$

Not long afterwards, PÉLOUZE published conclusions varying somewhat from the preceding. He fixed the increase sustained by cellulose, upon its conversion into pyroxylin, at between 74 and 76 per cent., and was led by these numbers and by direct analytical data obtained with pyroxylin, to regard the formula

$$C_{24}H_{17}O_{17},\ 5NO_5(C_{12}H_{17}O_{21}N_5)$$

as correctly representing the composition of that substance. The increase in weight which cellulose should sustain, by conversion into a substance of that composition, would be 74·9 per cent., a number which corresponds closely with the results obtained in these later experiments of PÉLOUZE.

Numerous researches on the composition of pyroxylin were instituted by Continental and English chemists at about the period of PÉLOUZE'S experiments, and the following are some of the formulæ assigned by different experimenters to gun-cotton, in 1846 and 1847*:—

PÉLOUZE (1846)	$C_{12}H_{11}N_2O_{21}$	$= C_{12}H_9O_9, 2(HONO_5)$.
PÉLIGOT	$C_{12}H_9N_3O_{24}$	$= C_{12}H_9O_9, 3NO_5$.
VON KIRCHHOFF and REUTER .	$C_{12}H_9NO_{14}$	$= C_{12}H_9O_9, NO_5$.
FEHLING	$C_{12}H_{10}N_2O_{20}$	$= C_{12}H_{10}O_{10}, 2NO_5$.
PORRET and TESCHEMACHER . .	$C_{24}H_{16}N_8O_{56}$	$= 2(C_{12}H_8O_8, 4NO_5)$.
PÉLOUZE (1847)	$C_{24}H_{17}N_5O_{42}$	$= C_{24}H_{17}O_{17}, 5NO_5$.
SCHMIDT and HECKER	$C_{12}H_5N_5O_{30}$	$= C_{12}H_5O_5, 5NO_5$.
GLADSTONE	$C_{24}H_{15}N_5O_{40}$	$= C_{24}H_{15}O_{20}, 5NO_4$.
W. CRUM	$C_{12}H_7N_3O_{22}$	$= \begin{cases} C_{12}H_7O_7, 3NO_5. \\ C_{12}H_7O_{10}, 3NO_4. \end{cases}$

Most of the published results of individual experimenters exhibit considerable variation among themselves, and in several instances the mean results are only approximately represented by the formula adopted.

The very considerable discrepancies presented by the results of independent investigations are unquestionably due, in part, to the difficulties which have to be encountered in attempts to obtain trustworthy analytical results from so highly explosive a material as gun-cotton. The methods of analysis which have been adopted have been almost as numerous as the formulæ deduced from their results; and in several instances the quantity of material operated upon has been too small to permit of the attainment of satisfactory results by methods in which the sources of error were not inconsiderable.

There is no doubt, however, that the different conclusions arrived at by many talented chemists with regard to the composition of gun-cotton, are to be mainly ascribed to the fact that the treatment of cotton-wool with nitric acid, or a mixture of nitric and sulphuric acids, has furnished, in the hands of different operators, products differing considerably in composition. That such is the case is clearly indicated by the statements made in several of the published researches with regard to the increase of weight sustained by the cotton upon treatment with acid. Thus PÉLOUZE, in his first paper on the composition of pyroxylin, states that he found the increase of weight constantly comprised between 68 and 70 per cent. In his next publication he fixes the increase of weight at between 74 and 76 per cent., the theoretical increase, according to the formula which he fixed upon, being 74·9 per cent.; and Von KIRCHHOFF and REUTER obtained an increase of 76 per cent. GLADSTONE also found the increase of weight to be between 73 and 76 per cent. PORRET and TESCHEMACHER obtained an increase of only 54 per cent.; TESCHEMACHER afterwards found the increase to be 69 per cent. GREGORY and SCHMIDT and HECKER arrived at a similar result; while W. CRUM, whose experiments

* The notation employed by the several experimenters is retained in this statement.

were made with very carefully purified cotton, obtained an increase of 78 per cent. The increase of weight which, in other instances, the cotton must have sustained for the attainment of the analytical results quoted, must have been even more various: thus RANSOME'S results would indicate an increase of weight of only 65·4 per cent., while those of PÉLIGOT correspond to a gain of 94·4 per cent.

Other indications of differences in the characters of the products operated upon by different chemists are furnished by statements made with regard to the action of solvents upon them. Their solubility in mixtures of alcohol and ether evidently varied considerably; and in one instance of these earlier experiments (namely those of MM. MÉNARDE and DOMONTE in 1846), a description of gun-cotton soluble in ether and alcohol was described as obtained together with a proportion of an insoluble product. The analysis of the latter furnished results which correspond very closely to those demanded by the formula

$$C_{12}\left\{\begin{matrix} H_8 \\ 2N\,O_4 \end{matrix}\right\}O_{10}.$$

BÉCHAMP instituted some researches upon gun-cotton in 1852, in which he obtained, by the action of ammonia upon a soluble form of gun-cotton, a substance to which he assigned the formula

$$C_{24}\,H_{17}\,O_{17},\ 4N\,O_5\ (C_{24}\,H_{34}\,O_{17},\ 4N_2\,O_5),$$

viewing it as pyroxylin from which one equivalent of nitric anhydride had been abstracted; he therefore considered that the formation of this substance confirmed PÉLOUZE'S view of the composition of gun-cotton.

It was believed by some chemists at about this period that pyroxylin was itself only slightly soluble in mixtures of alcohol and ether, but that these mixed solvents either modified its character, or separated it into two distinct explosive bodies, the one being soluble, and the other insoluble in the ether and alcohol. Others regarded the difference in solubility exhibited by gun-cotton, according to the manner in which it had been prepared, as ascribable to differences of molecular condition and not of composition.

But all the early investigators of this subject appear to have agreed in the opinion that the action of nitric acid, or the mixed acids, was completed in a few minutes, and that, however much the treatment with acids was protracted, no further change was effected.

GERHARDT, in his 'Traité de Chimie Organique' (1854), states that, as no gas is disengaged in the production of pyroxylin (a point upon which PÉLOUZE lays stress in his earlier papers), this substance may be affirmed to contain the elements of cellulose *plus* two or three proportions of the elements of nitric anhydride, and that it may be represented as cellulose in which two or three atoms of hydrogen are replaced by their equivalent of peroxide of nitrogen. This view of the composition of gun-cotton, which was first enunciated by CRUM, received very strong support from the interesting researches of HADOW, published in 1854. The experiments of this chemist furnished conclusive

evidence of the possibility of producing four distinct varieties of pyroxylin, by submitting cotton-wool to the action of different mixtures of nitric and sulphuric acids. Moreover, by carefully determining the increase of weight sustained by the cotton upon immersion in acid mixtures of different composition, and also by applying a new process to the examination of the products, HADOW succeeded in establishing the composition of three of these substances.

By repeated immersion of pure cotton in a mixture of the strongest sulphuric and nitric acids, HADOW obtained an increase of 81·34 per cent., a number considerably higher than that obtained by previous experimenters, and nearly corresponding to the theoretical gain (83·3 per cent.) which cotton would sustain by its conversion into a product of the formula

$$C_{18}H_{21}O_{15},\ 9NO_2,\ \text{or}\ C_6\left\{\begin{matrix}H_7\\3NO_2\end{matrix}\right\}O_5,\ \text{or}\ C_{12}H_{14}O_7,\ 3N_2O_5 (C_{36}H_{21}O_{30},\ 9NO_4,\ \text{HADOW}).$$

By determining, in the form of nitric acid, the oxide of nitrogen contained in the product, and reproducing the cotton from the latter by the action of potassic sulphhydrate, HADOW moreover obtained numerical results closely agreeing with those which should be furnished by trinitro-cellulose or trinitric cellulose, and therefore confirmatory of the conclusion which was based upon the weight of the product furnished by as complete a treatment as possible of the cellulose with the strongest nitric and sulphuric acids. Similarly, HADOW established the composition of two lower nitric-products, having respectively the formulæ

$$C_{18}H_{22}O_{15},\ 8NO_2 (C_{36}H_{22}O_{30},\ 8NO_4)$$

and

$$C_{18}H_{23}O_{15},\ 7NO_2 (C_{36}H_{23}O_{30},\ 7NO_4),$$

and differing from the highest compound in being soluble in mixtures of ether and alcohol.

Not long after HADOW'S researches were made known, BÉCHAMP published a continuation of his experiments with soluble gun-cotton. In this paper he adheres to the conclusion that PÉLOUZE'S formula for pyroxylin ($C_{24}H_{17}O_{17},\ 5NO_5$) is correct, because he obtains, by the action of ammonia and potassa upon that substance, products the composition of which he represents by the formulæ

$$C_{24}H_{17}O_{17},\ 4NO_5 \text{ and } C_{24}H_{17}O_{17},\ 3NO_5.$$

REDTENBACHER, SCHRÖTTER, and SCHNEIDER, in a joint report prepared by them in 1863 on gun-cotton manufactured by Baron von LENK, adopted the view that the most explosive variety of gun-cotton was trinitro-cellulose, and quoted several satisfactory analytical results in proof of their assertion that gun-cotton prepared according to LENK'S directions was that substance in a nearly pure condition.

The composition of the most explosive gun-cotton was indeed very generally regarded as definitely established to be trinitro-cellulose, or trinitric cellulose, until the publica-

tion (in 1864) of the memoir of PÉLOUZE and MAURY, in which that view is combated, and a new formula,

$$C_{24}H_{18}O_{18},\ 5NO_5\ (C_{24}H_{36}O_{18},\ 5N_2O_5),$$

is assigned to that substance, which differs, by the elements of one equivalent of water, from PÉLOUZE'S second formula, adopted in 1847.

Some analytical results are referred to by PÉLOUZE and MAURY in support of their view of the composition of gun-cotton; but they base their new formula principally upon the increase of weight which they have found cotton to sustain by treatment with the mixed acids, and which they now fix at 78 per cent. (the numbers formerly arrived at by PÉLOUZE being from 68 to 70 and from 74 to 76 per cent.). The theoretical increase of weight which *pure cellulose* should sustain upon complete conversion into a substance of the composition assigned to it by PÉLOUZE and MAURY is 77·78 per cent.; while, if gun-cotton were completely converted into trinitro-cellulose, it should gain in weight 83·3 per cent.

It would appear that these numbers are sufficiently far apart to preclude any uncertainty with regard to the correctness of a conclusion in favour of either formula, if based upon careful and sufficient experiments. Nevertheless, PÉLOUZE and MAURY state, on the one hand, that they base their somewhat complex formula upon the results of many experiments, variously instituted; while, on the other hand, the results arrived at by HADOW, which are not in any way referred to by PÉLOUZE and MAURY, and have never yet been called into question, appear to furnish very strong evidence in favour of the more simple formula.

Early in 1863, by desire of the Secretary of State for War, I entered upon a detailed investigation of the manufacture of gun-cotton, the composition of the material when produced upon an extensive scale, its behaviour under circumstances favourable to its change, and other subjects relating to the chemical history of this remarkable body.

The continuation of these investigations was afterwards entrusted to me by my colleagues, upon the appointment of a Government Committee on Gun-cotton.

The circumstance that the manufacture of the supplies required for artillery- and other experiments has been carried on under my direction, has enabled me to institute numerous experiments upon a considerable scale, in some of which the conditions of manufacture have been varied, while in others the quantity of product furnished has been carefully determined. By combining such experiments with a very extensive series of analytical and synthetical laboratory investigations, I have endeavoured to render both rigorous and exhaustive the examination into the uniformity of the process of manufacture of gun-cotton as perfected by Von LENK, and into the composition of the product.

I.—MANUFACTURE OF GUN-COTTON.

The system of manufacture of gun-cotton which is the result of Von LENK'S persevering endeavours to perfect this material, does not, at first sight, present any important

features of novelty, when compared with the methods of operation prescribed by SCHÖNBEIN, BÖTTGER, OTTO and others, and pursued upon an extensive scale, for a short time, at Messrs. HALL'S gunpowder works, and at Bouchet. Acids of the specific gravity prescribed by Von LENK and mixed in very similar proportions to those which he indicates, were employed; in some instances the cotton was submitted to a preliminary purification, as directed by him, and the product, after being washed in water, was also submitted to treatment with an alkaline bath, the mode only of carrying out this process of purification differing somewhat from that which Von LENK adopts. But the application, upon a manufacturing scale, of the system which has been pursued under LENK'S direction at the manufactory at Hirtenberg, brings to light several details of considerable value, the adoption of which unquestionably ensures the attainment of greater uniformity and purity of the product of manufacture than could be secured by the earlier modes of operation.

The important steps in Von LENK'S system of manufacture are briefly as follows:—

1. The carded cotton is spun into a loose yarn, varying in size and strength according to the applications it is to receive; and the yarn is made up into hanks of convenient size (weighing about three ounces).

2. The cotton is submitted to preliminary purification by boiling it for a few minutes in a solution of potassic carbonate, of specific gravity 1·02, separating the alkaline liquid by means of a centrifugal extractor, and washing the cotton thoroughly in water.

3. The cotton is perfectly dried by artificial heat, immediately before its treatment with acid.

4. The acid used for the production of the gun-cotton is prepared by mixing one part by weight of nitric acid, of specific gravity 1·52, with three parts of sulphuric acid of specific gravity 1·84. This mixture is allowed to become perfectly cold before use.

5. The dry cotton is immersed by small quantities (about six ounces, or two hanks, at one time) in a bath of the mixed acids, which is kept as cool as possible. When the cotton has become thoroughly saturated and has been moved about in the acids for a few minutes, it is removed from the bath to a ledge placed over it, where a portion of the acid absorbed is separated by gentle pressure; the hanks are then transferred to small covered stoneware vessels, in which they are preserved for forty-eight hours, the proportion of acid with which they are allowed to remain saturated for that period being 10·5 parts by weight to 1 of the original cotton. The vessels containing the gun-cotton and acid are kept as cool as possible by being surrounded with water.

6. The acid removed from the bath by each successive quantity of cotton immersed, is replaced by the addition of a corresponding quantity of the fresh mixture, before another quantity of cotton is treated.

7. After the lapse of forty-eight hours, the acid is separated from the gun-cotton as completely as possible by mechanical means (*i. e.* by means of the centrifugal extractors). The expressed acids are not employed again.

8. The hanks are then drenched with water, singly, as rapidly as possible; they are

afterwards washed by hand until no longer acid to the taste, and are afterwards placed in crates or perforated boxes and kept immersed in flowing water for about three weeks.

9. At the expiration of that time the water is separated mechanically from the gun-cotton, and the moist skeins are boiled for fifteen minutes in a solution of potassic carbonate of specific gravity 1·02. When the alkaline liquor has been expressed, the skeins are once more immersed in flowing water for a few days; the finished gun-cotton is then dried by exposure to air.

10. It is afterwards allowed to soak for about one hour in a cold solution of sodic silicate of specific gravity 1·072. The liquid is then expressed from the hanks in the usual manner; after which they are allowed to dry thoroughly, again washed for five or six hours in running water, and finally by hand. The thorough desiccation of the gun-cotton then completes its manufacture.

The employment of the cotton in the form of hanks of loosely spun yarn, instead of simply in the loose carded condition, considerably facilitates its conversion and purification. The proper impregnation of the cotton by the acids is more rapidly accomplished with the hanks; such manipulations as attend the separation of the main quantity of acid from the converted material, and its first rapid and complete immersion (while still saturated with the concentrated acids) into water, are much more readily carried out with the cotton in the spun form; and, again, the exposure of the latter to the full purifying effects of a current of water is much more simply and perfectly effected than if carded cotton be used, while the mechanical loss of wool and of gun-cotton, in the several operations of washing and expressing, is much reduced. I have perfectly satisfied myself of the advantages just pointed out, by operating upon considerable quantities of carded cotton-wool. In these experiments it was found impracticable, moreover, except by application of very powerful pressure, to reduce the proportion of acid which the wool retained after immersion (and which had to be left in contact with it, as prescribed) below that of fourteen parts to one of cotton, whereas with the yarn there is no difficulty in reducing the quantity, by moderate pressure, to ten parts, or even lower. The consumption of acid is therefore economized by using the cotton in a spun form.

The preparation of the mixture of nitric and sulphuric acids, as directed by Von Lenk, involves no important point of novelty; the necessity of employing the mixture cold, and therefore of either submitting it to refrigeration before use, or preparing a stock of the mixture some time before it was required, was well known to the earlier operators*.

* An observation made by Béchamp, in his papers on Pyroxylin, that the production of a soluble or an insoluble product was determined simply by conditions of temperature, when the conversion was effected by means of sulphuric acid and saltpetre, induced me to ascertain by experiment whether the solubility, in alcohol and ether, of the product obtained with the employment of the prescribed mixture of nitric and sulphuric acids, increased, if the temperature of the latter was raised to about 70° C. That temperature was fixed upon for the experiment as being the average of the freshly prepared mixture of nitric and sulphuric acids, usually employed for producing gun-cotton for photographic purposes, and which, in experiments instituted, furnished soluble gun-cotton yielding transparent collodion. The products obtained by the action of the warm mixture

In the treatment of the cotton with the mixed acids, the following precautions, viz. the immersion of uniform quantities of the perfectly dry cotton in the bath of acid, the adherence to a fixed proportion in weight between the cotton and the acid with which it is left in contact, and the regular replacement of the acids removed from the bath at each successive immersion of cotton, by a corresponding quantity of fresh mixture, combine to exert no unimportant influence upon the uniformity of the product. That such is the case has been established by manufacturing experiments. For example, on one occasion some hanks of cotton were immersed in the bath of acids without addition to the latter of the quantity of fresh acid proportionate to the amount removed in the previous operation of immersion. The resulting product, which was in all other respects treated as usual, exhibited a decided difference, both in its composition and its explosive powers, when compared with gun-cotton previously produced, strictly according to rule, in the same bath of acids.

As regards the period during which the cotton is allowed to remain immersed in the acids, the precise time fixed upon by LENK (forty-eight hours) appears to be arbitrary, but there is good reason for prolonging for several hours the contact between the acids and the product. That a few minutes' immersion of a small quantity of cotton may be sufficient to convert it into a highly explosive and even to a great extent into the most explosive product, is indisputable; but a considerable period elapses before the cotton, especially when it is spun and when at least 6 oz. are operated upon at one time, is converted, as *completely as possible* by one single treatment, into the most explosive product.

In operating upon small quantities of cotton, when the proportion of acids employed is always considerably in excess of that prescribed by Von LENK, an immersion of the cotton for two hours has been found to furnish results quite as perfect as those obtained by protracting the immersion for forty-eight hours. Even when the proportion of acid to cotton was reduced, in small experiments, as nearly as possible to that employed in a manufacturing operation, the results of twelve and twenty-four hours' immersion were quite equal to those produced by treatment for the full period; indeed, decided evidence was obtained that the very long-continued contact of gun-cotton with the acids gave rise to a slight loss, a small proportion of the product being eventually dissolved by the acids. But when the duration of the treatment of even small quantities of cotton (between three and four grammes) with a large excess of acid was limited to ten minutes, the conversion was comparatively very imperfect, and the products contained considerable proportions of soluble gun-cotton.

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upon the cotton-wool exhibited no difference as regards its insolubility, from the ordinary products furnished by the cold mixture. Neither was insoluble gun-cotton rendered at all soluble by being submitted to treatment with the warm mixture. HADOW has shown that a more dilute mixture of acids which, when cold, furnishes an almost insoluble product, will, if employed at a temperature of 55° C., yield perfectly soluble gun-cotton, giving a fluid transparent collodion.

A careful examination of products of manufacture, prepared by continuing the contact of the acids with the gun-cotton for only one-half of the usual period (twenty-four hours), failed to indicate any difference between them and products obtained by the full period of immersion; on the other hand, a prolongation of the immersion to seventy-two hours did not furnish results more closely in accordance with theoretical demands than the ordinary treatment.

It was found, by experiments with several hundred pounds of spun cotton, that a considerable increase beyond the prescribed proportion of acid left in contact with the gun-cotton (eighteen or twenty parts instead of ten parts to one of cotton) furnished products which differed from those obtained by a strict adherence to LENK'S directions, only in containing somewhat smaller proportions of foreign matters than products in the manufacture of which ten parts of acid had been used.

The heat resulting from the chemical action of the nitric acid upon the cotton, and from the union of the acids with the liberated water, is considerable; it is therefore quite as important that the bath of acid in which repeated immersions are effected should be kept cool by being surrounded with cold water, as that the acid mixture should in the first instance be perfectly cold. Moreover, the precaution which Von LENK adopts (excepting in cold weather) of keeping the closed vessels, in which the gun-cotton remains for forty-eight hours in contact with the acids, surrounded by cold water, is also very essential; for otherwise the accumulation of heat by the contents of the vessel, in consequence of the gradual conversion of some portions of the cotton, after its removal from the bath, may occasionally become sufficiently considerable to establish a destructive action of the acids upon the gun-cotton.

There can be no question as regards the necessity of employing some method, such as that adopted by Von LENK, for rendering as sudden and complete as possible the first immersion into water of the gun-cotton which is still saturated with acids (though these have been separated from it as far as possible by means of a centrifugal extractor); for if the hanks are simply thrown or dipped into water, the heat generated by the gradual penetration of the latter into the compact mass of gun-cotton, saturated with concentrated acids, suffices to establish in some parts a destructive action of the latter upon the gun-cotton, which is rendered evident by the disengagement of nitrous vapours, and which, though it is very speedily checked, as the acid becomes largely diluted by water, may give rise to the production of small quantities of substances of comparatively unstable character, not removed from the gun-cotton by the subsequent purification. The most effectual plan of rapidly diluting the acid in the gun-cotton is to throw the skeins just removed from the extractor singly *into* a cascade of water, whereby the instantaneous penetration of the mass of cotton by a large body of water is accomplished with ease and certainty.

The subsequent continuous immersion of the gun-cotton for at least three weeks in a stream of water, as directed by Von LENK, is unnecessarily long, as the gun-cotton is afterwards still subjected to treatment with an alkaline water, and to a final washing.

In the manufacturing operations carried on at Waltham Abbey, where only a very slow stream of water was available for the purposes of purification, the period for which the gun-cotton was allowed to remain in the water, after the preliminary washing in the cascade, was in some instances forty-eight hours, in others from ten to fourteen days. There is no question that the latter period was excessive, especially with the improved methods there adopted of exposing the gun-cotton to the purifying action of the water. Indeed there can be no doubt that this first washing is of minor importance, as effecting the ultimate purity of the product, compared to the treatment with alkaline liquid which it receives, and which, according to Von LENK'S directions, consists in boiling the gun-cotton for about fifteen minutes in a solution of potassic carbonate of specific gravity 1·02. The gun-cotton, manufactured nearly three years ago at Waltham Abbey, which was submitted to a first washing of only forty-eight hours, but was washed for a fortnight after treatment with alkali, has proved in every respect equal in permanence to products of more recent manufacture which have been submitted to the long-continued first washing. The curtailment of this washing operation, if compatible with perfect security, would be important, not only on account of the time saved in the manufacture, but also because, if the gun-cotton remains immersed in spring- or river-water in localities where light cannot be perfectly excluded, vegetable growth is speedily established upon it, and the perfect separation from it of extraneous organic matter becomes afterwards a very difficult and time-consuming operation. But, although the perfect permanence, for a period of nearly three years, coupled with very great power of resisting the destructive effects of heat and light, possessed by products in the manufacture of which the long-continued washing was postponed until after the alkaline treatment, warrant the belief that this method of operating secures the proper purification of the product, I have obtained indications, in other manufacturing operations, that a very considerable curtailment of the *total* purification, by washing, which the gun-cotton receives, in addition to the treatment with alkali, somewhat diminishes its power of resisting destructive influences. The omission of the treatment with an alkaline bath affects to a much more decided extent the permanence of the gun-cotton; indeed it is doubtful whether, even if the washing were protracted considerably beyond the full time prescribed by Von LENK, the gun-cutton would be as perfectly purified as it is by being washed only for a short time and then boiled for a few minutes in an alkaline solution.

If it were possible to operate on a large scale upon *pure* cotton fibre, the functions of the alkaline bath, used as a purifying agent, would simply be to neutralize and remove from the pyroxylin any traces of acid not separated by washing. But as it is only possible to submit cotton to very partial purification in manufacturing operations, its treatment with the acid must partially, or completely, convert into oxidized products the small quantities of resinous and other foreign substances still retained by the tubular fibre. An examination of many specimens of gun-cotton has shown that at any rate some of these products, which may be comparatively unstable in character, are much less readily removeable from the gun-cotton by simple washing than the acids with

which it is impregnated; the solvent action of the alkaline bath upon these is therefore very probably one of its most important functions.

As the difficulties attending the perfect removal of the acid with which gun-cotton remains impregnated after its conversion are mainly attributable to the tubular structure of the cotton fibre, and to the circumstance that the latter contracts considerably upon conversion into pyroxylin, the complete purification of the material is very greatly facilitated by reducing the gun-cotton fibre to a fine state of division, similar to that of the pulp used in paper manufacture, in which form it appears likely that gun-cotton will receive advantageous application. By submission to the "pulping" process, the gun-cotton is divided into very minute fragments, and is at the same time violently agitated for some considerable time with a very large volume of water (rendered slightly alkaline if necessary), which is afterwards thoroughly expressed when the pulp is converted into cylinders or other forms; so that a more searching supplementary process of purification can scarcely be conceived than this disintegration of the gun-cotton.

The treatment of the purified gun-cotton with a solution of soluble glass, which constituted a prominent feature in Von LENK'S system of manufacture when the latter first became known in this country, has been shown by SCHRÖTTER, REDTENBACHER and SCHNEIDER, by myself, and more recently by PÉLOUZE and MAURY, to possess no important merits. If gun-cotton, which has been thus treated, has ever been found to resist the destructive effects of exposure to elevated temperatures longer than equally pure gun-cotton to which no silicate has been applied, this must be ascribed to the introduction between the fibres of the gun-cotton of small quantities of substances which would exert a neutralizing action upon minute traces of acid not removed from the gun-cotton by the purifying process, or of any acid liberated or generated by the influence of heat.

Some hydrated calcic and magnesian silicates, produced by the decomposition of the alkaline silicate when the gun-cotton is washed in spring-water after its impregnation with soluble glass and desiccation, and possibly some small proportion of alkaline carbonate and silicates, which have escaped removal in the final washing, may exist in the gun-cotton submitted to the silicating treatment, and may act to some extent as protectives, in the manner pointed out. The examination of Austrian and other specimens of gun-cotton which had been submitted to the silicating process showed that some or all of those substances existed in these in small and variable quantities. But other specimens, such as the general products of manufacture at Waltham Abbey, to which no soluble glass had been applied, but which had remained for many days immersed in somewhat hard water, were found to contain calcic and magnesian carbonates, in proportions sufficient to exert quite as great a protective action as the substances deposited in the gun-cotton by submission to Von LENK'S "silicating" treatment. In the account which I hope before long to give of the action of light and heat upon gun-cotton, it will be shown that the impregnation of the material with small proportions of alkaline or earthy carbonates is likely to prove a very important protective measure; but it need hardly be stated that there are much more simple and certain methods of distributing

such substances uniformly through a mass of gun-cotton than the treatment with soluble glass and subsequent washing. Thus, considerable quantities of gun-cotton have been uniformly impregnated at Waltham Abbey, for experimental purposes, with sodic carbonate (in the proportions of 0·5 and 1 per cent.), simply by soaking the finished gun-cotton in solutions of that substance, of definite strength, expressing the excess of liquid in the usual manner, and then drying the skeins.

It will be seen from the foregoing observations on the Austrian system of manufacture, which are almost exclusively based upon the results of experience in the manufacture of considerable quantities of the material during the last three years, that General Von LENK has not actually initiated any new principle as applied to the production of gun-cotton, but that he has, by long experience and persevering investigation of the subject, so perfected the process of converting cotton-wool into the most explosive form of gun-cotton and of purifying the product, as to render a simple attention to clear and definite regulations alone necessary to ensure the manufacture of a very uniform material, which is unquestionably much more perfect in its nature than the products obtained in the earlier days of the history of gun-cotton. Such being the case, too much stress cannot be laid upon the fact that deviations from the prescribed process, which at first sight may appear very trivial (such as a slight reduction of the strength of the acids, the neglect of proper cooling arrangements, &c.), are certain to lead to variations in the products of manufacture affecting their explosive characters, or their permanence, or both. In discussing the composition of gun-cotton manufactured by LENK'S system, I shall have to refer to several samples of the material, produced at Hirtenberg and at Stowmarket, which differed widely in their composition and properties from the normal product of manufacture. I have obtained abundant and most conclusive proof that these exceptional variations are solely ascribable to the neglect of a uniformly strict adherence to the prescribed process of converting the cotton; and I am strongly of opinion that their occurrence has almost always been due to the employment of nitric acid which exhibited a fictitious specific gravity, from the presence either of considerable quantities of peroxide of nitrogen, or of some other impurity (such as sulphuric acid). A searching examination of the ordinary products of manufacture obtained at Waltham Abbey, where the quality of the nitric acid employed received uniformly strict attention, has shown that, without any exception, the variations in their composition were embraced within very narrow limits.

II.—COMPOSITION OF GUN-COTTON.

The researches instituted by me into the composition of gun-cotton have been conducted partly with ordinary products of manufacture, obtained from Waltham Abbey and from the gun-cotton factories at Hirtenberg and Stowmarket, and partly with products prepared in the laboratory with purified and very finely carded cotton-wool. The latter was more particularly employed in experiments instituted for the purpose of accurately ascertaining the maximum increase of weight which cotton-wool will sustain

by treatment with mixed nitric and sulphuric acids, while the products of ordinary manufacture have been employed in the analytical experiments.

The loosely spun cotton-wool from which these products are obtained varies somewhat in purity, even after the preliminary treatment with alkali and washing which it undergoes previous to conversion. The material, as supplied to Waltham Abbey by the cotton-spinners, always contains seed fragments, which are only very partially removed by the purifying process, but are in most instances completely dissolved or mechanically removed during the processes of conversion and purification. The purified cotton is always considerably inferior in whiteness to the converted material. The loss sustained by the cotton in the treatment with potassic carbonate and subsequent washing, ranged between 5 and 10 per cent. An average sample of the cotton used was submitted to analysis after having been purified in the usual manner. It contained 0·044 per cent. of ash, and the following percentage proportions of carbon and hydrogen:—

	Found.	Cellulose.
Carbon	44·26	44·44
Hydrogen	6·05	6·17
Oxygen	49·69	49·39

Hygroscopic moisture existing in gun cotton.—The amount of water absorbed and retained by gun-cotton under normal atmospheric conditions is very uniform; the average proportion is 2 per cent.; and although gun-cotton will gradually absorb as much as 6 per cent. of water if exposed for a sufficient period to a very moist confined atmosphere, the proportion which it retains upon re-exposure to open air rarely exceeds 2 per cent. This amount is rapidly reabsorbed by gun-cotton, after perfect desiccation *in vacuo* over sulphuric acid.

Mineral constituents of gun-cotton.—The proportion of mineral constituents (or ash) in gun-cotton has been carefully determined in a large number of products of manufacture. The mode of operation consisted in thoroughly moistening the dried and weighed gun-cotton (about 4 grms.) in distilled water, and then projecting it, in small fragments, into a deep platinum vessel of known weight heated to low redness. The decomposition of the gun-cotton under these conditions is so gradual, that there is no risk of the mechanical dispersion of any of the ash. After the combustion of the gun-cotton was completed, the temperature of the vessel was raised sufficiently to burn off minute quantities of carbon which had separated during the slow combustion. The variation in the amount of ash obtained from different samples of gun-cotton manufactured at the same works was but slight; 1 per cent. was the average proportion existing in gun-cotton manufactured at Waltham Abbey. A few samples examined contained a somewhat higher proportion, and some specimens, obtained from Hirtenberg, furnished an average proportion of nearly 2 per cent. An analysis of the ash in these instances indicated that the gun-cotton had been submitted to the "silicating" treatment adopted by LENK. The ash furnished by gun-cotton not thus treated con-

sisted principally of calcic carbonate and other impurities (sand, clay, &c.) deposited between the fibres during the immersion of the gun-cotton in the stream.

Proportion of the gun-cotton dissolved by ether and alcohol.—HADOW found that the highest product which he obtained by the action of nitric and sulphuric acids upon cotton-wool, and the composition of which agreed closely with the requirements of the formula

$$C_6 H_7 O_5, 3N O_2, \text{ or } C_{12} H_{14} O_7, 3N_2 O_5,$$

was perfectly insoluble in any mixture of ether and alcohol; but that the lower products, obtained by the action of acid-mixtures containing larger proportions of water, were more or less readily soluble in ether, used alone or in admixture with alcohol. Although, in operating upon small quantities of carefully purified cotton-wool with a considerable proportion of the acid-mixture, the most explosive gun-cotton can be obtained without difficulty in an almost pure condition (containing only mere traces of matters extractable by ether and alcohol) by one single treatment of the cotton, it could scarcely be expected that, in a manufacturing operation, more than a close approximation to this result could be arrived at, when it is remembered that a considerable time elapses before the action of the acids upon the entire quantity of cotton with which they remain in contact is completed, and that, during the period occupied by the conversion of the last portions of cotton, the acid in contact with the fibres becomes diluted by the water eliminated in the reaction, and does not therefore retain to the last the composition required for the production of the most explosive gun-cotton. But it is remarkable how very close and uniform an approximation to complete conversion of the cotton into the most explosive product is attained by properly carrying out VON LENK'S instructions.

A very large number of the ordinary products from Waltham Abbey have been carefully examined, with the view of determining the average percentage of soluble matter in the gun-cotton. In the first experiments, the weighed gun-cotton (between 2 and 3 grms.) was packed closely into a tube of about 12 millims. diameter and constricted to a fine opening at the lower extremity. The mixture of ether and alcohol which was poured on to the gun-cotton in the tube filtered through it very slowly. When the filtrate furnished what appeared an unimportant quantity of residue, the cotton in the tube was dried and its loss in weight determined. Upon examining the samples of gun-cotton thus treated, they were found, however, still to contain matter soluble in the ethereal mixture, and it was evident that, by this mode of treatment, either the soluble matter could not be separated from the insoluble fibre, or only the most readily soluble portions (which furnish a tolerably limpid solution) were carried through by the liquid; while those less easily dissolved, and which were, indeed, more glutenized than actually dissolved, remained in the tube. A different mode of operating was therefore resorted to. From 8 to 10 grammes of the gun-cotton were digested in a stoppered bottle for from thirty to fifty hours (according to the apparent extent of action of the solvent) with from 60 to 100 centimetres of the ethereal mixture. At the expiration of this

digestion the contents of the bottle were agitated slightly, a small portion of the gun-cotton was removed and placed as a plug in the apex of a funnel, through which the liquid was filtered into an evaporating dish. The gun-cotton was then transferred to a suitable instrument, placed over the funnel, and the liquid expressed; it was afterwards returned to the bottle, in which it was digested for a second (and sometimes a third) similar period with fresh solvent, the washings of the funnel, &c. being returned to the bottle. When the gun-cotton had been two or three times digested and expressed, it was washed upon the funnel. The liquid thus obtained never contained more than two or three minute fibres of the gun-cotton; it was generally of a very pale straw colour, and slightly opalescent. When evaporated nearly to dryness it became gelatinous, and gradually dried to a yellowish substance of somewhat resinous appearance.

The following results were obtained in this manner, a different sample being operated upon in each instance:—

	Description of gun-cotton.	Percentage of soluble matter.
Made in 1863.	Coarse yarn	1·70
,, ,,	Fine yarn	1·33
,, ,,	Coarse yarn	1·91
,, ,,	Fine yarn	1·53
Made in 1864.	Coarse yarn	2·00
,, ,,	,,	2·60
,, ,,	,,	1·81
,, ,,	,,	2·12
,, ,,	,,	2·31
,, ,,	,,	1·99
,, ,,	Fine yarn	2·35
,, ,,	,,	2·25
,, ,,	,,	1·83
,, ,,	,,	2·34
,, ,,	Coarse yarn	1·62
Made in 1865.	,,	2·30
,, ,,	,,	2·22
,, ,,	,,	1·93
,, ,,	,,	2·21
,, ,,	,,	2·22

Mean average of matter soluble in alcohol and ether, from results of examination of twenty samples of ordinary products of manufacture at Waltham Abbey . . . . . 2·03 per cent.

Extreme results obtained . . . . . =1·3 and 2·6 ,,

Soluble matter in gun-cotton prepared by twenty-four hours' treatment with acids . . . . . 1·99 ,,

Soluble matter in gun-cotton prepared by seventy-two hours' treatment with acids . . . . . 2·34 per cent.
Soluble matter in gun-cotton submitted to a second treatment for forty-eight hours with the usual acids . . . . . 2·40 „

Somewhat higher results were obtained by submitting the material to long-continued agitation with ether and alcohol, and repeating the digestion and agitation several times with fresh solvent; but the gun-cotton became so disintegrated by this treatment, that it was very difficult to filter the liquid so as to obtain it free from fibres; it was moreover found that a considerable proportion of the finely-divided mineral matter attached to the gun-cotton became suspended in the liquid and could not be separated. Repeated experiments showed that, after the second digestion of Waltham Abbey gun-cotton, there were only very small quantities of soluble matter extracted, which it appeared almost impossible to remove perfectly by this mode of treatment; the above numbers may therefore be accepted with confidence, as representing a close approximation to the average proportion of matter soluble in ether and alcohol contained in the normal products of gun-cotton manufactured according to Von LENK's prescription.

I was led to submit the products of the Waltham Abbey manufacture to a particularly searching examination, with reference to the proportion of matters extractable by ether and alcohol, because an examination of several of the samples of gun-cotton obtained from the Stowmarket and Hirtenberg factories, furnished results differing considerably from each other and from those obtained with the first Waltham Abbey samples examined.

The following are the proportions of soluble matter found in gun-cotton manufactured in Stowmarket in 1864:—

Specimen.	Per cent.	Specimen.	Per cent.
1	4·0	9	3·68
2	3·2	10	4·24
3	3·41	11	3·34
4	4·10	12	4·65
5	12·55	13	8·50
6	2·85	14	5·10
7	4·10	15	4·07
8	4·35		

The variations exhibited by these numbers, and the comparatively large proportion of soluble matter existing in some of the samples, must unquestionably be ascribed to some irregularity in the treatment with acids, as practised at Stowmarket, due perhaps to exceptional circumstances existing at the time these samples of gun-cotton were manufactured; the examination of several products of more recent date obtained from Stowmarket, has furnished much more uniform results, the majority of which correspond nearly to those obtained with the Waltham Abbey gun-cotton.

Several of the specimens of gun-cotton obtained from Hirtenberg were also found to contain comparatively large quantities of soluble matter, and the proportions in two or three samples were very high. The following are the results obtained with those which differed from the Waltham Abbey products:—

Specimen	Per cent.	Specimen.	Per cent.
1	8·60	6	14·21
2	7·44	7	3·02
3	14·10	8	3·66
4	5·02	9	5·32
5	4·50		

Another Austrian specimen* contained so high a proportion soluble in alcohol and ether that the yarn was entirely broken up by a brief digestion with the solvent; a large quantity of nearly transparent solution was separated from it, but the proportion of gun-cotton remaining insoluble could not be determined with any accuracy. A few other specimens of Hirtenberg gun-cotton corresponded closely to the Waltham Abbey products, as regards the proportion of soluble matter they contained.

The character of the soluble matter extracted from the Waltham Abbey products by ether and alcohol was very uniform.

The dry extracted matter, when digested with hot alcohol alone, dissolved to a very considerable extent, and a light yellow solution was obtained, which, on evaporation, furnished a yellow amorphous residue, almost entirely soluble in ammonia or sodic carbonate; the neutral liquids furnishing precipitates with lead- and silver-solutions. When the substance was heated with potassic hydrate, ammonia was evolved. When gradually exposed to heat on platinum or bibulous paper, it first fused and then deflagrated. The portion insoluble in alcohol dissolved in the ethereal mixture, the solution furnishing on evaporation a semiopake film, which contracted and split up into small horny particles when quite dry. The extracts from Stowmarket and Hirtenberg gun-cotton contained the same product soluble in alcohol alone, and generally in about the same proportion; but in most of those instances in which the specimen had furnished a considerable proportion of soluble matter, the part insoluble in alcohol yielded by solution in ether and alcohol, a liquid which approached in its character to photographic collodion; the film left by its evaporation being more or less tough, and nearly transparent. In two instances very good photographs were obtained with the collodion extracted from specimens of Austrian gun-cotton.

* This specimen, when I received it, was in distilled water, in which it had been preserved for twelve months. It need hardly be stated that the great solubility of the gun-cotton could not be ascribed to its having been thus preserved. The water containing it was perfectly neutral, and the gun-cotton exhibited no signs of having undergone change since its manufacture. A sample of Waltham Abbey gun-cotton, in which the soluble matter had been determined, was placed by me in distilled water at the time that the specimen above referred to was received. It has since been examined, having been in the water fifteen months, and was found perfectly unchanged.

The proportions of matter soluble in alcohol alone, and in the ethereal mixture, were successively determined in a few samples of gun-cotton, and furnished the following results:—

Description of gun-cotton.	Alcoholic extract. Per cent.	Ethereal extract. Per cent.		Total soluble matter.	Result obtained by direct extraction with ether and alcohol. Per cent.
Waltham Abbey, 1863 . .	0·75	1·31	=	2·06	1·91
„ 1864 . .	0·72	1·35	=	2·07	1·93
„ „ . .	0·95	1·48	=	2·43	2·21
„ „ . .	0·90	1·42	=	2·32	2·60
Stowmarket . . „ . .	0·78	1·18	=	2·96	3·00
„ exceptional . .	0·95	11·78	=	12·73	12·55

The foregoing results show that, in the general products of manufacture obtained by properly following Von LENK'S instructions with regard to the conversion of the cotton, the proportion extracted by alcohol alone is somewhat below 1 per cent., and consists of nitrogenized matter, of acid character, which has evidently been produced by the action of nitric acid upon the resinous or other foreign substances contained in the cotton at the time of its conversion. The portion soluble in ether and alcohol, but insoluble in spirit, varies in amount between 1 and 2 per cent., and consists of the very small proportion of gun-cotton which has escaped conversion into the most explosive product. The occurrence, in a few quite exceptional instances, of comparatively large proportions of soluble gun-cotton, of the kind produced by the action of a warm somewhat dilute acid mixture upon cotton, affords important evidence of the necessity for adhering strictly to the mode of treatment, and the precautions, which considerable experience and a careful examination of products have proved to be indispensable to the attainment of uniform results in the manufacture of gun-cotton.

With regard to the matter soluble in ether and alcohol found to exist in gun-cotton, the following observations possess some interest, as bearing upon the cause of its production in the manufacture of the substance.

1. The mean proportion of soluble matter furnished by the very concordant results of examination of gun-cotton manufactured at Waltham Abbey in 1863, in the preparation of which the acids, left in contact with the gun-cotton, were in the proportion of 18 parts by weight to 1 of cotton, is 1·62 per cent.; while the mean proportion furnished by the results of examination of sixteen samples of Waltham Abbey products, in the manufacture of which only 10 parts of the acids were left in contact with the gun-cotton, is 2·13 per cent. All the results obtained with the first gun-cotton were below 2 per cent., while out of sixteen results, obtained with the last, eleven were above 2 per cent. Here we have a decided indication that the prolonged contact with acid has some influence upon the composition of the product; the employment of the higher proportion of acid furnished results more nearly approaching perfection than those when the gun-cotton was left in contact with a smaller proportion of the acid mixture. As far as can

be judged at present, however, from the general properties of the products, the difference observed when the larger or the smaller proportion of acid is used, is not of sufficient importance to render necessary the consumption of the larger quantity of acid in the manufacture.

2. The following experiment was instituted with a portion of one of the specimens of gun-cotton from Stowmarket, which had been found to contain 11·5 per cent. of matter soluble in ether and alcohol (after removal of the portion soluble in alcohol only). The gun-cotton, having been perfectly dried and carefully weighed, was digested for three hours with mixed nitric and sulphuric acids, of the kind always employed. It was afterwards submitted to long-continued washing with distilled water; precautions being taken to prevent mechanical loss. The dry gun-cotton was found to have increased in weight 0·3 per cent. But the original gun-cotton contained 1·71 per cent. of mineral matter, while, after having been digested with acids and washed, it furnished only 1·01 per cent. of ash. The difference between these numbers had therefore to be added to the increase in weight which the gun-cotton sustained by this second treatment with acids, which consequently amounted to 1 per cent. The substance now no longer contained any appreciable amount of soluble matter. Assuming that the soluble gun-cotton originally existing in the sample was either one of those whose composition has been determined by HADOW,

$$(C_{18}H_{22}O_{15},\ 8N\,O_2,\quad \text{or}\quad C_{18}H_{23}O_{15},\ 7N\,O_2),$$

the increase sustained by the imperfect sample, if completely converted into the most explosive and insoluble product, should have amounted in the one instance to 0·61 per cent., and in the other to 1·29 per cent. Considering that neither of these substances would be likely to exist alone in the imperfectly converted material, the actual increase of 1 per cent., sustained by the gun-cotton, must be regarded as a close approximation to the theoretical proportion of imperfectly converted gun-cotton, and proves decisively that, on the one hand, the treatment of the cotton with the acids had not in the first instance been quite perfect, while on the other a further digestion of imperfectly converted gun-cotton with acids will convert soluble gun-cotton which it contains, into the most explosive or insoluble variety.

Determination of the carbon, hydrogen, and nitrogen contained in gun-cotton.—The difficulties which attend the application of the ordinary analytical methods to determining the composition of so highly explosive a substance as pyroxylin, need scarcely be dwelt upon. Several special methods of proceeding have been pointed out by different experimenters; and others have been elaborated in the course of these researches; but even the most simple and perfect require great care and some experience in their employment, for the attainment of trustworthy results. The following is a brief account of the most successful methods tried for determining the carbon, hydrogen, and nitrogen, and of the results which each has furnished.

In the majority of instances the specimens of gun-cotton analyzed were ordinary products of manufacture. The material operated upon was always purified as far as pos-

sible, by repeated digestion and washing, from matters soluble in ether and alcohol; and, in calculating the results, allowance was made for the mineral constituents of the gun-cotton operated upon.

Carbon determinations. Method I.—The gun-cotton yarn was cut into small pieces, dried, and the fragments introduced singly into a very long combustion-tube, each portion being separated from the next by about 5 centimetres of oxide of copper. When the tube had received the entire quantity to be burned, about 15 centimetres of the anterior portion were filled with oxide of copper, and the remainder (about 20 centimetres) with porous fragments of reduced copper. The potassa-apparatus, used for absorbing carbonic acid, had a small chloride-of-calcium tube attached to it, which was weighed together with the apparatus, before and after the combustion. Although the greatest care was taken to proceed as slowly as possible with the heating of those portions of the tube containing the gun-cotton, the successful completion of the operation was a matter of great uncertainty, as the explosive combustion of some small portion of the gun-cotton would very frequently throw the surrounding oxide of copper forward, thus closing the necessary passage in the front part of the tube. This method was therefore abandoned after about two dozen experiments had been made, of which only four were brought to a satisfactory termination. The results of these were as follows:—

	Substance employed.	Carbon found.	
I.	0·2219 grm.	23·71 per cent.	Mean 24·02 per cent.
II.	0·3204 „	24·00 „	
III.	0·3790 „	24·26 „	
IV.	0·1996 „	24·12 „	

Method II.—The weighed substance was saturated with distilled water, and the latter removed as far as possible by pressure. The moist yarn was then cut into eight or ten pieces and introduced separately into one end of a long combustion-tube open at both extremities, and divided in the centre by a plug of asbestos. The shorter portion of the tube contained only the fragments of gun-cotton placed at distances of about 12 millimetres from each other; the longer portion was previously filled with long layers of oxide of copper, oxidized copper turnings, and porous reduced copper. This part of the tube was connected with a desiccating apparatus, to which were attached the potassa-bulbs with the small weighed chloride-of-calcium tube, fixed on to the outer limb. The extremity of that part of the combustion-tube which contained the gun-cotton was connected with an arrangement for passing an easily regulated current of pure dry air through the apparatus. The two portions of the tube were separated in the furnace by a screen. When the front part of the tube had been raised to a full red heat (at which it was maintained throughout the operation), the pieces of gun-cotton were consecutively made to undergo slow combustion, the portion nearest the asbestos plug being first heated, and the resulting gases and aqueous vapours being carried forward by the slow current of air continuously passed through the apparatus. This passage of air served

to oxidize minute portions of carbon separated from the gun-cotton, when the whole tube was raised to a red heat at the close of the operation. The proportion of reduced copper employed was so regulated, that a considerable quantity remained unoxidized at the conclusion of the experiment. Great care was required in the application of heat to the parts of the tube containing the moist gun-cotton, there being otherwise considerable risk of its fracture by the water expelled from the heated substance.

The following are the results of eight carbon determinations made by this method in different specimens of gun-cotton manufactured in 1863. The quantities of material operated upon ranged from 0·2634 grm. to 0·4115 grm.

24·29 per cent.	24·35 per cent.	Mean = 24·42 per cent.
24·58 „	24·59 „	
24·66 „	24·11 „	
24·52 „	24·18 „	

Method III.—A weighed quantity of gun-cotton, moistened as in the preceding experiments, was placed in a capacious strong Bohemian glass tube, sealed at one end; a small quantity of oxide of copper was introduced into the tube just in front of the gun-cotton. The other extremity of the tube was now constricted, and was sealed when the air in the tube had been exhausted. Heat was then carefully applied to the sealed tube until the gun-cotton had undergone slow combustion, and the oxide of copper was afterwards shaken to that part of the tube where a minute carbonaceous deposit had been left by the gun-cotton. The tube was placed in a gas-furnace and connected at one end with an apparatus for delivering pure air and oxygen, and at the other with a long combustion-tube, in a separate furnace, containing layers of oxide of copper and porous reduced copper, to which were attached a large chloride-of-calcium tube and the potassa-apparatus. The two Bohemian tubes were connected by a narrow india-rubber tube, about 12 centimetres long, fitted with a screw clamp, so that communication between the tubes could be cut off or gradually increased. The long tube having been raised to a red heat, the point of the sealed tube which was enclosed in the caoutchouc connexion was broken, and the confined gases were allowed to pass gradually over the heated oxide of copper and metal. When no further escape of gas from the tube took place, the other extremity, connected with the apparatus for delivering air, was broken, and the whole of the products of decomposition of the gun-cotton were gradually conveyed into the heated tube. Pure oxygen was finally passed through the apparatus, and the tube in which the gun-cotton had been burned was heated to redness.

The gun-cotton for these experiments was taken from various products of Waltham Abbey manufacture obtained in 1863 and 1864; the quantity employed varied between 0·2257 grm. and 0·39 grm. The following proportions of carbon were obtained:—

23·85 per cent.		24·06 per cent.	Mean 24·15 per cent.
23·90	,,	24·57	,,
23·91	,,	24·12	,,
24·26	,,	24·60	,,
24·15	,,		

Method IV.—The gun-cotton was reduced, by cutting, to an extremely fine state of division, and mixed when dry as intimately as possible with a very large proportion of chromate of lead, in the first few experiments, and of finely-divided oxide of copper in the remainder. Long layers of oxide of copper and porous reduced copper were employed as usual, and at the close of the combustion a current of pure oxygen, and finally pure air, was passed through the tube. With care and some experience, the combustion of the substance was brought perfectly under control by this comparatively simple method of proceeding; in a few instances, however, the operation was terminated prematurely by the stopping up of the tube, in consequence of the explosive combustion of a small accumulation of the finely-divided gun-cotton.

The following are the results obtained in carbon determinations with different specimens by this method. (The quantity of substance varied between 0·2263 grm. and 0·4839 grm.)

Coarse yarn, made in 1863.

Carbon found.			
24·88 per cent.		24·36 per cent.	
24·04	,,	24·67	,,

Coarse yarn, made in 1864.

Carbon found.			
24·67 per cent.		24·37 per cent.	
24·64	,,	24·52	,,
24·48	,,	24·54	,,
24·66	,,	24·70	,,

Medium yarn, made in 1864.

Carbon found.			
24·54 per cent.		24·46 per cent.	
24·69	,,	24·70	,,
24·87	,,	24·61	,,
24·76	,,	24·78	,,

Fine yarn, made in 1864.

Carbon found.			
24·34 per cent.		24·39 per cent.	
24·39	,,	24·66	,,
24·21	,,	24·23	,,
24·31	,,	24·75	,,

Mean result of 28 determinations=24·57 per cent.

The several mean results arrived at by the four different methods employed for determining the carbon in gun-cotton, manufactured by Von LENK's process, are 24·02, 24·42, 24·15, and 24·57; the mean of 49 determinations is therefore 24·29. But the results, upon the accuracy of which the most perfect reliance is to be placed, are unquestionably those furnished by the fourth method, which ranged between 24·04 and 24·88 per cent., the mean being 24·57 per cent.

Determination of Hydrogen.—The hydrogen was determined at the same time as the

carbon, by the method of operating last described. The results of all the combustions (eight in number), conducted with different samples of gun-cotton yarn, were so remarkably uniform, that they were regarded as furnishing ample numerical data, with respect to this constituent element. The following were the proportions of hydrogen found:—

2·41	per cent.	2·56	per cent.	Mean 2·46 per cent.
2·46	,,	2·44	,,	
2·40	,,	2·47	,,	
2·55	,,	2·44	,,	

Determination of Nitrogen.—The method of DUMAS was employed for determining, by volume, the proportion of nitrogen contained in gun-cotton. A rather wide combustion-tube, about 82 centimetres long, was drawn out at one end so as to admit of being connected with a carbonic acid apparatus provided with a regulating tap; and was fitted at the other end with the usual form of delivery tube. 5 centimetres of the tube were first filled with coarse porous fragments of oxide of copper, a layer of 3 centimetres of fine oxide of copper followed, and then the very finely cut gun-cotton, mixed with a large proportion of oxide of copper; the mixture occupying about 25 centimetres of the tube. The next 22 centimetres were filled partly with coarse porous oxide of copper, and partly with finely powdered oxide; a layer of 20 centimetres of reduced copper followed, and finally, the tube was plugged with coarse porous oxide, occupying a length of about 5 centimetres. The combustion was conducted very slowly, with the usual precautions, pure carbonic acid being passed through the apparatus for the requisite period before commencing, and at the conclusion. The gas collected was found, in one instance only, to contain traces of nitric oxide, and this determination was consequently rejected. The quantity of substance operated upon varied between 0·3006 grm. and 0·415 grm. The following are the percentage proportions of nitrogen calculated from the corrected volumes of gas observed:—

Description of gun-cotton.	Nitrogen found.	Description of gun-cotton.	Nitrogen found.
Coarse yarn, made in 1863	13·36 per cent.	Coarse yarn, made in 1864	13·60 per cent.
	13·79 ,,		13·68 ,,
Fine yarn, made in 1864	13·44 ,,		13·63 ,,
	13·71 ,,		13·79 ,,
	13·58 ,,		13·78 ,,
	14·30 ,,		14·03 ,,
Medium yarn, made in 1864	14·60 ,,		14·20 ,,
	14·26 ,,	Medium yarn, made in 1864	13·97 ,,
	13·59 ,,		13·73 ,,

The results of these eighteen analyses of various products from Waltham Abbey ranged, therefore, between 13·36 and 14·60, and give the number 13·83 as the mean percentage of nitrogen contained in the material.

Deductions from the Analytical Results.—The formula adopted by HADOW, as representing the most explosive product of the action of mixed nitric and sulphuric acids upon cellulose,—which is the same as that first suggested for gun-cotton by W. CRUM, afterwards adopted as probable by GERHARDT, and recently supported by SCHRÖTTER, REDTENBACHER, and SCHNEIDER,—demands the following percentage proportions of its constituent elements:—

$$C_6 H_7 N_3 O_{11} = C_6 \left\{ \begin{matrix} H_7 \\ 3N O_2 \end{matrix} \right\} O_5.$$

Carbon	72	24·24
Hydrogen	7	2·36
Nitrogen	42	14·14
Oxygen	176	59·26
	297	100·00

The formula recently adopted by PÉLOUZE and MAURY, as agreeing closely with the results which they obtained in their experiments, requires the following numerical proportions:—

$C_{24} H_{18} O_{18}$, $5N O_5$, or $C_{24} H_{36} O_{18}$, $5N_2 O_5$.

Carbon	288	25·00
Hydrogen . . .	36	3·13
Nitrogen	140	12·15
Oxygen	688	59·72
	1152	100·00

The following statement shows the relation which the extreme and mean results, obtained in the numerous analytical examinations of gun-cotton manufactured at Waltham Abbey, bear to the two above formulæ:—

Trinitro- or trinitric cellulose.		Results of analysis. Extremes.		Means.	Formula of PÉLOUZE and MAURY.
Carbon . .	24·24	23·71	24·26	24·02	25·00
		24·11	24·59	24·42	
		24·06	24·60	24·15	
		24·21	24·78	24·57	
Hydrogen .	2·36	2·40	2·47	2·46	3·13
Nitrogen . .	14·14	13·36	14·60	13·83	12·15
Oxygen . .	59·26				59·72

In comparing the experimental results with the requirements of the two different formulæ, it is necessary to bear in mind the following circumstances:—

1. The gun-cotton examined has not been obtained from *pure* cellulose (for the production of which the most elaborate system of purification has been proved to be

necessary), but has been prepared from cotton separated from foreign matters as far as it is possible by the ordinary method of purification adopted.

2. Ample proof has been furnished, by most extensive and rigorous experiments, of the invariable existence in the purified gun-cotton (as produced by the most complete action of the strongest acids upon cotton-wool, purified by treatment with alkali and washing) of notable proportions of substances which owe their existence to the presence of foreign matters remaining in the cotton fibre after its ordinary purification, and also of products resulting from the less perfect action of nitric acid upon small portions of the cellulose.

3. Although these two varieties of impurities were extracted as far as possible by repeated digestion and washing with ether and alcohol, from the pyroxylin analyzed, their perfect removal from the fibre, by the application of any feasible method of purification, is extremely difficult, if not impossible.

4. The existence of even small proportions of these impurities in a sample of pyroxylin will have the effect of raising somewhat the percentage of carbon, obtained by analysis of the substance, above that which would be furnished by the pure material, and also, consequently, of reducing to a trifling extent the proportion of nitrogen obtained, below the theoretical requirement.

A proof of this is furnished by the analytical results obtained with specimens of the matter soluble in ether and alcohol, which had been extracted from Waltham Abbey gun-cotton.

These results are as follows:—

	Carbon.	Hydrogen.	Nitrogen.
Specimen 1	30·50	2·91	
Specimen 2	29·18 29·28		11·85
Mean results furnished by the gun-cotton after digestion with ether and alcohol	24·15	2·46	13·83

It is believed that the foregoing circumstances must be admitted to account perfectly for the slight variations exhibited, among themselves, by the numerous analytical results which have been quoted. The whole of the carbon-percentages obtained by the most trustworthy method of analysis (Method IV.) are somewhat higher, and the great majority of the results of the nitrogen determinations are a little lower than required by the formula

$$C_6\left\{\begin{matrix} H_7 \\ 3NO_2 \end{matrix}\right\}O_5, \text{ or } C_{12}H_{14}O_7, 3N_2O_5.$$

On the other hand, making even very full allowance for errors of analysis, and assuming for an instant the possibility that the substance analyzed could be an absolutely pure product, the individual as well as the mean results of the carbon, hydrogen, and nitrogen determinations, are far more closely in accordance with those theoretical requirements, than with the percentage results which should be furnished by a pure

substance having the composition more recently assigned to pyroxylin by PÉLOUZE and MAURY, viz.,

$$C_{24}H_{36}O_{18}, 5N_2O_5.$$

The analytical results of gun-cotton manufactured at Waltham Abbey according to Von LENK'S directions confirm, therefore, the correctness of the conclusions that the most explosive known variety of gun-cotton is *trinitro-cellulose* or *trinitric cellulose*; and that cotton-wool is converted into this substance by the complete action upon it, in the cold, of a mixture of one part by weight of nitric acid of specific gravity 1·52, and three parts of sulphuric acid of specific gravity 1·84.

In addition to the data furnished by the analytical experiments described in the foregoing, others, bearing upon the composition of gun-cotton, have been furnished by different systems of experimental inquiry.

The relation between the nitrogen and carbonic acid obtained by oxidation of gun-cotton has been determined. For this purpose, LIEBIG'S method of operating was adopted in the first instance; the gun-cotton being prepared and arranged for combustion as in the case of the nitrogen determinations, and the mixed gases collected in successive proportions and examined*. A few experiments rendered it evident, however, that this method, when applied to the examination of gun-cotton, did not furnish trustworthy results. In the decomposition of this substance, when distributed through a very large proportion of oxide of copper, the oxidation of the carbon does not proceed uniformly; small portions of that element evidently escape oxidation in the first instance, and are only subsequently burned when the nitrogen has already been in great proportion liberated. The proportion which the carbonic acid bears to the nitrogen in the gases successively collected varies therefore, frequently, as the combustion proceeds; and it would consequently be necessary to collect the entire quantity of gases furnished by the gun-cotton operated upon, in order to arrive at a correct result.

The following statement of the relative proportions by volume of the gases collected successively in two operations of this kind, will serve to illustrate the variable composition of the gas collected at successive stages of one and the same operation. In both experiments the gas had been allowed to escape for some time, before the first collection, for expulsion of the air in the combustion-tube.

Experiment I.

	Carbonic acid.	Nitrogen.
1st tube.	80	20
2nd „	78·75	21·25
3rd „	79·29	20·71
4th „	79·15	20·85
5th „	83·42	16·58

Experiment II.

	Carbonic acid.	Nitrogen.
1st tube.	77·45	22·55
2nd „	79·76	20·24
3rd „	79·45	20·55
4th „	79·83	20·17
5th „	78·56	21·44
6th „	77·06	22·94

* This method of examination appears, from the description given in their report, to have been the one adopted by PÉLOUZE and MAURY in their determinations of the relative proportions of carbonic acid and nitrogen furnished by gun-cotton.

The majority of results obtained in each of the above experiments are concordant among themselves, and agree closely with the percentage proportions (by volume) of carbonic acid and nitrogen which should be furnished by trinitro-cellulose (namely 80 of carbonic acid to 20 of nitrogen). But in each experiment somewhat discordant results were obtained, and therefore this method of determining the relation between the carbon and nitrogen in gun-cotton was abandoned as not sufficiently trustworthy. It should be observed, however, that even the mean of the several results obtained in each experiment corresponds much more closely with the volume-proportion which should be furnished by trinitro-cellulose, than with that demanded by the formula which PÉLOUZE and MAURY adopt, as the following comparison shows:—

	Theory.		Experiment.	
	$C_{24}H_{36}O_{18}5N_2O_5$	$C_6H_7O_5 3NO_2$	1.	2.
Nitrogen . .	17·2	20	21·28	19·88

Several determinations of the relative proportions of carbonic acid and nitrogen have been made by BUNSEN'S method. The mode of operating was as follows: into a very stout wide Bohemian glass tube, about 22 centimetres long and sealed at one end, were introduced, first some reduced copper, then about 0·1 to 0·15 grm. of the dry gun-cotton, and afterwards sufficient oxide to fill about 4 centimetres of the tube. The open extremity of the latter was constricted, and sealed when air had been exhausted. The gun-cotton was then decomposed by applying the flame of a lamp for a short time to the tube. After the oxide of copper had been distributed over the surface of the tube (to the interior of which it adhered, in consequence of the deposition of water from the exploded gun-cotton upon the glass), the latter was introduced into a vessel of wrought iron, within which it was compactly surrounded on all sides by very fine sand. The vessel consisted simply of a piece of gas-pipe about 25 centimetres long and of 3 centimetres internal diameter, closed at one end by means of a plug welded into it, and provided at the other extremity with a screw-cap. A few small perforations were drilled into the sides of the pipe. The glass tube was exposed in this envelope to a red heat for about one hour; when cold, it was opened under mercury, and the gas transferred and examined in the usual manner. The results thus arrived at, which will be quoted presently, were very concordant, and stood in close relation to the results obtained by the separate determinations of carbon and nitrogen in gun-cotton.

The reproduction of cotton from pyroxylin by HADOW'S method has been made the subject of many experiments, with the view of controlling by its means the analytical and synthetical results obtained. It was found that by submitting purified insoluble gun-cotton to the action of an alcoholic solution of potassic sulphhydrate, as directed by HADOW, the amount of cotton obtained corresponded closely to the theoretical proportion to be furnished by trinitro-cellulose.

The following results may be quoted as examples. They were obtained with gun-

cotton which contained only small proportions of matter soluble in ether and alcohol. From 4·064 grms. to 4·898 grms. of substance were employed.

Description of gun-cotton.	Cotton obtained.	Cotton to be furnished by trinitro-cellulose.
Austrian, coarse yarn	55·24 per cent.	
,, ,, ,, ...	55·08 ,,	
Waltham Abbey, coarse . . .	55·38 ,,	
,, ,, fine	55·30 ,,	
Laboratory products, No. 1 . .	54·22 ,,	54·54 per cent.
,, ,, No. 2 . .	54·48 ,,	
,, ,, No. 3 . .	54·85 ,,	
,, ,, No. 4 . .	54·16 ,,	
,, ,, No. 5 . .	53·64 ,,	

In conducting experiments on this method of examination, a liability to mechanical loss was observed when a very strong solution of the potassic sulphhydrate was employed, in consequence of the fibre becoming to a considerable extent disintegrated during the digestion; but this can be easily avoided by employing the reagent in a more dilute form. The solution best adapted for effecting the complete reduction of gun-cotton by digestion in the cold without breaking up the fibre, was obtained by preparing a saturated solution of potassic hydrate, completely saturating this with sulphhydric acid, and diluting the liquid thus obtained with half its volume of alcohol.

A small loss of product occurs generally, even when the sulphhydrate-solution is not stronger than just described, in consequence of a feeble solvent action exerted by the liquid upon the *reduced* cotton*. In one experiment a sample of cotton obtained from gun-cotton sustained a loss of 0·6 per cent. by digestion in the cold for forty-eight hours with the sulphhydrate.

A slight excess (about 0·5 per cent.) is sometimes exhibited by the weight of the reduced cotton over the amount which should be furnished, theoretically, by pure trinitro-cellulose. In order to ascertain how far this might be ascribed to the retention of sulphur by the cotton under treatment, a very careful examination of several specimens was instituted. A faint odour of sulphurous acid was sometimes observed when the reduced cotton was burned, and in two or three instances the cotton sustained a slight loss (from 0·1 to 0·3 per cent.) upon being digested and washed with carbonic bisulphide; but in other instances the proportion present was only very minute, and the cotton was generally found to be quite free from sulphur.

A comparison between the ash existing in the gun-cotton operated upon, and the quantity remaining in the reduced cotton, showed that no proportion of an excessive result can be ascribed to an accumulation of that constituent. Although the amount of

* Cotton, in the original form of carded wool, is not dissolved by the potassic sulphhydrate.

gun-cotton operated upon is about double that of the cotton recovered, the latter was found to contain the smallest proportion of ash. Thus,

Expt.	Gun-cotton employed contained	Cotton obtained contained
1.	1 per cent.	0·56 per cent.
2.	1 „	0·74 „

It is evident that the mineral impurities which, during the washing operations, have attached themselves to the gun-cotton fibre, become partially detached during the digestion in potassic sulphhydrate, and the subsequent washing.

Some combustions made of the reduced cotton furnished proportions of carbon and hydrogen which, though according fairly with the requirements of pure cellulose (allowance being made for the ash in the specimens analyzed), were somewhat below the theoretical numbers:—

	Experiment 1.	Experiment 2.	Cellulose.
Carbon . . .	43·98	43·85	44·44
Hydrogen . .	6·11	6·15	6·17

The specimens analyzed were carefully examined for nitrogen, and very small quantities were detected. The deficiencies of the carbon obtained from them may, therefore, be to a slight extent ascribable to minute portions of the nitro-product having escaped reduction. A still greater influence upon the results must, however, be exerted by the invariable existence of small quantities of foreign organic substances in the samples operated upon.

The slight excess obtained, in many instances, above the theoretical amount of cotton may, it appears, be occasionally due to some extent to accidental causes, but it is mainly to be ascribed to the presence in the specimen examined of a proportion of material resulting from the less perfect action of nitric acid upon some portions of the cotton fibre. Unfortunately, however, the fluctuations in the results which may be furnished by different examinations of the same specimen of gun-cotton by this method, though they might be regarded as not very important in an ordinary analytical process, may be equivalent to differences which would be caused by very considerable variation in the amount of soluble gun-cotton present in the substance.

The proportions of cotton which should be furnished by pure trinitro-cellulose, and by the lower products which HADOW has examined, are as follows:—

		Cotton.
$C_6H_7O_5$, $3NO_2$, or $C_{18}H_{21}O_{15}$, $9NO_2$	furnishes	54·54 per cent.
Compound B . .	$C_{18}H_{22}O_{15}$, $8NO_2$ „	57·45 „
Compound C* . .	$C_{18}H_{23}O_{15}$, $7NO_2$ „	60·67 „

* A product possessing the properties of compound C, described by HADOW, and agreeing closely in its composition with the requirements of the formula assigned to that body, has been manufactured in considerable quantities at Waltham Abbey, for experimental purposes, by submitting cotton-yarn to digestion for the customary

Supposing that the matter soluble in ether and alcohol in a specimen of gun-cotton amounted to 2 per cent., and consisted of the compound C, the result of the analysis should be affected by that impurity to the extent of about 0·1 per cent. An excess of 0·5 per cent. obtained in the examination of a sample should therefore indicate the existence of 10 per cent. of compound C (readily soluble gun-cotton) in the sample; or if the specimen contained that percentage of compound B, this would only affect the result by 0·3 per cent. It cannot be confidently asserted that the errors of the method itself are ever less than from 0·3 to 0·5 per cent.

It is evident, therefore, that this method of examining gun-cotton, though useful as a mode of controlling the results obtained by determining the increase of weight which cotton sustains by treatment with nitric acid, under varied circumstances, is not susceptible of affording sufficiently definite and trustworthy results to render it applicable as a method of ascertaining the degree of freedom from soluble gun-cotton, of products of manufacture.

Experiments on the increase sustained by cotton in its conversion into gun-cotton.—HADOW found that cotton-wool, by treatment with the strongest mixture of nitric and sulphuric acids, sustained an increase of 81·34 per cent., that the gun-cotton produced was quite insoluble in mixtures of ether and alcohol, and that the increase of weight which cellulose should sustain by conversion into the trinitro-cellulose agreed very nearly with the results of his experiment.

PÉLOUZE'S earlier experiments fixed the *maximum* increase in weight sustained by cotton upon conversion into gun-cotton at 76 per cent. But in the recent report of PÉLOUZE and MAURY it is stated that, in a number of laboratory experiments in which the composition of the acid-mixture, the proportions borne by the acid used to the cotton treated, and the duration of the treatment, were variously modified, the increase in weight of the cotton fluctuated within narrow limits, and did not exceed 78 per cent. The authors are led, mainly by these results, to adopt the formula

$$C_{24}H_{36}O_{18}, 5N_2O_5,$$

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period with an acid-mixture which differed from that employed in the manufacture of insoluble gun-cotton, in containing $3H_2O$ in addition.

The substance possessed feeble explosive properties, was readily soluble in ether and in glacial acetic acid, with the exception of a small proportion of foreign matter, which rendered the solution slightly turbid. The results obtained by determinations of carbon and nitrogen in the substance corresponded very closely to the proportions which should be furnished by $C_{18}H_{23}O_{15}, 7NO_2$, as the following comparison shows:—

		Theory.		Experiment.		
Carbon . . .	18 =	216 =	26·97	27·08	27·01	27·17
Nitrogen . . .	7 =	98 =	12·23	12·42	12·41	
Hydrogen . .	23 =	23 =	2·87			
Oxygen . . .	29 =	464 =	57·93			
		801	100·00			

because cellulose, by conversion into a substance having the percentage-composition which that formula demands, should sustain an increase of weight of 77·78; a number which is very slightly *below* the maximum result obtained in their experiments.

It should be stated that they describe the acids employed by them in all their experiments as follows: the sulphuric acid had a density of 66° BAUMÉ (which corresponds to a specific gravity of 1·767), and the nitric acid had a specific gravity of 1·50 at 9° C.

It will be observed that these acids, but more especially the sulphuric acid, are very notably inferior in strength to those prescribed by Von LENK, which have been used in all the experiments now described, and are always employed in the manufacture of gun-cotton at Waltham Abbey; namely, sulphuric acid of specific gravity 1·833 to 1·84 (somewhat above 69° BAUMÉ), and nitric acid of specific gravity 1·52 at 15° C. It appears most probable, from many of the experimental observations included in these researches, that such discrepancies as exist between the results arrived at by PÉLOUZE and MAURY, and by HADOW, the German chemists and myself, are to be mainly ascribed to the differences in the strength of acids employed.

The subjoined results of very numerous experiments will, I believe, be admitted not only to establish satisfactorily the correctness of HADOW's statement, that cotton-wool may be made to sustain an increase in weight above 81 per cent., but also to show that the results of other experimenters who have found the increase sustained by cotton not to exceed 78 per cent., are in perfect harmony with the conclusion that the product of the complete action, upon cotton-wool, of certain mixtures of the strongest nitric and sulphuric acids, *is the substance*

$$C_6 H_7 N_3 O_{11},$$

in a nearly pure condition.

The following statement shows the increase of weight which finely carded cotton-wool of very high quality, previously purified by treatment with alkali and washing, has sustained by single and successive digestions, for different periods, with the prescribed acid-mixture. The products were always purified by careful washing with distilled water.

No. of experiments.	Quantity of cotton operated upon.	Proportion of acid to cotton.	Duration of treatment.	Temperature of acid used.	Increase in weight on 100 of cotton.
1	3·704 grms. submitted to six successive treatments.	From 60 to 70 parts of acid to 1 part of cotton.	1st treatment, 1 hour.	15° C.	79·40
			2nd treatment, 3·5 hours.	,,	79·96
			3rd treatment, 18 ,,	,,	80·26
			4th treatment, 18 ,,	,,	82·13
			5th treatment, 48 ,,	,,	81·28
			6th treatment, 48 ,,	,,	80·26
2	3·087 grms.	50 to 1	48 hours.	,,	81·86
3	1·132 grm.	,,	24 ,,	,,	82·57
4	1·263 ,,	,,	24 ,,	,,	82·04
5	1·083 ,,	14·6 to 1	24 ,,	,,	80·07
6	3·222 grms.	10 to 1	48 ,,	,,	78·79
7	1·907 grm.	10 to 1	12 ,,	,,	78·13
8	2·468 grms.	50 to 1	10 minutes.	,,	62·43
9	1·668 grm.	50 to 1	15 ,,	55° C.	78·98

Experiment 1 shows that a repeated immersion of the gun-cotton in a fresh mixture of the acids raised the weight of 100 parts of cotton to 182·13, a number somewhat higher than that obtained by HADOW; but that, by protracting the treatment beyond the point when the product ceased to increase in weight, a slight but continuous loss was sustained, which, there appears no doubt, from the results of confirmatory experiments, is to be ascribed to the solution of small quantities of gun-cotton in the strong acids with which it was left in prolonged contact.

The following results show that the *repeated* immersion of cotton in an acid-mixture of somewhat less strength, does not effect, nearly as rapidly or as completely, its conversion into insoluble gun-cotton, as does a single treatment with the acid-mixture prescribed by Von LENK.

(*Experiment* 10.)—2·12 grms. of pure dry cotton were submitted to two successive treatments with a cold mixture of acids having the composition

$$\left.\begin{matrix}HNO_3\\H_2SO_4\end{matrix}\right\}+3H_2O*.$$

Period of first immersion three hours, increase in weight . . 62·34 per cent.
Period of second immersion nine hours, increase in weight . 65·14 per cent.

The product was then digested for three hours in the cold with the strongest acid-mixture, after which the total increase in weight was 77·51 per cent.

Experiments 2, 3, and 4 prove that, by a single treatment of cotton with a considerable proportion of the strongest acid-mixture, results may be obtained closely in accordance with the number given by HADOW, and with the theoretical requirement of trinitro-cellulose. The mean of these three experiments fixes the maximum increase in weight which cotton is capable of attaining by this treatment at 82·16 per cent.; the theoretical number is 83·3 per cent.

Experiments 5, 6, and 7 show that, even in operating upon small quantities of comparatively very pure cotton, if the proportions of the acid-mixture used be limited to such as are employed in manufacturing operations (10 to 14 parts to 1 of cotton), the conversion into trinitro-cellulose cannot be as completely accomplished. In these instances, the increase of weight sustained by the cotton is between 78 and 80 per cent. As might have been anticipated, the products contained notable proportions of matter soluble in ether and alcohol, while those obtained in experiments 2, 3, and 4 yielded a minute trace to the solvent.

Experiment 8 demonstrates the importance of continuing the digestion with acids longer than is merely necessary for the production of an explosive material, if it is desired to effect as complete a conversion as possible into insoluble gun-cotton. By immersion for ten minutes only, the cotton increased in weight only 62·43 per cent.,

* This is the composition of the mixture which HADOW believes to be the weakest which is capable of producing insoluble gun-cotton by repeated immersions. The nearest expression of the composition of Von LENK's acid-mixture is $\left.\begin{matrix}10\,HNO_3\\19\,H_2SO_4\end{matrix}\right\}$.

and the product was to a considerable extent soluble in ether and alcohol. In another experiment, a still more soluble product was obtained by immersion for only three minutes. Experiments 6 and 7 indicate that, the quantity of acid used being limited, digestion for twelve hours is scarcely sufficient to ensure the maximum attainable increase of weight; and the results of experiments 3 and 4, compared with those of 1 and 2, indicate that under equal conditions, the result obtained by immersion for twenty-four hours is quite equal to that furnished by more protracted digestion. This observation is fully borne out by the results of manufacturing operations, as pointed out in the first part of this memoir. There is no doubt that an actual loss of product, though only slight, is sustained by prolonging the contact of the acids with the gun-cotton much beyond the period necessary for its perfect production.

Experiment 9 shows that a very brief treatment of cotton with a warm acid-mixture effects its conversion into insoluble gun-cotton as completely as a long-continued treatment with cold acids (the proportion of the latter being limited). This experiment was made for the purpose of ascertaining whether, with the employment of the strongest acids, heat exerted a similar influence upon the character of the product to what it does when weaker acid-mixtures, or mixtures of saltpetre and sulphuric acid are employed. This is evidently not the case, for the product obtained was as slightly soluble as the general products of manufacture at Waltham Abbey. It was also found that a few minutes' immersion in a warm acid-mixture converted an imperfect product, obtained by a few minutes' treatment with *cold* acids and containing much soluble matter, into a gun-cotton of the ordinary kind.

The following results were obtained by submitting samples of cotton-yarn (taken from ordinary supplies for the manufacture of gun-cotton) to treatment with the usual mixture of acids, the cotton having previously been boiled in an alkaline bath and washed; after which treatment it still retained a very few fragments of seed.

Experiment.	Cotton employed.	Duration of immersion.	Increase in weight on 100 parts of cotton.
11	4·777 grms.	48 hours	78·43
12	8·076 „	48 „	78·19
13	6·0206 „	24 „	80·77
14	6·901 „	24 „	80·79
15	9·2147 „	48 „	78·14

In all these experiments a considerable excess of acids (about 60 parts to 1 of cotton) was employed. They afford decided evidence of the influence which the quality of the cotton employed must exert upon the quantity of product obtained even in a laboratory operation; and show that the results furnished, under most favourable circumstances, by cotton of ordinary commercial quality, fluctuate between 78 and 81 per cent., never quite reaching the latter number. The results also point, as did some of those obtained with the purer cotton, to a tendency of the gun-cotton to dissolve in the acid-mixture when the immersion is continued for a very long period. Both results (experiments 13 and

14) obtained by treatment of the cotton for twenty-four hours are notably higher than those furnished by the forty-eight hours' treatment. The loss of product ascribable to this cause is doubtless somewhat greater in these experiments than in manufacturing operations, when the proportion of acid to the cotton used is considerably lower*.

A comparison of the weight of cotton, obtained from samples of gun-cotton, with the original weight of cotton employed in their production, affords data which are strongly in support of the conclusion that the differences between the increase in weight which cotton should sustain by conversion into trinitro-cellulose,

$$C_6 H_7 N_3 O_{11},$$

and the results furnished by as perfect a treatment of different specimens of cotton as is practicable, are to be ascribed, not merely to the presence, in the products, of small quantities of imperfectly converted soluble gun-cotton, but also to the existence in them of substances which are foreign to the cotton, and which are only partially removeable by simple washing with water.

The following are the results of very careful experiments made with finely-carded and specially purified cotton-wool, and with ordinary cotton-yarn, purified by boiling with potassic carbonate. The increase sustained by the cotton upon its conversion into gun-cotton having been noted, the product was reconverted into cotton by HADOW'S method, special care being taken to avoid mechanical loss in the several operations. The weights of the cotton recovered compared with those of the original cotton, and with the increase of weight sustained by the latter when converted into gun-cotton, are as follows:—

Description of cotton.	Proportion of acids to cotton.	Increase sustained by conversion.	Cotton employed.	Cotton recovered.	Loss upon the original cotton.
		Per cent.	grms.	grms.	Per cent.
Finely carded and purified.	50 to 1	82·57	1·132	1·119	1·14
Ditto.	Ditto.	82·04	1·263	1·2526	0·83
Ditto.	14·6 to 1	80·07	1·083	1·0695	1·24
Cotton-yarn, ordinary quality.	60 and 70 to 1	78·43	4·777	4·574	4·43
Ditto.		78·19	8·076	7·561	6·34
Ditto.		80·77	6·0206	5·6862	5·55
Ditto.		80·79	6·901	6·5319	5·36

It will be seen from the above statement, that the cotton which was recovered from the laboratory products, furnished by comparatively very pure cotton which had sustained an increase of weight of 82 and 82·6 per cent. (the theoretical increase being

* Upon reconversion into gun-cotton of some specimens of the reduced cotton, which is always in a friable condition very favourable to solution, the weights of the resulting products indicated that a more considerable proportion of the gun-cotton produced was dissolved than when the original cotton was operated upon.

One sample sustained an increase of weight of only 73·91 per cent., and a second 73 per cent. by immersion for the usual period. A third sample, submitted to a brief treatment, gave an increase of 77·61 per cent., and upon being immersed a second time for twenty-four hours, the weight of the product indicated an increase of only 75·15 per cent.

83·3 per cent.), amounted to only about 1 per cent. less than the cotton originally taken; and that when the employment of a limited quantity of acid (as in the third experiment) yielded a product the weight of which represented about 2 per cent. less increase than these, the cotton recovered was in this instance also only about 1 per cent. below the quantity employed, the difference in the weight of the nitro-product having been due only to the formation of a somewhat larger proportion of soluble gun-cotton. It appears from these results, and estimating the proportion of loss which the processes of conversion and reduction may involve at about 0·5 per cent., that the particular cotton-wool operated upon contained about 0·5 per cent. of matter foreign to cellulose, which was eliminated in the course of the transformation and reproduction of the latter. But, when less pure samples of cotton were converted as completely as practicable into insoluble gun-cotton, and furnished results from 1·75 to 4 per cent. lower than those obtained by similar treatment of the pure material, the weight of the recovered cotton indicated a loss upon the original substance employed of from 4·4 to 6·3 per cent., an increased loss which must be due to the larger proportion of foreign matters existing in the cotton operated upon. These facts surely afford strong support to the conclusion that the deficiency in weight exhibited by the products obtained from ordinary cotton-wool, even after its purification with alkali, as compared with those furnished under the same circumstances by purer cotton-wool, is due to the presence of foreign matters in the cotton, which, though partially retained by the gun-cotton, exist there in the form of products whose formation does not add, in so high a proportion, to the original weight of the cotton as does the production of trinitro-cellulose.

It follows from the above results, obtained by treatment of the ordinary cotton-wool with a considerable excess of acid, that if the same cotton be treated with the limited proportion of acid-mixture (10 to 14 parts by weight to 1 part of cotton) employed in the ordinary course of manufacture, the products must then exhibit somewhat less increase of weight (lower proportions, therefore, than 178 or 180 from 100 of cotton), because, under those circumstances, the production of larger proportions of the lower cellulose-products (soluble in ether and alcohol) comes into play to cause a reduction in the weight of the product beyond that which is ascribable mainly to the influence of the foreign matters in the cotton.

Two quantitative operations have been conducted in the ordinary course of manufacture at Waltham Abbey, with the view of ascertaining the actual quantity of gun-cotton furnished by 100 parts of cotton in the ordinary course of operating with considerable quantities of material.

In one experiment the cotton employed, which contained about the average quantity of seed, and had as usual the peculiar colour of unbleached fibre, was submitted to the ordinary purification in the bath of potassic carbonate, and was dried as usual for twenty-four hours at 50° C. before immersion in acids. Its weight, when dry, was 31 lbs. 6 oz. It was afterwards treated in all respects like an ordinary product of manufacture. The weight of the air-dry gun-cotton showed an increase upon the original dry cotton of

74·3 upon 100 parts. The weight of the thoroughly dry product corresponded to an increase of 71 upon 100.

In another experiment, made with a somewhat higher quality of cotton, an increase of 76 per cent. was obtained.

The products of these operations were quite similar in character to those usually obtained, and to the results furnished by the laboratory-experiments just now described, which were conducted with samples of the same description of cotton. A difference of about 9 per cent. between the latter results and the lowest number furnished by the quantitative manufacturing experiments has therefore to be accounted for. The following statements will show that this deficiency is not greater than would be anticipated.

In the cotton operated upon, besides the resinous and other impurities which are partly removed by solution in the acid and by subsequent extraction in the purifying processes, and which also occasion a notable loss in the laboratory-experiments with this kind of cotton, as already pointed out, there exists a more or less considerable proportion of seed, of which only minute particles are here and there observed in the finished gun-cotton. To this source of loss upon the weight of the cotton employed, has to be added the mechanical loss of product unavoidably attending the repeated submission of the gun-cotton to the expressing and long-continued washing processes. But the principal loss of product, and one which alone suffices to account for the difference observed between the results of the laboratory-experiments and those of ordinary manufacturing operations, occurs in boiling the gun-cotton in the alkaline bath. The brief digestion of the material in the weak solution of potassic carbonate not only abstracts a considerable proportion of the products foreign to gun-cotton, resulting from the action of the acids upon the impurities which the cotton fibre obstinately retains, but also causes a very notable proportion of the gun-cotton itself to pass into solution.

A quantity of Waltham Abbey gun-cotton which had, in the ordinary course, already been submitted to the treatment with alkali, was boiled for ten minutes in a solution of potassic carbonate precisely similar to that usually employed (of spec. grav. 1·02). The liquid became of an amber colour, and the gun-cotton, when dried, was found to have sustained a loss of 3·7 per cent. The same gun-cotton was again boiled for twenty minutes in the same alkaline bath, which deepened in colour considerably during this second employment. The total loss sustained by the material, after this second treatment, amounted to 12·09 per cent.*

9·22 grms. of cotton yarn, previously purified by treatment with alkali and carefully freed from seed, were converted into gun-cotton in the ordinary manner, excepting that about three times the ordinary proportion of acid was used, whereby the solution of

* The treatment of gun-cotton with a boiling solution of potassic carbonate of the prescribed strength, even if greatly prolonged, does not affect the composition of the mass, but evidently acts by dissolving, and transforming into other products, portions of the fibre, or of its surfaces. The combustion of a specimen of ordinary gun-cotton which had been boiled for one hour in the alkaline bath furnished 24·48 per cent. of carbon (the theoretical number of trinitro-cellulose being 24·24 per cent.).

foreign matters in the acid was promoted. The product, after long-continued washing in distilled water, was dried and weighed. The increase sustained by the cotton amounted to 78·14 per cent. (a number closely corresponding to the laboratory-results previously described). The gun-cotton was then boiled for eleven minutes in a solution of potassic carbonate of the usual strength. When washed and again dried, it was found to have lost considerably in weight, and the finished product showed an increase of weight upon the original cotton equivalent to 69·8 upon 100, which was therefore 1·2 per cent. less than the lowest result obtained in the manufacturing operations. It is easily conceivable that, in the smaller operations, the gun-cotton, though submitted only for exactly the usual period to treatment with an alkaline bath of the ordinary strength, should sustain a somewhat greater loss than a large compact mass of the material, such as is always operated upon. But the results of these experiments establish a source of loss in the usual process of manufacture, which fully accounts for the discrepancies exhibited between the yields of usual manufacturing operations and of laboratory operations conducted with the same description of cotton, in which the treatment with boiling alkaline water has been omitted.

Comparison between analytical and synthetical results.—The relative proportions of carbonic acid and nitrogen furnished by the complete oxidation of gun-cotton, afford the means of instituting a comparison between the analytical and synthetical results, of which the details have been given, and, it is believed, of demonstrating beyond dispute the correctness of the conclusion, that the product of the complete action upon cotton-wool of the mixture of strongest acids prescribed by Von LENK is most correctly represented by the formula

$$C_6 H_7 N_3 O_{11},$$

of which the expression

$$C_6 H_7 O_5, 3N O_2$$

appears to be the most rational interpretation. The method of determining the relative proportions of the two gases furnished by gun-cotton has been already described. The following results were furnished by four samples of gun-cotton:—

	Volume proportions of carbonic acid and nitrogen.		Proportions required by
	I.	II.	$C_6 H_7 N_3 O_{11}$.
Carbonic acid . .	62·25=81·22	76·899=80·91	80
Nitrogen . . .	14·40=18·78	18·144=19·09	20
	III.	IV.*	$C_{24} H_{36} O_{18} 5N_2 O_5$.
Carbonic acid . .	83·64=80·91	72·397=80·91	82·8
Nitrogen . . .	19·73=19·09	17·082=19·09	17·2

* A sample of gun-cotton which had been left in contact with acids for five days, and a second sample, which had been twice submitted to the ordinary treatment with acids, furnished the following results:—

	5 days in acid.	Twice dipped.	Trinitro-cellulose.
Carbonic acid . . .	80·574	80·37	80
Nitrogen	19·426	19·63	20

The proportion of nitrogen furnished by the first experiment, though somewhat low, is nearer to the requirements of the trinitro-cellulose formula than to those of the formula adopted by PÉLOUZE and MAURY; the proportions of the gases observed in the other three experiments, which happen to be identical in their results, correspond with the requirements of $C_6 H_7 N_3 O_{11}$ as closely as could possibly be expected when operating upon a substance of approximate purity only.

Upon calculating the proportion which the nitrogen found in these experiments bears to the mean percentage of carbon (24·6) obtained by the most trustworthy method employed for the determination of that element, the following numbers are obtained:—

	I.	II., III., & IV.
Carbon	24·6	24·6
Nitrogen	13·32	13·59

These percentage-proportions of nitrogen are not only in perfect accordance with a considerable number of the results obtained by direct determination of the volume of nitrogen furnished by samples of Waltham Abbey gun-cotton, they are also as close approximations to the theoretical percentage of nitrogen in trinitro-cellulose as the analysis of products containing small proportions of lower nitro-compounds could be expected to furnish; and lastly, the increase in weight which cotton of average purity should sustain by conversion into nitro-cellulose-products which furnish these proportions of nitrogen, corresponds closely to the average results obtained by operating upon moderately pure cotton with the mixed acids of *prescribed strength* and in the proportion (about 10 parts to 1 of cotton) indicated by Von LENK.

The general conclusions to be deduced from the experimental results described in this memoir are as follows:—

1. The products obtained by submitting cotton-wool to treatment with the prescribed mixture of nitric and sulphuric acids, and to purification as directed by Von LENK, are very uniform in character; they consist almost entirely of the most explosive known variety of gun-cotton or pyroxylin, which is insoluble in mixtures of ether and alcohol. This substance, when produced upon a manufacturing scale, contains from 1 to 2 per cent. of mineral substances, and a small proportion, varying with the quality of the cotton, of matters soluble in alcohol, partaking of acid properties, and consisting chiefly, if not entirely, of products of the action of nitric acid upon resinous or other bodies enclosed in the cotton fibre. There is also always present in the gun-cotton a small quantity (from 1 to 3 per cent.) of cellulose-products of a less explosive character, soluble in mixtures of ether and alcohol, which result from the incomplete action of nitric acid upon small portions of the cotton operated upon.

2. The gun-cotton, when purified as far as it is possible from foreign substances, soluble in alcohol and in ether and alcohol, furnishes analytical results which agree much more closely with those demanded by the formula

$$C_6 H_7 N_3 O_{11}, \text{ or } C_6 H_7 O_5, 3N O_2,$$

than with the requirements of the formula

$$C_{24}H_{36}O_{18}, 5N_2O_5,$$

recently adopted for gun-cotton by PÉLOUZE and MAURY.

3. If cotton-wool of great purity is digested for a period of about twenty-four hours with a considerable proportion of the prescribed acid-mixture (about 50 parts to 1 of cotton), it sustains an increase of weight ranging between 81·8 and 82·6 upon 100 of cotton. Lower results (between 78 and 80 per cent. increase) are obtained by digesting the cotton for a short period only, or for very considerable periods, by using a limited proportion of the acid (from 10 to 14 parts to 1 of cotton), by employment of acids of slightly lower specific gravities than those specified, and by operating upon cotton of somewhat lower quality. The digestion, for a second or third time, of products which have exhibited a comparatively low increase of weight, in an acid-mixture of the kind first used, or of greater strength, has the effect of raising the weight of the product to within the higher limits above named.

The increase in weight which 100 parts of pure cellulose should sustain, theoretically, by complete conversion into a substance of the composition $C_6H_7N_3O_{11}$, is 83·3, while, if converted into a substance of the formula

$$C_{24}H_{36}O_{18}, 5N_2O_5,$$

the increase sustained by it only amounts to 77·8 upon 100 parts.

4. Cotton-wool always contains, even after careful purification, small proportions of foreign organic substances, the presence of which, in the material submitted to treatment with the acids, must affect to some extent the quantity of the product obtained.

5. It is extremely difficult, indeed apparently impossible, even in operating under most favourable conditions upon small quantities of cotton-wool, to convert this substance *completely* into the highest nitric product—the perfectly insoluble gun-cotton. Small quantities of gun-cotton soluble in ether and alcohol can always be extracted from the products; the quantities are only minute in the highest laboratory-products, but they are always very appreciable in the most perfect manufacturing products. Their invariable formation must unquestionably cause the increase of weight sustained by cotton to be somewhat less than that which theory would demand.

6. The long-continued digestion of the gun-cotton in the acid-mixture, the several mechanical operations to which it is submitted in the course of its purification, and above all, the solvent action exerted not only upon certain bye-products, but also upon the gun-cotton itself by the alkaline liquid, in which it is boiled for a short time, are all sources of loss which, in examining into the results of a system of manufacture, must not be disregarded, and the existence of which explains satisfactorily the difference observed between the weights of laboratory-products and those of manufacturing operations.

7. In accepting the formula proposed by PÉLOUZE and MAURY for gun-cotton, it

would be necessary to assume that the cotton-wool operated upon was pure cellulose; that the operation of conversion was an absolutely perfect chemical process; that there were no possible sources of loss in the production of the material; and that in all laboratory operations which had furnished an increase of weight above the theoretical demand (77·8 per cent.), some substance, differing in composition from the ordinary products of manufacture, must have been obtained.

8. The identity in their characters, and close resemblance in composition, of the most perfect products of laboratory operations and of the *purified* products of manufacture, the very close approximation in the weight of the former to the theoretical demands of the formula

$$C_6 H_7 N_3 O_{11}$$

(which may be expressed as

$$C_6 H_7 O_5, 3N O_2, \text{ or } C_{12} H_{14} O_7, 3N_2 O_5),$$

and the satisfactory manner in which the unavoidable production of somewhat lower results in the manufacturing operations admits of practical demonstration, appear to afford conclusive evidence of the correctness of either of those formulæ as representing the composition of the most explosive gun-cotton, and to demonstrate satisfactorily that the material, prepared strictly according to the directions perfected by Von LENK, consists uniformly of that substance (now generally known as *trinitro-cellulose*) in a nearly pure condition.

The products furnished by the explosion of gun-cotton under varied conditions are at present being investigated by me; and the behaviour of the substance (as obtained in ordinary manufacturing operations), when exposed to light, heat, and other agencies tending to promote chemical change in bodies of unstable character, is also being carefully examined into. The results of these branches of the general inquiry into the history of pyroxylin will be communicated to the Royal Society in due course; meanwhile it should be stated that numerous experiments already instituted, which bear upon the stability of gun-cotton, have furnished results differing in very important respects from those recently published in France.