

XI. THE BAKERIAN LECTURE.—*Researches on Gun-cotton*.—Second Memoir.
On the Stability of Gun-cotton. By F. A. ABEL, F.R.S., V.P.C.S.

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THE earlier of the published researches into the composition and properties of gun-cotton were speedily followed by accounts of the spontaneous decomposition which the substance was, in many instances, observed to undergo upon more or less protracted exposure in confined spaces to strong or diffused light. These indications of instability, in conjunction with the occurrence of several serious explosions during the manufacture of gun-cotton in France and England, afforded apparently good grounds for the general conclusion,—arrived at within a brief period after the announcement of SCHÖNBEIN'S discovery, and adhered to until quite recently in all countries except Austria,—that this remarkable explosive agent did not in itself possess the quality of uniform permanence essential to its safe manufacture, or to its employment with any degree of security from accident, in warlike or industrial operations.

It is unnecessary to refer in detail to the results of the numerous observations published before 1860 upon the nature of the spontaneous changes which particular specimens of gun-cotton had suffered. In the brief prefatory review of published investigations upon the production and composition of gun-cotton, contained in the paper on those subjects which I communicated to the Royal Society last year, it has been shown that the products obtained by individual operators in submitting cotton to the action of nitric acid varied greatly in composition, and that, with only one or two exceptions, these could not be viewed as representing the definite substance producible by the most complete action at a low temperature of a mixture of the strongest nitric and sulphuric acids upon purified cotton-wool (or nearly pure cellulose). The behaviour and results of the decomposition of such specimens, or of others of more recent date prepared (for lectures or similar experimental purposes) without special regard being paid to their composition or purity, afford but little information that can be accepted as bearing upon the question of stability of gun-cotton when produced by a system of operation which is now known to furnish uniform products in a condition of comparative purity.

There can be no question that the variations in composition of the different specimens of gun-cotton, the decomposition of which has received investigation at different hands, exerted a most important influence upon the period for which they withstood the destructive effects of heat and light, and upon the *degree of rapidity* with which chemical change, when once established, proceeded from stage to stage. The *products* of change described by different observers have also varied somewhat in their characters, partly

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on account of the variations in the gun-cotton itself, and partly because different experimenters have examined the products of its metamorphosis at different stages.

The accounts published by DE LUCA, BONET, and BLONDEAU, between 1861 and 1865, of their investigations into the changes which gun-cotton undergoes spontaneously, include nearly all the results previously described in one or other of the published papers on this subject.

The following is a general statement of the changes which gun-cotton, preserved in bottles partly or perfectly closed, has been observed to undergo by exposure to light, and of the nature of the products of decomposition.

In the first instance nitrous vapours make their appearance, the atmosphere in the vessel becoming sometimes of a deep orange tint. The gun-cotton acquires considerable acidity, exhibits a peculiar pungent odour, and gradually contracts, so that it eventually occupies only a small proportion of the original volume. During this period a considerable proportion of nitric acid accumulates in the mass, and the decomposition proceeds after a time with increased rapidity, especially if the vessel be exposed to sunlight. The contracted gun-cotton gradually becomes more or less friable, its explosiveness is notably reduced, it yields a highly acid extract to water, in which, besides nitric acid, small proportions of glucose, of formic and oxalic acids, and of cyanogen have been detected. The material sometimes contracts to such an extent as to form a very compact somewhat hard mass, but in general it ultimately passes over with more or less rapidity into a brownish gum-like mass, which at first is rendered very porous by the evolution of gas-bubbles, and which becomes lighter in colour and friable after a time. This ultimate product of the decomposition of gun-cotton has been found to contain glucose and oxalic acid in considerable proportions, besides a gum-like substance, formic acid, cyanogen, and an organic acid which by some observers is considered to possess novel characters, while DIVERS believes that he has identified pectic and parapectic acids in the product of a decomposed specimen*. The amorphous mass has also been found to evolve ammonia when heated with a solution of potassic hydrate.

In some instances the gun-cotton is described as having undergone other intermediate changes, but the greatest discrepancies exist between the observations of even the most practised experimenters regarding the periods within which the decomposition of gun-cotton has become manifest, and the conditions under which the changes have occurred.

* The observations of DIVERS regarding the occurrence of the pectic acids among the products of decomposition of gun-cotton, have been confirmed by the results of examination of a very large number of specimens obtained by the decomposition of gun-cotton at high temperatures under various conditions. The reactions of pectic and of para- and meta-pectic acids have been so frequently obtained that these substances must be regarded as general products of the gradual decomposition of gun-cotton. On the other hand, although the most careful search has frequently been made for glucose, only two instances of its existence were established by the fermentation test. It appears probable that the reduction of cupric salt from an alkaline solution has in many instances been accepted as a sufficient indication of the presence of glucose, while, in reality, this reaction has been furnished by the pectic acids produced. Small quantities of cyanogen have on several occasions been detected among the products of very gradual decomposition of gun-cotton by heat.

In some instances the first signs of decomposition were observed after exposure of the gun-cotton to daylight for several years, in others a few days' exposure sufficed to establish the change. Some observers state that the material has been preserved in the dark for very protracted periods without change, others (*e. g.* quite recently DE LUCA and BLONDEAU) show that, even in the dark, gun-cotton undergoes decomposition within a comparatively short period. Such conflicting observations afford convincing proof of great variations in the composition or degree of purity of the materials experimented upon.

The exposure of gun-cotton to heat has, by most observers, been found to accelerate its decomposition considerably; but here again great discrepancies are presented by different accounts of the behaviour of the material under the influence of different temperatures; thus, its spontaneous explosion has been brought about in some instances by brief exposure to a degree of heat which, in others, has only produced a comparatively very gradual decomposition.

The most interesting and important of recent observations upon the influence of heat on the stability of gun-cotton are those described by PÉLOUZE and MAURY in their recent report upon Baron Von LENK's system of manufacturing gun-cotton, and upon the composition and properties of the products which it furnishes. They describe a number of results obtained with specimens of gun-cotton which, it is to be inferred, were all produced according to Von LENK's directions, and which, therefore, provided these were strictly adhered to, and such an adherence ensured the uniformity of the products, should have furnished reliable data regarding the powers of purified gun-cotton to resist the destructive effects of heat. The principal results arrived at by PÉLOUZE and MAURY are as follows: they found that all specimens which were heated to 100° C. became decomposed in more or less time; a few minutes' exposure to that temperature sufficed in every instance to determine the evolution of nitrous vapours. They describe the results of decomposition as susceptible of variation at will; either the gun-cotton might be brought to explode, or the various forms of decomposition already described by other chemists might be established; or finally, it might be made to furnish simply a small black residue presenting the appearance of carbon, from which ammonia might be disengaged. Identically the same results were obtained by exposing specimens of gun-cotton to temperatures of 90° and 80° C., with this difference, that the phenomena of decomposition, instead of appearing in a few minutes, were not exhibited until after the lapse of several hours. It is further stated that pyroxylin is decomposed at 60° C. (140° F.), and even at 50° C. (122° F.); after the lapse of several days dense vapours filled the vessel containing the specimens, but no explosions of gun-cotton occurred in the experiments conducted at those temperatures. Great stress is laid, however, upon an instance of explosion which occurred with a specimen of gun-cotton prepared according to Von LENK's process, immediately upon its coming into contact with the metal of an oil-bath, the temperature of which was only 47° C. (116°·6 F.) at the time. PÉLOUZE and MAURY afterwards refer to the instances of spontaneous decomposition of gun-cotton at ordinary temperatures observed by other chemists, and to certain specimens, among a number prepared at

Bouchet in 1847, which had undergone alterations such as have already been described. These were examined for sulphuric acid, and none was detected; hence the conclusion is drawn that these samples had been perfectly washed, and that their spontaneous change could not be ascribed to imperfect purification. It is argued that instances of change have been observed to occur under ordinary atmospheric conditions, similar to those established in gun-cotton at higher temperatures; that, because exposure to the latter had occasionally brought about spontaneous explosion, it is possible for instances of spontaneous decomposition at *ordinary* temperatures to result in explosions, and that, consequently, it is right to conclude that the storage of large quantities of gun-cotton is attended by great risk of explosion. In further support of this conclusion the observations are recorded, that the most perfectly washed gun-cotton becomes acid by long exposure to sunlight; that some pyroxylin, which was alkaline at first, after exposure for several weeks to light, in contact with the sides of a glass flask, exhibited an acid reaction; and that, even when gun-cotton is preserved in the dark, this acidity invariably becomes manifest in course of time. Finally, without referring to any single instance in which an explosion or even an appreciable development of heat has been observed as resulting from protracted exposure of gun-cotton to strong daylight or sunlight, PÉLOUZE and MAURY conclude that the indications of gradual decomposition furnished by certain specimens of gun-cotton under those conditions, are sufficient proof of the liability of this material, as now manufactured, to explode spontaneously, when stored in considerable quantities.

The researches into the manufacture, composition, and properties of gun-cotton, upon which, as a member of the Government Gun-cotton Committee, I have been engaged for nearly four years, have included, from their very commencement, careful observations and a great variety of experiments, with both small and large quantities of material, bearing upon the influence exerted by light and heat, and by various modifications introduced into the system of manufacture, upon the stability of gun-cotton produced in accordance with the general directions laid down by Von LENK. It is obvious that, although most of these experiments have furnished very decisive results within a comparatively brief period, there are others which become the more valuable and the more fully conclusive in their character, the longer the period of their duration. It is considered, however, that the data which even the latter class of experiments has already furnished possess sufficient scientific interest and practical importance to warrant their present publication, in addition to those obtained by numerous experiments instituted with the view to ascertain whether and to what extent the results of researches recently published in France upon the spontaneous changes of gun-cotton, apply to the material manufactured in this country during the last four years.

The experiments and observations carried on at Woolwich may be classed as having for their objects,—

(a) The determination of the influence of light and of long protracted storage, under ordinary conditions as to temperature, upon the stability of gun-cotton;

(*b*) The investigation of the behaviour of gun-cotton upon exposure, under varied conditions, to artificial temperatures, and to such elevated natural temperatures as are occasionally experienced in particular localities;

(*c*) The examination of the influence exerted upon the stability of gun-cotton by special modes of preparing and preserving it.

A few observations have been made upon specimens of gun-cotton which either were prepared by myself or came into my possession previous to the commencement of the present inquiry, but all actual experiments have been instituted with samples of products of manufacture obtained at Hirtenberg, Stowmarket, and Waltham Abbey, some modifications having been introduced, in special instances, in the ordinary system of operation at the last-named manufactory, with the view to ascertain the nature and extent of their influence upon the stability of the product.

PART I.—ACTION OF LIGHT UPON GUN-COTTON.

The want of uniformity in power to resist the destructive action of light, exhibited by different specimens of gun-cotton with which chemists have experimented, has been additionally exemplified by the behaviour of numerous specimens of gun-cotton which have from time to time come into my hands or were prepared by me, previous to 1862. I will limit my notice of such specimens to two examples.

In the autumn of 1846 a small quantity (one or two pounds) of gun-cotton was prepared by me at the Royal College of Chemistry according to the directions which had been made public in Germany a short time previously. The product, which was insoluble in mixtures of ether and alcohol, was obtained by immersing carded and purified cotton-wool of very high quality for a few minutes in the prescribed mixture of nitric and sulphuric acids, afterwards exposing it for several hours to a current of water, then digesting it in a cold dilute solution of potassic carbonate, and finally washing it in pure water. The larger proportion of the product was gradually expended in lecture-experiments, but a specimen has been preserved by me up to the present time. For sixteen years it was simply enveloped in paper and kept in a drawer much used; at the expiration of that period, when it was found to be perfectly unchanged, not exhibiting the slightest acidity or odour, it was transferred to a stoppered bottle, in which it has been since exposed to diffused daylight for four years. This specimen still remains perfectly unchanged.

Messrs. HALL of Faversham had the goodness, about three and a half years ago, to disinter at my request a sample of a large quantity of gun-cotton manufactured by them in 1847, and which they buried upon the occurrence of the disastrous explosion at their works in that year. This sample was much discoloured when received, but the fibre was strong, and the material did not appear to have undergone any change. Its explosive properties were, however, considerably inferior to those of gun-cotton prepared according to SCHÖNBEIN'S or VON LENK'S directions; and, upon analysis, it furnished

results corresponding very nearly with those required by the formula $C_{18}H_{23}O_{15}7NO_2$, the compound C, or collodion gun-cotton, of which the composition was determined by HADOW. It was, moreover, readily soluble in a mixture of ether and alcohol, and furnished a good collodion-film. It is most probable, therefore, that a deficiency in the strength of the acids employed in its production had led to the manufacture, in this instance, of soluble and less explosive gun-cotton by Messrs. HALL. A specimen of this material, after having been very carefully washed, was dried and enclosed by me in a stoppered bottle, in which it has remained exposed to diffused daylight for upwards of three years. A piece of litmus-paper, enclosed with the gun-cotton, exhibited faint signs of reddening within three months after the first exposure, and within twelve months it was bleached. At this time the gun-cotton possessed a faint but decided cyanic odour; no nitrous vapours were perceptible within the bottle, either then or at any more recent period up to the present time, though the odour of the gun-cotton has now become more pronounced, and is indicative of nitrous acid. The substance has at present a marked acid reaction; it has not as yet altered either in explosiveness, strength of fibre, or other properties, but the odour and slight development of acid are undoubted indications that the material which for sixteen years was preserved in a moist condition in the dark without any apparent change, has during three years' exposure to light furnished slight indications of spontaneous change. It was a specimen of gun-cotton prepared by Messrs. HALL in 1847, and preserved by PERCY since that year in a stoppered bottle, exposed to light, which had gradually become converted into a light-brown semifluid gum-like mass, described by HOFMANN as having exhibited all the properties of ordinary gum, and as being interspersed with crystals of oxalic acid. It is therefore not improbable that the specimen of Messrs. HALL'S manufacture above referred to may, by long-continued exposure to light, eventually furnish more important indications of spontaneous change than have hitherto been developed in it.

There can be little doubt that the quality of cotton operated upon by Messrs. HALL in the production of the specimens above referred to (and certainly in the instance of that examined by me), was considerably inferior to that of the material employed by me in 1846, and the character of the gun-cotton produced demonstrates that the conditions essential to the production of the most explosive material were not fulfilled by the method of manufacture pursued by those gentlemen in 1847. It is equally certain that the great importance of as complete a purification as possible of the cotton employed and of the product obtained was not fully recognized at that period, and that consequently, although a small laboratory operation carefully conducted according to the prescribed directions might furnish a pure product of great stability, the operations of manufacture had not been established with the precision essential to the attainment of satisfactory results.

The following are the results obtained up to the present time by exposure to light, under various circumstances, of gun-cotton prepared and purified according to Von LENK'S directions.

Exposure to strong daylight and to sunlight, either in the open air or in confined spaces for a few days (two to four), develops in the gun-cotton a very faint aromatic odour; and if litmus-paper be allowed to remain in close contact with the confined material, it acquires a rose-coloured tinge similar to that produced by carbonic acid, and recovers its original colour after brief exposure to air. If, after exposure to light in open air for some days, the gun-cotton be placed in the dark, in cases which are not air-tight, the odour becomes gradually fainter, and the effect upon litmus-paper slighter; if the packages containing the gun-cotton are air-tight, the odour and action upon litmus do not increase during storage for several years (the actual experience gained at Woolwich extends over nearly four years).

If the gun-cotton be exposed for protracted periods to daylight with free access of air, it speedily loses all odour and power of affecting litmus. If exposure to diffused daylight in confined spaces be continued, the first results of the action of light are, of course, retained; but up to the present time no single indication of their increase has been observed; indeed, the very faint acid reaction described, which was developed at first, has frequently disappeared, probably in consequence of the neutralizing action of small quantities of earthy carbonates contained in the gun-cotton.

But if the material be exposed continuously in a perfectly confined space to the action of sunlight or strong daylight, it furnishes, after a time, much greater evidence of change than that already described. The acidity gradually becomes more manifest; the odour increases, and becomes in time somewhat pungent and indicative of the presence of very small quantities of nitrous acid; and litmus-paper, if confined in the vessel with gun-cotton thus exposed, becomes entirely bleached after two or three months. Although specimens of gun-cotton always undergo some spontaneous change under these very special circumstances, the decomposition proceeds with extreme slowness; and the results of the observations instituted by me are, therefore, in this respect quite at variance with those recently published by DE LUCA, who states that the specimens operated upon by him decomposed upon exposure to sunlight, some on the first day of the experiment, others after several days' exposure.

The following account of special experiments instituted with gun-cotton manufactured at Waltham Abbey, will serve to illustrate the rate and nature of the decomposition suffered by this material when exposed to the action of sunlight in confined spaces.

Experiments 1 and 2.—16.37 grms. of air-dry gun-cotton were introduced into a large bulb blown at the extremity of a barometer tube of 10 millims. internal diameter, the length of which below the bulb was 812 millims. The bulb-tube was supported with the open extremity dipping into mercury.

19.12 grms. of the same gun-cotton were placed in a bulb-tube with a stem of the same length. The extremity of this tube was also dipped into mercury; but a small quantity of water was afterwards passed up into the end of the tube, so that the gun-cotton in the bulb might receive the maximum proportion of moisture which it was capable of absorbing. On the 20th of October, 1863, these two samples of gun-cotton were

placed in a very exposed position out of doors in front of a brick wall, where sunlight had access to them during the greater part of the day; moreover, during the summer months, the heat radiated from the wall immediately behind the bulbs was considerable. The appearance of the gun-cotton and of the atmosphere in the bulbs was carefully examined periodically, but the former retained its original appearance, and no coloration by nitrous acid was ever observed in the latter. On the 1st of December, 1864 (more than thirteen months after the commencement of the experiments), the tube enclosing the gun-cotton in a moist atmosphere was accidentally broken. The contents of this bulb were therefore removed and examined. The gun-cotton was found to have a powerful acid reaction and a somewhat pungent odour, its fibre had become tender, but its explosiveness had not sustained any important diminution. The aqueous solution yielded upon evaporation only a very small amorphous residue, which consisted partly of alkaline and earthy salts derived from the gun-cotton. By exhausting one gramme of the material with water, neutralizing the solution with sodic carbonate and concentrating by evaporation, abundant evidence of the presence of nitric acid was obtained. The aqueous extract acquired a yellowish colour upon addition of potassic hydrate, and a small quantity of cupric salt added to the alkaline liquid was reduced when heat was applied.

After treatment with water the gun-cotton furnished about 18 per cent. of matter soluble in a mixture of ether and alcohol. The solution, upon evaporation, did not furnish a tough film, but a horny brittle residue, which contracted and split up into small particles upon complete desiccation. This residue was explosive, and appeared to possess the characters of the lower nitrocellulose, $C_{18} \left\{ \begin{smallmatrix} H_{22} \\ 8NO_2 \end{smallmatrix} \right\} O_{15}$. The acidity of the gun-cotton was determined in 5 grms. of the specimen, and was found to correspond to 2 per cent. of HNO_3 .

A portion of this altered gun-cotton was placed in a stoppered bottle immediately upon removal from the bulb, and set aside in a cupboard to which light had imperfect access. After the lapse of two years (upwards of three from the commencement of the experiment) the specimen was again examined. Upon opening the bottle a faint odour of nitrous acid was perceived. A number of small very hard crystals were found firmly attached to the glass; and similar crystals were interspersed through the material itself, which still retained the appearance of the original gun-cotton, having, however, contracted to some extent. On removal from the bottle it was found to be quite pulverulent; it speedily attracted moisture from the air, passing over into a very adhesive mass; it was soluble in water; the solution, which was turbid only from suspended mineral matter, reduced cupric salts abundantly, and gave the reactions of parapectic acid, but was not found to contain glucose.

A portion of the specimen of air-dry gun-cotton which had been enclosed with ordinarily dry air in a bulb-tube at the same time as the sample just referred to, was also examined after it had been exposed for thirteen months, the remainder being left in

the bulb, and its exposure continued for a further period of two years. The effects upon this specimen of more than one year's exposure in a confined space to strong daylight, frequent sunlight, and considerable heat radiated from the wall during the summer months, were as follows:—the gun-cotton had a somewhat pungent odour, in which, however, nitrous acid could not be recognized; its reaction was decidedly, though not powerfully, acid; the strength of its fibre and its explosiveness had not become affected. By exhaustion with boiling water it furnished a somewhat acid liquid, which contained a very small quantity of organic matter; a yellowish tinge was imparted to it by addition of potassic hydrate, but it did not reduce cupric salts.

After treatment with water, the gun-cotton was carefully exhausted with the usual mixture of ether and alcohol, and was found not to furnish a higher proportion of extract than the original material.

The remainder of this sample, after further exposure in the bulb-tube for two years (*i. e.* upwards of three years from the commencement of the experiment), had not altered in appearance, and was found to be in the following condition.

There was scarcely any perceptible odour in the tube on removing the extremity from the mercury; and the gun-cotton itself, when extracted from the bulb, had decidedly less odour than when examined two years previously.

It was still highly explosive, and the toughness of its fibre had very slightly diminished. Water extracted only 1·3 per cent. of soluble matter; the extract had a faint acid reaction; a minute quantity of nitric acid was detected in it, but no oxalic acid; and it exerted to a very slight extent a reducing action upon cupric salts. The gun-cotton yielded 25·5 per cent. of soluble product to the mixture of ether and alcohol.

Experiments 3 and 4.—It was considered very probable that the gradual metamorphosis sustained by gun-cotton upon exposure to sunlight would be attended by the disengagement of gaseous products, and that the rate of generation of these might furnish an indication of the comparative rapidity with which different specimens were affected. With this view two bulb-tubes, similar to those used in the experiments just described (the stems being 812 millims. long and 10 millims. in diameter), were respectively charged with 15 grms. of air-dry gun-cotton of the same manufacture as used in the preceding experiments. These tubes were then carefully exhausted over mercury, by means of a long narrow glass tube inserted into them, and extending from the mouth of the tube to within the bulb. The column of mercury in each tube was thus raised to within 16 millims. and 17 millims. of the height of the barometer. A small quantity of water was afterwards passed up into one of the tubes, so as to form a layer upon the mercury 3·5 millims. in height. These bulb-tubes were exposed in the middle of October 1863, side by side, in the position already described.

During exposure to light for the first four (autumn and winter) months, the depression of the mercury was not considerable in either instance, but it was nearly twice as great in the bulb-tube which enclosed water as in the other (88 millims. in the latter and 31 millims. in the former). During the next six months (from spring to autumn) the

depression was more considerable; but at the expiration of twelve months' exposure to strong daylight and sunlight, it was only 115 millims. in the dry bulb-tube, and 220 millims. in the bulb-tube enclosing water. During the ensuing winter months the development of gas was again very trifling, though it continued to be greater in the tube which enclosed water. After two years' exposure to light the mercury was expelled from this tube, but the depression of the mercury in the dry tube amounted only to 340 millims., and after the third year's exposure the extent of depression in the latter was 660 millims. Neither of the specimens had undergone any alteration in appearance after exposure for three years and four months. They were then removed from the bulbs, and the following were the results of their examination.

Gun-cotton from the dry tube.

Slightly altered in explosiveness and strength of fibre. Slightly pungent odour, 0.77 per cent. extracted by water. Aqueous solution very faintly acid, contained a minute quantity of nitric acid, no oxalic acid, reduced cupric salts slightly: 27 per cent. of soluble gun-cotton.

Gun-cotton from the tube which enclosed water.

Not greatly changed in explosiveness or strength of fibre. Odour more pungent than in the other sample, 1.4 per cent. extracted by water. Aqueous solution faintly acid, contained a small quantity of nitric acid, no oxalic acid, reduced cupric salts: 39.7 per cent. of soluble gun-cotton.

These four experiments show that—

1. Gun-cotton in an ordinarily dry condition undergoes very slow change indeed when freely exposed in closed vessels (either containing air or with air excluded) to strong daylight and to the light and heat of the sun, the effects upon the material, during upwards of three years' exposure, being to diminish its explosiveness somewhat by the reduction of a portion of the trinitrocellulose to lower cellulose-products. The material, when purified by washing in alkaline water after this very severe exposure to light, is still gun-cotton possessing useful explosive properties, and exhibiting no greater tendency to change than the original material.

2. If the space in which the gun-cotton is enclosed be kept saturated with aqueous vapour, the substance undergoes decidedly more rapid and considerable change, though, even under these circumstances, gun-cotton prepared according to the system now in use is much less rapidly decomposed by severe exposure to light than has been the case with specimens of gun-cotton previously experimented upon.

Samples of gun-cotton which had been submitted to a less perfect purification than usual, afforded indications of being somewhat more rapidly affected by prolonged exposure to strong daylight and sunlight.

Experiment 5.—A quantity of gun-cotton, after removal from the acids, was exposed to the purifying effects of flowing water for one day only, and was afterwards submitted to treatment with the hot alkaline bath as usual. 19.85 grms. of this sample were introduced into a dry bulb-tube from which the air was exhausted over mercury, and

were then exposed to light, and occasionally to radiated heat, in the locality selected for these experiments. For the first few months the depression of the mercury-column was only very slight; in seven months it amounted to 15 millims.; after that period (during bright spring weather) it became more considerable, being 155 millims. after ten months' exposure. During the following year the depression of the mercury continued steadily; in one year and nine months it amounted to 497 millims.; and at the expiration of the three following months (about two years from the commencement) the mercury was expelled from the tube, a result corresponding to that obtained with the gun-cotton confined with aqueous vapour. After exposure for $2\frac{1}{2}$ years the condition of the gun-cotton was as follows: it had a somewhat pungent odour, its explosiveness and strength of fibre were slightly reduced; water extracted 0.6 per cent. of soluble matter; the solution had a slight acid reaction, contained a small quantity of nitric acid, no oxalic acid, and reduced cupric salt to a slight extent. The proportion of soluble matter amounted to 27 per cent.

Experiment 6.—A sample (19.8 grms.) of gun-cotton which had been submitted to long-continued purification in flowing water, but had not been digested in an alkaline bath, was exposed to light in a dry globe, like the other specimens, and by the side of it was placed another globe containing an equal quantity of the same gun-cotton, but covered with black calico, so as to have light excluded from it but to be subject to the effects of considerable heat during summer weather. After the first six (autumn and winter) months' exposure, the depression of the mercury-column in the perfectly exposed tube amounted to 51 millims. (being therefore considerably greater than in the case of the specimen washed with alkali). During this period the gun-cotton in the dark globe exhibited no signs of evolving gas. After nine months' exposure the depression of mercury in the uncovered tube amounted to 320 millims. (against 155 millims. in ten months produced by the sample which had been washed in an alkaline bath). The covered bulb-tube which had been frequently exposed to the heat of the sun during the spring months, exhibited at this time a depression of 38 millims. After the expiration of twelve months the depression of the mercury-column in the perfectly exposed tube amounted to 585 millims., and the mercury was completely expelled from this tube after the lapse of sixteen months.

Although, however, gas had been more rapidly disengaged from this tube than from the one referred to in the previous experiments, the change which the gun-cotton had sustained at the expiration of about $2\frac{1}{2}$ years was not as great as that observed in the specimen which had been treated with the alkaline bath but washed for a short time only. The specimen had only a very faint odour, its explosiveness and strength had not undergone any appreciable change; water extracted only 0.3 per cent. of soluble matter; a trace of nitric acid was detected in the extract, but no oxalic acid and no reaction upon cupric salts could be obtained. The proportion dissolved by ether and alcohol amounted to 16 per cent.

Neither of these specimens, in the preparation of which the complete system of puri-

fication had not been pursued, were found to be as injuriously affected by the very severe exposure as was anticipated. The specimen which had been exposed in the blackened bulb has up to the present time exhibited but slight indications of change (by development of gas), and only when the heat radiated upon it from the wall behind, and absorbed from the sun's rays, has been very considerable. It has not been disturbed for examination, as there is no reason whatever to believe that it would differ in any respect from other portions of this imperfectly purified sample which have been preserved in the dark in well-closed boxes, and which only exhibit a slight acidity after $2\frac{1}{2}$ years' preservation.

Experiment 7.—A sample (19.8 grms.) taken from a large quantity of gun-cotton which, for purposes to be hereafter described, had been impregnated with 0.5 per cent. of sodic carbonate, was exposed to strong light in the same way as the preceding specimens. During six months (between August and March) only a very slight indication of alteration was obtained; the depression of the mercury amounted to 15 millims. at the end of that period. Soon afterwards gas was more abundantly evolved, the depression amounting to 133 millims. after ten months' exposure. After eighteen months' exposure the amount of depression was 324 millims., which had increased to 432 millims. when the sample had been exposed for two years. After the lapse of $2\frac{1}{2}$ years the mercury had not been entirely expelled from the tube. The gun-cotton was not altered in appearance or toughness of fibre, nor did it exhibit any appreciable diminution of explosiveness. It had a slight odour and faint acid reaction; the aqueous extract amounted to 1.5 per cent. (a portion of which was due to soda); it contained no oxalic acid, a small quantity of nitric acid, and reduced cupric salt slightly; ether and alcohol extracted 10 per cent. of soluble matter. This sample had therefore suffered less change than any of the others. The disengagement of gas was manifestly due in part to the decomposition of the sodic carbonate, by small quantities of acid developed after a time by the exposure of the gun-cotton as described. This sample, after having been washed in water, exhibits no difference whatever in character from specimens of freshly prepared gun-cotton, in which the proportion of soluble cellulose-products is above the ordinary average.

The observations made in experiments 1–4, that the preservation of gun-cotton in an atmosphere saturated with moisture rendered it somewhat more prone to alteration by long-continued exposure to light, have been confirmed by other experiments still in progress, in which known quantities of moist and wet gun-cotton are exposed to light in confined spaces, in comparison with dry gun-cotton. Thus, in one of these experiments 43.71 grms. of perfectly dry gun-cotton and 40.045 grms. of gun-cotton in a damp condition have been enclosed in large stoppered bottles and exposed side by side to strong daylight and sunlight. After the lapse of two (summer) months they were carefully dried and their weights determined. The sample which had been exposed to light saturated with water had lost 0.33 per cent., the weight of the dry sample indicated a loss of only 0.02 per cent. They were then again exposed in the wet and dry condition for four months; the total loss in weight of the sample exposed in a wet condition was

then found to amount to 0·6 per cent., that of the dry sample only to 0·14 per cent. (after six months' exposure).

A trifling oxidation at the expense of oxygen in the water, established by the agency of sunlight, is doubtless the cause of the slight but decided influence which, under these circumstances, water has been observed to exert upon the permanence of gun-cotton; an influence which is quite opposed to that exerted by the presence of water in gun-cotton stored in the dark, or exposed to high temperatures, as will be presently demonstrated.

The statement made by DE LUCA*, that when once decomposition has been established in gun-cotton, resulting in the development of nitrous acid, the progress of the change cannot be arrested, is not borne out by the results of numerous observations made by me. Many specimens of gun-cotton which, by exposure to high temperatures (100° and 90° C.) or by very long-continued exposure to lower temperatures (50° to 65°), have suffered considerable change, resulting in the development of nitric peroxide and of other products, have been afterwards preserved in glass bottles, both tightly closed and partially open, and freely exposed to light for periods ranging from one to three years, without undergoing additional change. In a few exceptional instances, further decomposition has after a time been established by the influence of light; but in those the gun-cotton was impregnated to a considerable extent with free (nitric) acid. Such specimens, in case they were then thoroughly washed, a slightly alkaline solution being employed in their first purification, have afterwards not been found, up to the present time, to exhibit any greater tendency to decomposition by exposure to light, than the original gun-cotton.

PART II.—EFFECTS OF HEAT UPON GUN-COTTON.

The behaviour of gun-cotton under exposure even to comparatively high temperatures is subject to very considerable modifications, which may be in great measure determined by the conditions of treatment. Illustrations of this were obtained at an early period of these investigations, in experiments instituted with the view to ascertain the average temperature at which gun-cotton explodes.

The following is a summary of the observations made on this head.

Exploding-point of gun-cotton.—The apparatus employed in the experiments on this subject consisted of a small air-bath fitted with a thermometer and closed with a mica-plate, having a little circular opening in the centre, through which the gun-cotton might be introduced, and which was kept closed when not in use. The mode of operating was modified in various ways. In the first instance the gun-cotton was combed out into a very loose condition, and allowed to rest upon metal in the air-bath. The temperature of the latter was then raised very gradually from 15° C. to 204°, or 205° C. When the time occupied in the passage to the maximum temperature was two hours and upwards, the gun-cotton did not explode at all (in six experiments), but gradually

* Comptes Rendus, vol. lix. p. 487.

became dark brown, quite friable, and deprived of all explosive properties. When a considerably shorter time (about one hour) was occupied in the attainment of the maximum temperature, the gun-cotton exploded on one or two occasions, but not until its temperature had reached 205° C.

In the next experiments, the gun-cotton was employed in very small compact masses, and, resting upon a wooden support, was exposed to a continuously increasing temperature. The passage from 15° C. to the exploding-point ranged in these experiments from forty-five minutes to two hours.

Temperature at commencement of Experiment = 26° C.

No. of experiment.	Time occupied.	Exploding-point.
8	Forty-five minutes	137°·5 C.
9	One hour twenty-five minutes	136° „
10	One hour	137°·5 „
11	One hour	138°·5 „
12	Two hours	138° „

Another series of experiments was instituted for ascertaining in what particular mechanical condition the gun-cotton exploded most readily and at most uniform temperatures; and ultimately the material was employed in the form of pieces of loosely-twisted strand about 20 millims. long, and its exploding-point was determined by first raising the atmosphere of the air-bath to 105° C., then allowing the specimen to fall upon a diaphragm of wire gauze in the air-bath, at once increasing the temperature as rapidly as possible, and carefully reading the thermometer until the explosion occurred. The results of eight observations thus conducted were as follows:—

No. of experiment.	Exploding-point.
13	151°·5 C.
14	151° „
15	151° „
16	150°·5 „
17	150°·5 „
18	148°·5 „
19	151° „
19a	147° „

These last experiments, which appear the most trustworthy, indicate that the average temperature at which the gun-cotton explodes when in a condition most favourable to its rapid heating, is about 150° C. In two observations, in which the gun-cotton was in a very open condition, the temperature being raised more rapidly than usual, the explosions occurred when the thermometer indicated 145° and 143°·5 C.; and in the experiments preceding these, which were differently conducted, compact gun-cotton being exposed to heat for a considerable time, the point of ignition ranged between 136° and

138°·5 C. SCHRÖTTER, REDTENBACHER, and SCHNEIDER, in their report upon Von LENK's gun-cotton, mention that 136° C. is the *lowest* temperature fixed by Von EBNER at which this material explodes.

EFFECTS UPON GUN-COTTON OF EXPOSURE TO 100° C.

PÉLOUZE and MAURY, in their accounts of the effects of heat upon gun-cotton, describe several kinds or stages of decomposition as occurring, or producible at will, by its exposure to a temperature of 100° C., and state that in every instance they found a few minutes' exposure to that temperature sufficient to produce a disengagement of nitrous vapours.

A large number of experiments has been instituted with gun-cotton prepared at Waltham Abbey and Stowmarket according to Von LENK's direction, and also with some specimens of Austrian gun-cotton, with the view of ascertaining the effect upon them of exposure to 100° C. The gun-cotton was exposed to heat in sealed tubes and in open vessels arranged in different ways. The quantities operated upon and other conditions in the experiments were varied, as will be presently particularized, the objects contemplated being, in the first instance, to examine into the effects of exposure of gun-cotton to heat, and, afterwards, to ascertain if possible by what circumstances those effects might be subject to modification.

The following is a condensed account of the observations made.

I. *Experiments in sealed tubes.*—Experiment 20. Air-dry gun-cotton (coarse yarn, manufactured in 1863), enclosed in a stout glass tube hermetically sealed, was maintained at 100° C. in a water-bath. The tube was filled with deep orange vapours in about three hours. The vapours gradually diminished in intensity, after a time, until the gun-cotton was converted into a gum-like mass, the transformation occurring most rapidly at the upper end of the tube, where the water produced during the change condensed and returned, charged with acid, upon the gun-cotton. When the sealed tube was opened, after continuation of the heat for three or four days (seven hours daily), nitric oxide escaped under considerable pressure. Upon closing the tube again, after the escape of gas, and continuing the application of heat, the gun-cotton was gradually converted into a black pitch-like mass.

This experiment, several times repeated, always furnished closely similar results.

Experiment 21.—A tube containing fine gun-cotton thread, manufactured in 1863, was exhausted and sealed. After four hours' exposure to 100° C., it exploded with great violence, tearing open the stout copper water-bath in which it was heated. Portions of unburned gun-cotton were scattered about.

Experiment 22.—Another tube, containing some of the same gun-cotton, was opened after seven hours' heating, to allow the gas to escape, and again sealed. On the second day, after heating for three or four hours, it exploded violently.

Experiment 23.—Several experiments were made with perfectly dry gun-cotton, and furnished results quite similar to those obtained with the air-dry material.

Experiment 24.—Fine gun-cotton thread was introduced into a tube sealed at one

end; the other extremity of the tube was constricted, then exhausted and filled with nitrogen, these operations being repeated three times; the tube was afterwards sealed and heated to 100°C . in a water-bath. After forty-five minutes faint red vapours were observed. In another quarter of an hour the colour of the vapours was very deep; in a short time nitrous acid began to condense in the cool part of the tube. After continuing the heat for $1\frac{1}{4}$ hour longer, the coloured vapours had entirely disappeared. The gun-cotton had become highly bleached, and in the upper extremity of the tube it was partially converted into the gummy substance. Nitric oxide escaped when the tube was opened.

Experiment 25.—A sample of gun-cotton impregnated with about 0.4 per cent. of alkaline carbonate, was exposed to 100° in an exhausted sealed tube, for the purpose of collecting the gases evolved. When the tube had been heated six hours daily for five days, it was opened under mercury, and the gas, which escaped under considerable pressure, collected. The tube was again closed and heated for two days, when gas was once more collected from it. The experiment was interrupted, after the gun-cotton had been further heated for two days, the tube being fractured by the effects of an explosion in its vicinity. The collected gases were found to consist of 50.2 per cent. of carbonic acid, 4.7 per cent. of nitric oxide, and 45 per cent. of nitrogen.

These experiments, in which the gun-cotton was submitted to the influence of 100°C . under the most severe conditions, appear to indicate that nitric peroxide or nitrous acid is liberated by the first decomposition of the gun-cotton, and at once establishes a further destructive action upon the substance, becoming reduced to nitric oxide, nitrogen being eventually liberated by complete reduction of the latter*. The extent of surface of gun-cotton presented to the action of heat, and of the liberated acid, appears to exert, as might be anticipated, an important influence upon the change. Exposure of fine gun-cotton thread to heat under the same conditions as those which were safe with coarse yarn gave rise to explosions, due possibly to the increased pressure of gas in the tubes, but more probably, judging from their great violence, to the sudden decomposition of the gun-cotton at a particular period. The characters exhibited by the products of decomposition of gun-cotton obtained in experiments 20 and 24, were similar to those already described by other chemists, and have been referred to in the preceding parts of this paper.

II. *Experiments in vessels open to the air.*—The following experiments, conducted with considerably larger quantities of gun-cotton than before employed, were made with the view of obtaining, at one time, several distinct data regarding the decomposition of gun-cotton at 100°C . Direct evidence was sought of the development of heat in gun-cotton upon continued exposure to that temperature. The period was carefully noted when decomposition was first indicated by the disengagement of nitrous acid, after commencement of the experiment. In some instances, the loss of weight sustained by the

* Similar results were observed in experiment 109.

gun-cotton was determined at intervals (*e. g.* at the close of six hours, or one day's exposure to heat), the nitrous acid contained in the vessel being first displaced.

The vessels employed in these experiments were globe-flasks fitted by means of perforated corks, with long narrow glass tubes, and in most instances with thermometers graduated from 100° C. upwards. The flasks were of a size to receive the gun-cotton in a compact condition, and the thermometer-bulbs were inserted into the centre of the mass. Continuous observations were made in safety during the experiments, through a small glass let into a wooden screen, which was placed in front of the water-bath containing the heated flask. The results obtained are tabulated for convenience of comparison.

TABLE I.

No. of experiment.	Description of gun-cotton.	Quantity employed.	Total exposure to 100° C.	Interval between first exposure to 100° C., and first signs of decomposition.	Loss of weight sustained by the gun-cotton.	Temperature observations.	Other observations.
26	Coarse yarn made in 1864, Waltham.	grms. 15.55	20 hours (in 4 days).	4 hours	1 per ct. in 6 ^h , 12.91 per ct. in 12 ^h 30 ^m , 13.91 p. c. = total loss in 18 hours.	Not made in this experiment	The gun-cotton <i>exploded</i> violently soon after commencement of the 4th day's heating. Nitrous acid was copiously evolved just before the explosion.
27	Coarse yarn, Waltham.	22	5 ^h 30 ^m (30 minutes on the second day).	2 hours	8.35 per cent. in 5 hours.	The thermometer remained almost stationary during the first 4½ hours. It then rose continuously and reached to 109° C. in 25 minutes, when the experiment was interrupted. On 2nd day, when the thermometer reached 100° C., it continued to rise; within 30 minutes it indicated 122° C., and the gun-cotton <i>exploded</i> very shortly afterwards.	The evolution of nitrous acid, when it once commenced, continued copious throughout the experiment. The <i>explosion</i> of the gun-cotton was very violent.
28	Coarse yarn, Waltham.	6.5	24 hours (in 4 days).	8 hours	23.7 per cent. in 24 hours.	The thermometer did not rise above 100° C. on the first day. On the 2nd day, after 1½ hour's heating, it rose slowly till it reached 109° C. It remained nearly stationary at that point for 1½ hour, and then gradually fell to 100° C. towards the close of the 2nd day. No rise of temperature was observed on the 3rd and 4th days.	At the conclusion of the experiment the sample had contracted somewhat, and assumed a brown colour. It was quite friable, and had lost the properties of gun-cotton.
29	Fine yarn, Waltham.	6.5	21 hours (in 3 days).	3 hours	30 per cent. in 21 hours.	A slight increase of temperature was indicated at the close of the 3rd hour, the highest temperature, 110° C., being indicated 3 ^h 50 ^m after commencing the experiment. Shortly afterwards the thermometer began to fall; after the lapse of 1 hour it indicated 103° C., and had fallen to 100° C. before the close of the 1st day. No rise in temperature was observed on the 2nd or 3rd days.	The gun-cotton began to darken on the 2nd day. At conclusion of experiment it had contracted considerably, was dark brown, yielded a considerable proportion to water, in which the usual products of change were detected. The residue was nearly soluble in alcohol, and completely so in ether and alcohol.
30	Coarse yarn from Hirtenberg.	6.5	33 minutes ...	20 minutes		The thermometer began to rise 25 minutes after first exposure, and continued to do so very rapidly up to the time of explosion.	The gun-cotton <i>exploded</i> violently after 33 minutes' exposure to 100° C.
31	Coarse yarn from Austria (another specimen).	6.5	1 hour	15 minutes		The thermometer began to rise 45 minutes after first exposure, and continued to rise rapidly, indicating 129° shortly before the explosion.	The gun-cotton <i>exploded</i> violently after exposure to 100° C. for one hour.

These results indicated,—

(1) That sufficiently protracted exposure to 100°C . under conditions unfavourable to the rapid expulsion of the nitrous acid developed by the first action of the heat upon the gun-cotton, ensures the complete destruction of the original properties of this substance, and its conversion into a variety of volatile and fixed products.

(2) That the rapidity and violence of the decomposition resulting from the combined action of heat and of the acid generated, is regulated by the quantity of gun-cotton operated upon.

(3) That, as shown by experiments 28 and 29, conducted with coarse and fine yarn manufactured in precisely the same manner, the mechanical condition of the gun-cotton exerts an important influence over the rapidity of decomposition at 100° (a point also indicated by the results of experiments in sealed tubes).

(4) That a very important difference may exist between the behaviour of different samples of gun-cotton, even if operated upon in precisely the same manner, quantities, and mechanical conditions. This is illustrated by comparing experiments 30 and 31 (conducted with Austrian gun-cotton), with experiment 28, and with a considerable number (18) of precisely similar experiments instituted with different samples of Waltham Abbey gun-cotton, in not one of which was an explosion brought about by long-continued exposure of equal quantities (6.5 grms.) to 100°C . The two specimens of Austrian gun-cotton differed very greatly in composition from all the products of manufacture prepared at Waltham, according to Von LENK's system; and it will be shown presently that this circumstance may serve to account for the exceptional proneness of these specimens to very violent decomposition under the particular conditions of the above experiments.

It need perhaps scarcely be stated that the temperature-observations in these experiments (and others still to be described) were instituted more with the view to afford a good means of registering the comparative rapidity of decomposition of different specimens of gun-cotton operated upon under equal conditions, than with the idea of attempting to ascertain the actual moment of development of heat and progressive rise of temperature in a mass of gun-cotton. Such observations could only be correctly made with much larger quantities of gun-cotton, so confined as to prevent the escape of heat from the interior, and are therefore impracticable on the score of danger. A considerable number of these thermometric observations, which unquestionably recorded close approximations of the actual rise in temperature of the interior of the mass of badly conducting gun-cotton, showed that, when the temperature passes 110° to 112°C ., the development of heat proceeds with great rapidity, so that very speedily the rise of the thermometer does not keep pace with the heating of portions of the gun-cotton in close proximity to it, and therefore the explosion of the mass appears to occur at a temperature considerably lower than the actual exploding point of gun-cotton.

In continuation of the heat-experiments, several samples of gun-cotton from Waltham Abbey and Stowmarket, weighing 3 grms. each, in an air-dry condition, were exposed to

100° C. in conical assay flasks, into which long quill-tubes were fitted. The following results were observed.

TABLE II.

Number of experiment.	Nature of gun-cotton.	Nitrous vapours first observed after commencement of experiment.	Other observations.
32	Coarse yarn from Waltham Abbey, made in 1863.	In 5 hours, very faint colour.	The gun-cotton was heated 5 hours daily for 6 days. The nitrous fumes were never more than very faint, and were no longer visible after the close of the third day's experiment. At the close of the 6th day the gun-cotton had scarcely altered in appearance. The specimen was destroyed on the 7th day by the explosion of a neighbouring vessel. The atmosphere in the flasks was deeply coloured at the expiration of the 6th hour; the experiments were therefore interrupted.
33	Fine yarn from Waltham, made in 1864.	In 2 hours, faint colour.	
34	Fine yarn from Waltham, made in 1866.	In 2 hours.	
35	Medium sized yarn, Waltham, 1864.	In 1½ hour, very faint colour.	
36	Coarse yarn made at Waltham, 1864.	In 30 minutes.	The vessel was filled with deep-coloured vapours after 5 hours' exposure. The experiment was continued on the next day, when, after further exposure to 100° C. for 4 hours, the specimen <i>exploded</i> . Nitrous vapours were abundantly evolved within 10 minutes, and continued to increase until the experiment was arrested.
37	Stowmarket, coarse yarn, 1864 (early manufacture).	In 10 minutes.	
38	Stowmarket, coarse yarn (another specimen).	None observed during 9 days' exposure, 5 hours daily.	After 9 days' exposure no nitrous vapours were observed in the vessel. The specimen had an acid reaction and somewhat pungent odour, but was not otherwise altered.
39	A portion of the same sample as 38.	Very faint after 15 hours' treatment.	The nitrous vapours became more evident on the 4th day of the experiment.

These eight experiments, conducted precisely alike, point to very important differences in the powers of different specimens of gun-cotton to resist destruction by exposure to 100° C. Of five samples manufactured at Waltham Abbey, only one exhibited the effects of such exposure described by PÉLOUZE and MAURY as invariable, namely, the disengagement of nitrous vapours within a few minutes. One specimen did not exhibit this sign of change until after five hours' exposure, and then only to a very slight extent. Of two specimens of gun-cotton from Stowmarket, one decomposed with very considerable rapidity at 100° C., and the other did not, in one experiment, evolve any visible amount of nitrous acid during forty-five hours' exposure, in nine days, and exhibited very slight signs of change at the expiration of this severe treatment; while in a second experiment, with a portion of the same sample, slight decomposition became apparent at the close of the third day's exposure of five hours.

The cause of the latter difference in the behaviour of one and the same sample, upon different occasions, was traced to the circumstance that the specimen, in the condition in which it was first employed, contained a somewhat larger proportion of moisture than when the experiment was repeated with it, in consequence of its having been in a damp locality for a short time before the first portion was operated upon. Thus one possible reason for the different behaviour of several samples of gun-cotton prepared by one and the same process was indicated. In confirmation of the influence exerted by moisture in retarding the decomposition of gun-cotton exposed to a high temperature, the results of a preliminary experiment may be here recorded, which was instituted with a sample of gun-cotton found to be very readily affected by exposure to heat.

Experiment 40.—Three specimens, each of one grm., were exposed side by side in small long-necked flasks to 100° C., in three different conditions. The one was air-dry (and contained therefore about 2 per cent. of water), the second was dried immediately before the experiment by sufficient exposure to 50° C., and the third was saturated with water and pressed between bibulous paper. The dry sample showed signs of decomposition in ten minutes, the air-dry sample began to decompose in forty-five minutes, and the moistened specimen exhibited no acidity after exposure to 100° C. five hours daily for three days (further experiments on the protective power of water will be presently described). In all subsequent experiments upon the comparative effects of exposure of different samples to elevated temperatures, the gun-cotton was employed in a dry condition.

The discrepancies noticed above in the behaviour of different samples of gun-cotton under exposure to 100° C., led to a searching investigation into the composition of products of manufacture obtained from Waltham Abbey, Stowmarket, and Hirtenberg, the results of which were laid before the Royal Society last year.

It was established by this inquiry that gun-cotton manufactured at those establishments contains variable proportions of the following substances foreign to the most explosive gun-cotton, *trinitrocellulose*, or $\text{C}_6\text{H}_7\text{O}_5\text{N}_3$.

(1) Hygroscopic moisture, the proportion of which amounts very uniformly to about 2 per cent., except in special instances, when mineral impurities in the material exert an influence upon its hygroscopic properties*.

(2) Mineral matters, varying in amount with the character of water used in purifying the material, with the duration of its treatment with water, and with the circumstance whether the purified gun-cotton has been submitted to the treatment with soluble glass, recommended by Von LENK. These mineral matters include calcic and magnesian carbonates, silica, clay, and occasionally small quantities of sand and alkaline salts.

(3) Products of the less complete action of nitric acid upon cellulose, the nature of which has been investigated by HADOW. These products, which are less explosive than trinitrocellulose, and are more or less readily soluble in mixtures of ether and alcohol, were found to exist in very considerable proportion in some samples obtained from Hirtenberg and Stowmarket, and have also been found to the extent of about 2 per cent. in the most perfect products of manufacture. Their formation may be due to insufficiently protracted treatment of the cotton with the mixed acids, to the employment of acids of insufficient strength, and to the presence of hygroscopic moisture in the cotton at the time of its conversion. An elevation of temperature during the treatment of the cotton with the acids would also give rise to the production of soluble gun-cotton.

(4) Products of the partial oxidation, by nitric acid, of organic impurities existing in the cotton, even after the preliminary purification to which it is subject. These products,

* Several of the earlier products of manufacture obtained at Stowmarket were found to absorb from the atmosphere, under ordinary conditions, from 0.5 to 1.5 per cent. more moisture than the average proportion (2 per cent.) contained in Von LENK's gun-cotton.

which are formed from portions of seed-husk adhering to the cotton, and from small quantities of gum-like and other substances still retained within the fibre, escape complete removal from the gun-cotton, although the larger proportion passes into solution during the treatment with acids and upon the subsequent digestion in an alkaline bath. It need scarcely be stated that the proportion of these substances, existing in the finished gun-cotton, varies with the description and quality of cotton employed, with the duration of the digestion in acids, and the degree of perfection of the purifying processes to which the material has been submitted. They are discovered by treatment of the gun-cotton with alcohol, and no specimen has yet been examined by me which has been found entirely free from them, while comparatively considerable proportions have been found to exist in a few specimens from Hirtenberg and Stowmarket.

A description of the nature of these impurities, as far as it could be determined, has been given in the previous memoir*. They possess acid characters, and their origin leaves no room to doubt that they are less simple and definite, and therefore less stable in their characters, than are the products of the action of nitric acid at low temperatures upon pure cellulose.

It has been argued by SCHRÖTTER, REDTENBACHER, and SCHNEIDER in their official report upon Von LENK's gun-cotton, that an incomplete conversion of cellulose into the most explosive gun-cotton may be one cause of the want of stability observed in the early products of manufacture (at Bouchet, &c.); and consequently the existence in gun-cotton of a proportion of the third class of impurities above specified should, according to these chemists, give rise to, or promote a tendency to spontaneous change in the material. On the other hand, PÉLOUZE and MAURY consider it probable that a gun-cotton will be the more liable to spontaneous change the further it is removed in composition from the cellulose type, and that products prepared by prolonged immersion in large proportions of very concentrated acids will therefore be more liable to spontaneous ignition than the gun-cotton prepared by a brief immersion in less concentrated acids. No experimental data are given in support of either opinion.

The discordant results furnished by the heat-experiments just described, and the facts established by investigating the composition of the gun-cotton operated upon, led to the institution of a very considerable number of experiments with the view of ascertaining, if possible, whether the establishment of change in gun-cotton by its exposure to high temperatures has to be ascribed to the instability of trinitrocellulose itself, or whether it is to any extent ascribable to the injurious influence of less permanent bodies existing as impurities in the ordinary product of manufacture.

A careful comparative examination was instituted of the effects of exposure, under equal conditions, to 100° C. upon a number of samples in portions of which the matters soluble in ether and alcohol had been determined. One gramme of each sample was first dried in a water-bath at a temperature of 50° C.; it was then introduced loosely into a small flask having a neck about 220 millims. in length, and immersed in boiling water, the first indications of the disengagement of nitrous acid being afterwards care-

* Transactions Royal Society, vol. clvi. p. 285.

fully noted. The specimens were uniformly exposed to 100° C. for thirty hours (six hours daily for five consecutive days), unless, as was the case in a few instances, the gun-cotton had suffered complete change within a shorter period.

TABLE III.

No. of experiment.	Description of gun-cotton.	Percentage of matter extracted by ether and alcohol.	Period when nitrous vapours were first observed after commencement of experiment.	Other observations.
41	Coarse yarn, manufactured at different periods at Waltham Abbey, <i>not silicated</i> .	1·80	4 hours.	The atmosphere in the flask was only faintly coloured during the whole term of the experiment. At the conclusion the gun-cotton had darkened slightly in a few places, but had not altered in explosiveness or strength of fibre.
42		1·83	1 hour.	The atmosphere in the flask became only faintly coloured on the second day; the gun-cotton darkened and contracted, and its explosiveness was much reduced.
43		1·91	45 minutes.	The nitrous vapours were not considerable throughout the experiment, colour of the gun-cotton not altered, but the fibre weakened and explosiveness reduced.
44		1·99	2 ^h 30 ^m .	A faint coloration of the atmosphere in the flask was only observed on the first day. The colour and strength of fibre were not altered, but the explosiveness was greatly reduced.
45		2·00	14 hours.	Only very faint indications of nitrous acid at any time. After 30 hours' exposure the gun-cotton had not suffered any change in colour, strength of fibre, or explosive qualities.
46		2·00	1 ^h 30 ^m .	Towards the close of the second day, the atmosphere in the flask was only faintly coloured. Colour and strength of fibre not altered, but explosiveness notably reduced.
47		2·12	14 hours.	Only very faint indications of nitrous acid at any time. The gun-cotton sustained no change in colour, strength of fibre, or explosiveness.
48		2·21	4 hours.	Only faint indications of nitrous acid observed in either of these experiments. Neither of the samples were altered in appearance or strength of fibre, but the explosiveness of both was diminished.
49		2·22	1 ^h 20 ^m .	
50		2·25	45 minutes.	
51		2·30	45 minutes.	
52	Coarse yarn, manufactured at Stowmarket, <i>silicated</i> .	2·31	1 hour.	Nitrous vapours were somewhat more abundantly evolved in experiment 50 than in 51, only faint indications being obtained in the latter case. Neither sample was altered in colour, but the strength of fibre and explosiveness were reduced in both instances.
53		2·6	3 ^h 30 ^m .	The indications of nitrous acid were very faint after the first day's exposure. The gun-cotton was very slightly darkened in a few places, but strength of fibre and explosiveness were not affected.
54		2·85	45 minutes.	Very slight reduction in explosiveness at conclusion of experiment; no change in appearance. Faint indication of nitrous acid throughout the experiment; the gun-cotton was darkened, and its explosiveness somewhat reduced.
55		3·0	45 minutes.	Faint indications of nitrous acid. Fibre not altered in colour or toughness, but explosiveness much reduced.
56		3·41	10 minutes.	Nitrous acid evolved abundantly. The gun-cotton converted into a pulverulent, quite explosive substance.
57		3·34	17 hours.	Very faint indications of nitrous acid. Strength of fibre not altered, but explosiveness much reduced.
58		3·68	5 ^h 45 ^m .	Nitrous acid not considerable. Gun-cotton discoloured and friable, explosiveness destroyed.
59		4·0	2 ^h 15 ^m .	Nitrous acid abundant. Fibre of gun-cotton and explosiveness destroyed.
60		4·1	45 minutes.	Nitrous acid not abundant. Gun-cotton darkened in parts; strength of fibre and explosiveness slightly reduced.
61		4·15	5 hours.	Nitrous acid not abundant. Gun-cotton not darkened, but fibre rotten, and explosiveness very greatly reduced.
62	Coarse yarn, manufactured at Stowmarket, <i>silicated</i> .	4·24	5 hours.	Nitrous acid considerable. Gum-like mass produced.
63		4·3	10 minutes.	Nitrous acid very abundant. Gun-cotton converted into friable non-explosive material.
64		5·1	5 ^h 45 ^m .	Nitrous acid very abundant. Gum-like mass produced.
65		8·5	15 hours.	Very faint indications of nitrous acid. Gun-cotton slightly discoloured; strength of fibre and explosiveness very slightly reduced.
66		11·78	15 hours.	Faint indication of nitrous acid. Gun-cotton darkened; strength of fibre slightly diminished, and explosiveness much reduced.
67	Coarse yarn, Austria.	3·02	1 ^h 15 ^m .	Nitrous acid considerable on the second day, diminished afterwards. Gun-cotton darkened in some parts; strength of fibre and explosiveness much reduced.
68	Fine yarn, Austria.	3·66	30 minutes.	Nitrous vapours considerable, disappeared entirely towards close of experiment. Strength of fibre and explosiveness very greatly reduced.
69	Fine yarn, Austria.	4·50	3 ^h 30 ^m .	Faint indications of nitrous acid. Strength of fibre and explosiveness scarcely affected in either instance.
70	Fine yarn, Austria.	5·02	1 hour.	
71	Coarse yarn, Austria.	7·44	15 minutes (total exposure 12 hours).	Nitrous vapours very abundant. Gum-like mass produced, with a charred appearance in some parts.
72	Coarse yarn, Austria.	8·6	10 minutes (total exposure 12 hours).	
73	Coarse yarn, Austria.	14·2	10 minutes (total exposure 12 hours).	Nitrous vapours very abundant. Gun-cotton quite pulverulent and passing into gum-like mass.
74	Coarse yarn, Austria.	14·1	12 minutes (total exposure 15 hours).	
75	Fine yarn, Austria.	15	8 minutes.	Nitrous acid vapours considerable; strength of fibre and explosiveness considerably diminished.
76	Coarse yarn, Austria.	70 (about)	30 minutes.	Nitrous acid only faint after the second day. Fibre and explosiveness destroyed.

The following are the principal facts demonstrated by the foregoing experiments:—

1. The results furnished by the samples of Waltham Abbey gun-cotton demonstrate that different samples of the material, manufactured as far as possible in the same manner, are not alike affected by exposure for a fixed period to 100° C. under uniform conditions. Of thirteen samples of Waltham Abbey gun-cotton, four resisted in a remarkable manner the destructive effects of heat, and remained unchanged in physical properties and explosiveness after thirty hours' exposure to 100° C. This treatment only developed acid to a slight extent in these particular samples; but in the other nine specimens it produced somewhat greater alteration; nitrous acid was disengaged in more considerable proportions, the fibre of the gun-cotton was rendered more or less rotten, and its explosiveness was diminished in different degrees.

2. The comparative celerity with which nitrous acid is disengaged from different specimens of gun-cotton upon exposure to 100° C., does not afford a reliable indication of their relative susceptibility to rapid decomposition at that temperature. As illustrations of this the following instances may be selected from among those furnished by the results detailed in the preceding Table. Those specimens of Waltham Abbey gun-cotton which exhibited uniform powers of resisting the destructive effect of heat (experiments 41, 45, 47, and 52), furnished the first faint indications of development of acid vapours at one hour, four hours, and fourteen hours, respectively, after first exposure to 100° C. Three samples (experiments 44, 48, 49) which were altered alike, and slightly, by uniform exposure to 100° for thirty hours, exhibited the first symptoms of decomposition at 1^h 20^m, 2^h 30^m, and four hours after commencement of the experiment. Again, a sample which exhibited no sign of change beyond slight acidity at the close of the experiment (experiment 52) afforded faint indications of the development of acid in one hour, while another specimen which sustained comparatively considerable change (experiment 48) did not evolve any acid vapour until four hours after its first exposure to heat. An inspection of the results obtained with Stowmarket gun-cotton shows that, out of thirteen samples, five did not furnish signs of disengagement of acid vapours until after the lapse of five hours and upwards, while among the thirteen Waltham Abbey samples only three furnished no signs of change for four hours and upwards. On the other hand, these samples of Waltham Abbey gun-cotton were, after thirty hours' exposure, only very slightly affected, while the Stowmarket samples just referred to, all exhibited important signs of change. Two samples from Stowmarket (experiments 54 and 60), though they evolved acid vapours within forty-five minutes of their first exposure, were not very greatly changed by the thirty hours' treatment, while other two samples (experiments 62 and 64), which evolved no acid for five hours and 5^h 45^m, were completely decomposed by the close of the experiment.

A careful examination into the possible causes of these differences showed that they were to be ascribed, at any rate in very great measure, to variations in the proportion and character of the mineral matters contained in the specimens. Some few of the Waltham Abbey samples contained larger proportions of calcic and magnesian carbonates

(deposited upon the fibre by the hard water in which the material had been washed) than other samples. There was consequently present in such specimens a larger amount of matter capable of neutralizing acid, if liberated by the action of heat, than in others; and therefore the period would be proportionately delayed, in those instances, when the development of free acid would first become evident. The Stowmarket samples had been submitted to the "silicating" process, which consists in impregnating the gun-cotton with a dilute solution of soluble glass, afterwards drying it, and finally washing it in spring- or rain-water. The result of this treatment is that small proportions of alkaline and earthy carbonates are deposited upon the fibre in addition to what it would acquire by simple long-continued exposure to running water. This circumstance tends to explain why the Stowmarket gun-cotton experimented with, though generally much more seriously affected by protracted exposure to 100° C. than the Waltham Abbey samples, appeared to resist change in several instances for much longer periods than the latter.

The proportion and nature of the mineral matters in gun-cotton may, therefore, as shown by those experiments, exert a very notable effect upon the behaviour of the material when exposed to high temperatures. But the results of subsequent experiments have demonstrated most decisively that the influence which the presence of earthy or alkaline carbonates, mechanically distributed in small proportion through a mass of gun-cotton, exerts upon the effects produced by exposure to heat, is in many instances not confined to a simple delay of the *indications* of change furnished by the development of acid; it may also manifest itself in much more important directions, namely, by actually retarding and even considerably limiting, if not altogether preventing, the spontaneous decomposition of the gun-cotton itself. These effects are of such evident importance in connexion with the question of the stability of gun-cotton, that they have been made the subject of extensive experimental inquiry, the results of which will be given under a special head.

3. The different behaviour of the samples of gun-cotton operated upon in the foregoing experiments cannot be ascribed to differences in the *proportions* of matter soluble in ether and alcohol present in them. The four samples (experiments 41, 45, 47, 52) which withstood to the greatest extent the action of heat, contained 1·8, 2, 2·1, and 2·31 per cent. of soluble matter, which numbers represent the lowest, the mean, and almost the highest proportions of soluble matter in the Waltham Abbey gun-cotton. Again, some samples of Waltham Abbey products, containing identical proportions of soluble matter, behaved very differently, as may be seen by comparing experiments 41 and 42, 45 and 46, 51 and 52. The want of connexion between the proportion of matter soluble in ether and alcohol, and the stability of the sample, is perhaps even more strikingly demonstrated by results obtained with specimens of Stowmarket and Hirtenberg products. Samples containing equal proportions of soluble matter, as in experiments 56 and 57, 59 and 60, 65 and 72, behaved very differently, while others, in which the amount of soluble matter differed very considerably, exhibited similar behaviour upon

exposure to heat, as demonstrated by a comparison of experiments 57 and 66, 41 and 70, 56, 63 with 72, 73, and 74.

A comparison of the general results furnished by the Waltham Abbey and Austrian samples might be considered to afford some foundation for the conclusion that the gun-cotton which contains the largest proportion of the less explosive cellulose-products is the most susceptible of change, but it has already been shown that this conclusion is not supported by comparison of the individual experiments; and the following additional illustrations may be pointed out. A sample of Waltham gun-cotton containing 1.83 per cent. of soluble matter sustained decidedly greater change than Austrian samples containing 4.5 and 5.02 per cent., or than a Stowmarket sample containing 8.5 per cent.; and a specimen of Austrian cotton containing 3 per cent. of soluble matter did not sustain less alteration, and was much more rapidly affected than one from Stowmarket containing 11.78 per cent. Again, the specimen of Austrian gun-cotton which consisted chiefly of the lower nitro-products, was not so rapidly or completely changed as another Austrian specimen which contained only 7.4 per cent. of soluble matter (experiment 71), or a Stowmarket sample which contained but 4.3 per cent. (experiment 63).

4. A comparison of the *characters* exhibited by the matters which ether and alcohol extracted from different samples employed in these experiments, appeared to throw much greater light upon the causes of their different behaviour, than the comparison of the *proportions* of soluble matter which they furnished. Reference has already been made (p. 201) to the matters soluble in alcohol alone, which have been discovered in small but variable proportions in all samples of gun-cotton hitherto examined. Both the quantity and character of these substances extracted from different specimens of gun-cotton exhibit variations, as might be anticipated, when it is remembered that they are derived from impurities retained by the cellulose to an extent determined by the particular description and degree of purity of the cotton operated upon. In the Waltham Abbey specimens employed, the proportion of matter varied only slightly (between 0.72 and 0.9 per cent.); yet, although the comparatively slight differences in the effects of heat upon the different samples were in part ascribable to variations in the proportions of mineral matters present, indications were obtained that the gun-cotton which resisted the action of heat to the greatest extent contained the smallest proportion of nitrogenized organic matter not derived from cellulose. The Stowmarket samples afforded much more decided evidence of the influence of these foreign products upon the stability of the gun-cotton. Two specimens (experiments 56 and 63) from which nitrous acid-vapours were disengaged within ten minutes of their first exposure to 100° C., and three others (58, 62, and 64) which, owing apparently to the influence of mineral matters, did not furnish acid-vapours until after five hours' exposure, yielded extracts with ether and alcohol decidedly different in character from the other specimens; a comparatively large proportion consisted of nitrogenized acid matter of a resinous character, soluble in alcohol.

With two or three exceptions, the samples of Austrian gun-cotton exhibited decided

signs of less complete purification of the cotton previous to conversion, than the generality of samples of English manufacture. It should also be observed that the extract by ether and alcohol after treatment of the samples with alcohol, possessed in several instances the characters of photographic collodion (the solutions furnishing tough transparent films upon glass), which was not the case with any of the specimens of Waltham Abbey gun-cotton, and in only one or two instances among the samples from Stowmarket. The ordinary ethereal extract from the English samples furnished a horny brittle residue, contracting greatly upon perfect desiccation, and appearing to consist chiefly of the product "B" described by HADOW as having the formula $C_{18}H_{22}O_{15}8NO_2$. No decided evidence was obtained in support of the conclusion that this difference in the character of the ethereal extract affected the stability of the gun-cotton. On the contrary, the Austrian samples used in experiments 71 and 72, which did not furnish an extract having the properties of good collodion, and only yielded 7.5 and 8.5 per cent. of total soluble matter, decomposed far more rapidly and completely than the specimen (experiment 76) which consisted chiefly of collodion gun-cotton.

The destructive effect upon the structure of the fibre produced by the long-continued digestion of the gun-cotton in warm solvents, which is necessary for ensuring the extraction as completely as practicable of the soluble matters, renders it very difficult to obtain reliable indications of the effects of heat upon gun-cotton deprived of those substances. The following experiments appear, however, to afford considerable support to the inference drawn from some of the results of the heat-experiments just referred to, that the existence in gun-cotton of small proportions of organic impurities, resulting from partial oxidation of foreign matters enclosed in the cotton fibre, exerts a very prejudicial influence upon the stability of the material, and that there is no sound foundation for the opinion that any such influence is exerted by the lower cellulose-products, when associated in small or large proportion with trinitrocellulose.

Experiments 77–80.—Four specimens of gun-cotton were extracted with ether and alcohol, by being twice digested for periods of twenty-four hours, in a considerable volume of the mixture, and afterwards washed. The dry specimens were then exposed for twelve hours (in two days) to 100° C., side by side with portions of the original samples.

No. 1.—The *original* gun-cotton exhibited faint indications of disengagement of nitrous acid in ten minutes after first exposure; the vapours did not become more abundant throughout the experiment, and, at the conclusion, the gun-cotton, which was strongly acid, had sustained a loss of 18.5 per cent. The *extracted* sample did not, throughout the experiment; afford any indication of the disengagement of nitrous acid; its acidity at the close was comparatively very slight, and it had lost only 3.5 per cent.

No. 2.—This sample, as well as Nos. 3 and 4, contained considerably more soluble matter than No. 1 sample; the original gun-cotton behaved quite similarly to No. 1, but the portion treated with the solvent evolved nitrous vapours in about fifteen minutes, and sustained much more rapid and considerable decomposition than the gun-cotton in its original condition.

No. 3.—The *extracted* gun-cotton first exhibited signs of change, and nitrous vapours were evolved more abundantly than from the original sample, which only afforded faint indications of nitrous acid after several hours' heating. The latter had lost only 5·5 per cent. at the conclusion of the experiment, while the extracted gun-cotton had sustained a loss of 10 per cent.

No. 4.—Signs of change were exhibited by both samples at the same time; faint vapours made their appearance after eight hours' exposure to 100° C. Nitrous acid was afterwards somewhat more abundantly evolved from the extracted sample. The loss sustained by the latter after twelve hours' heating was 5 per cent., that of the original gun-cotton was 4·1 per cent.

In these experiments No. 1 sample, which contained the average proportion of matter soluble in alcohol existing in Waltham Abbey gun-cotton, and a comparatively very small proportion of matter soluble in ether and alcohol, was rendered very much less susceptible of change at 100° C., by extraction with the mixed solvents, while the other samples, apparently in consequence of the injury to the structure of the fibre resulting from the extraction of a comparatively considerable proportion of imperfectly converted gun-cotton by the ether and alcohol, were rendered somewhat more prone to change by the treatment received.

Experiments 81, 82.—Two specimens of gun-cotton, selected from those which in preceding experiments had been found most susceptible of decomposition at 100° C., were digested for some time in dilute acetic acid, afterwards thoroughly washed, first in slightly alkaline water, and then in distilled water. By this treatment such mineral impurities as might have an influence upon the rapidity of decomposition of the gun-cotton were removed. One-half of each sample was digested for twenty-four hours with ether and alcohol, afterwards washed with the mixture, and dried. The samples thus treated were exposed to 100° C. in a water-bath, side by side with corresponding quantities of the same specimen which had simply been extracted with acetic acid. The results observed were as follows:—

	No. 1.		No. 2.	
	Treated with acetic acid only.	Treated with ether and alcohol.	Treated with acetic acid only.	Treated with ether and alcohol.
Indications of change observed after first exposure to 100° C.	35 minutes.	7½ hours (3 hours on the second day).	30 minutes.	3h 45m, very faint.
Loss of weight after 4½ hours' exposure to 100° C.	17·9 per cent.	2·3 per cent.	20 per cent.	1 per cent.

The very marked difference in the stability of these specimens (which contained only very small proportions of soluble gun-cotton), when exposed to 100° C. in the two different conditions, appears to afford strong evidence that the abstraction of the matters soluble in ether and alcohol greatly increases the stability of the gun-cotton. The next-following experiments show, on the one hand, that this difference does not appear ascribable to the removal of the soluble gun-cotton from the trinitrocellulose, and indicate, on the

other hand, that the closing up of the fibres resulting from the solution (or gelatinization), but imperfect removal from the gun-cotton of the soluble portions, may, in the above experiment, have imparted to the material increased powers of resisting decomposition at a high temperature.

Experiments 83-87.—Four specimens of gun-cotton, containing small proportions of imperfectly converted material, were thoroughly saturated with a very weak solution of pure soluble gun-cotton (or collodion), then at once removed from the liquid and dried. The mechanical condition of the gun-cotton was not perceptibly altered by this treatment. These specimens were exposed to 100°C ., together with portions of the original samples (all of them being for this purpose packed lightly and uniformly in small flasks). In every instance the prepared gun-cotton resisted the action of heat for a much longer period than the unprepared material. The former exhibited the first very faint indications of disengaging of nitrous acid between twelve and fourteen hours after the first exposure, while the unprepared specimens evolved nitrous acid after one hour to $1^{\text{h}} 30^{\text{m}}$ exposure.

It would appear therefore from these experiments that the addition of less perfectly converted gun-cotton to the ordinary product does not have the effect of promoting its decomposition at 100°C ., but that, on the contrary, when applied as indicated above, it renders the material considerably less susceptible of change, probably because the fibres are partially sealed, or in some other way mechanically protected by the treatment with dilute collodion. That the partial or complete closing of the fibre does exert an important influence upon the power of gun-cotton to resist the action of heat was demonstrated by

Experiment 88.—An ordinary sample of dry gun-cotton was allowed to remain for eighteen hours in a confined space together with an open vessel containing the ether- and alcohol-mixture. It was afterwards dried and exposed to 100°C ., side by side with a portion of the sample in its original condition. The latter exhibited signs of decomposition within two hours, the sample which had been exposed to the action of the vapour only exhibited faint signs of change after eighteen hours' exposure.

Experiment 89.—A specimen of Stowmarket gun-cotton containing a large proportion of matter extractable by ether and alcohol was washed with alcohol only, and its behaviour at 100° was afterwards compared with the original gun-cotton. The washed gun-cotton resisted the action of heat only slightly longer than the original gun-cotton, but it was observed that the washing had effected the separation of much of the earthy carbonates mechanically attached to the fibre, and hence was deprived, by the alcoholic treatment, both of a protective and a destructive element. A portion of the washed gun-cotton was afterwards exhausted as far as possible with ether and alcohol. By this treatment the fibre was much disintegrated, and upon exposure of the insoluble gun-cotton to 100°C ., it exhibited signs of decomposition much more speedily than the original gun-cotton. The ethereal extract was evaporated, and the dry product was exposed for thirty hours (during six days) to 100°C . No indications of nitrous acid

were observed throughout the experiment, and the material was unaltered in character, excepting that it had become decidedly acid. It should be observed that this ethereal extract was not quite free from the matters soluble in alcohol which the gun-cotton contained, as it is apparently impossible to extract these perfectly by digestion and frequent washing with alcohol.

Experiment 90.—A specimen of Waltham Abbey gun-cotton was in the first instance digested with dilute acetic acid and thoroughly washed, the object of this treatment being to remove any mineral matters from the sample which might exert a neutralizing action and thereby influence the effects of exposure to heat. One half of this gun-cotton was then digested for two days with warm alcohol, and was afterwards repeatedly washed. On evaporation of the alcoholic extract the usual small yellowish resinous residue was obtained.

A small portion of the dry gun-cotton thus purified was heated to 100° C. in a glass tube side by side with some of the same specimen which had only been extracted with acetic acid. Early on the second day of the experiment, the latter specimen began to evolve nitrous acid; and about thirty minutes afterwards the sample extracted with alcohol exhibited faint signs of decomposition.

Eight grammes of each of these samples, and a similar quantity of the gun-cotton in its original condition, were afterwards introduced into very long-necked flasks, the openings of which were loosely closed with corks and exposed for six days, seven hours daily, to 65° C.; as none of the specimens exhibited any sign of change at the expiration of that period, the temperature of the water-bath was maintained at between 88° and 90° . After about nine hours' exposure to this temperature, the original gun-cotton began to decompose, and two hours later an extremely faint indication of nitrous acid was observed in the sample extracted with *acetic acid*. After two days' (twelve hours) further exposure to heat, the first signs of decomposition became apparent in the flask containing the sample which had been extracted with *alcohol*. The coloration of the atmosphere continued, however, to be only faint in the flasks containing both extracted specimens during ten days' exposure to about 90° .

The observation made in this experiment, that the treatment of the gun-cotton with acetic acid decidedly increased its power of resisting the destructive effects of heat, was quite at variance with the anticipated result; for, undoubted evidence having already been obtained of the retarding effect upon the decomposition exerted by the existence of earthy carbonates when deposited upon the gun-cotton during the washing operations, it was considered that the treatment of ordinary gun-cotton with the acid, if it in any way influenced the subsequent action of heat upon the material, would have an accelerating effect. Several additional experiments confirmed, however, the correctness of the above observations; the following results, furnished by different samples of gun-cotton, of which portions were extracted with acetic acid, may be quoted in illustration of this.

TABLE IV.

No. of experiment.	Nature of material.	Exposed to	Duration of exposure.	Nitrous acid disengaged after first exposure.	Loss of weight.	Other observations.
91	Ordinary gun-cotton, air-dry.	100 ^o	4 ^h 30 ^m	20 minutes	27 per cent....	The vapours were very deep-coloured in 20 minutes.
	Same sample, extracted with acid.	100	4 ^h 30 ^m	35 minutes	20 per cent....	The vapours were not deep-coloured until after 2 hours' heating.
92	Ordinary gun-cotton, quite dry.	100	4 ^h 30 ^m	10 minutes	24.4 per cent....	The vapours very deep-coloured in 15 minutes.
	Same sample, extracted with acid.	100	4 ^h 30 ^m	30 minutes	17.9 per cent....	The vapours were deep-coloured after 30 minutes' heating.
93	Ordinary gun-cotton	65	140 hours (in 20 days).	30 hours, 4th day very faint.	In one week 1.66 per cent.	The sample was greatly changed after 20 days' heating, being converted partly into the matter soluble in water, of the usual character, and partly into soluble gun-cotton.
	Same sample, extracted with acid.	65	140 hours (in 20 days).	38 hours (6th day).	1.0 per cent....	The sample had sustained a trifling change; it had contracted somewhat, and the soluble matter had increased a little.

Upon examining the extract obtained by digesting gun-cotton with acetic acid in the cold, it was found to contain a small quantity of organic matter of resinous character, insoluble in water, but soluble in alcohol alone and in ether and alcohol, containing nitrogen and deflagrating when heated; it was evident therefore that this treatment of gun-cotton had the effect of purifying it to some extent from the organic impurities more perfectly removed by the extraction with alcohol.

The treatment of gun-cotton with dilute hydrochloric acid was not found to effect the removal of any proportion of these organic impurities, while the carbonates were, of course, readily extracted thereby. When gun-cotton, thus purified and very thoroughly washed, was exposed to heat side by side with the material in its original condition, the latter exhibited decidedly greater power of resisting change, thus furnishing an important indication of protective power exerted by carbonates if present in gun-cotton, which will be presently examined into more fully.

It is considered that the foregoing experiments afford good grounds for the following conclusions:—

(1) That the invariable existence in gun-cotton of small proportions of organic impurities, resulting from the partial oxidation of foreign matters enclosed within the cotton fibre, exerts a very prejudicial influence upon the stability of trinitrocellulose.

(2) That there is no sound foundation for the opinion that any such influence is exerted by the lower cellulose-products, when associated in large or small proportions with trinitrocellulose.

The following additional experimental data may be quoted in support of the latter conclusion:—

A considerable quantity of perfectly soluble gun-cotton was prepared at Waltham in

1865, the ordinary process of manufacture having been strictly followed, with the exception of the necessary difference in the strength of the acid-mixture used. This gun-cotton was found to correspond closely in composition to the formula of HADOW'S compound "C" ($C_{18}H_{23}O_{15}7N\Theta_2$), as shown in my first Memoir*. It has exhibited no tendency whatever to change by long-continued exposure to diffused daylight; several comparative experiments have been instituted with it and with samples of ordinary Waltham-Abbey products, and it has never exhibited any indications of greater susceptibility to change than the most stable of these. Indeed, the following results would appear to indicate that any difference in stability which may exist between the different members of the nitrocellulose group is not in the direction assumed by REDTENBACHER, SCHRÖTTER, and SCHNEIDER.

Experiment 94.—A portion (about 1 grm.) of the soluble gun-cotton, which had been reduced to a fine state of division in a pulping-machine, was introduced into a wide-bulb tube, and a similar tube was charged with a corresponding quantity of ordinary gun-cotton in the same mechanical condition. Both specimens were air-dry. They were exposed in the same water-bath seven hours daily to $100^{\circ}C$. Not the slightest indication of change was observed in either specimen until towards the close of the seventh day, when a faint coloration by nitrous acid was observed on looking down the tube containing the ordinary gun-cotton. Very shortly afterwards a still fainter coloration was noticed in the tube containing the finely-divided *soluble* gun-cotton. Both samples continued from this time to undergo slow decomposition; but for several hours after the first commencement of change, the ordinary gun-cotton evolved nitrous vapours more abundantly than the soluble sample.

Experiment 95.—Larger quantities (11 grms. and 33 grms.) of ordinary gun-cotton and of the soluble gun-cotton, both in a fine state of division, were exposed day and night uninterruptedly to $60^{\circ}C$. After a period of one month the soluble gun-cotton had sustained not the slightest loss of weight, the ordinary gun-cotton having lost 0.058 per cent. At the expiration of another month's uninterrupted heating, the weight of the soluble gun-cotton was still found to have sustained no change, while the ordinary gun-cotton had only sustained a further loss of 0.02 per cent.†

These and other similar results appear to demonstrate satisfactorily that the lower nitrocellulose compounds, when prepared in a condition of equal purity with the ordinary gun-cotton, are certainly not more prone to change at high temperatures.

EXPOSURE OF GUN-COTTON TO $90^{\circ}C$.

It is stated by PÉLOUZE and MAURY that in their experiments the exposure of gun-cotton to 90° furnished identically the same results as those produced by the tempera-

* Philosophical Transactions, vol. clvi. p. 297.

† After continuous exposure of these samples at 60° , for a further period of four months, the soluble gun-cotton is found not to have sustained any loss in weight, while the total loss sustained by the ordinary gun-cotton amounts to 0.19 per cent.—June 8th, 1867.

ture of 100° C., excepting that the phenomena of decomposition, instead of appearing after a few minutes, only became manifest after several hours. This statement has been confirmed, by the results of comparative experiments which I have instituted at 90° and 100°, to this extent, that in all instances the first signs of change become manifest in the specimens heated to 100°, and that sometimes the interval of time between the first exposure to heat and the first indications of decomposition is much greater at the lower than the higher temperature. The following results furnished by exposure of equal quantities of the same gun-cotton, in the same condition, to 90° and 100° C., may be quoted in illustration of the comparative effects of the two temperatures.

TABLE V.

No. of experiment.	Total period of exposure to		First indications of change observed after commencement of exposure to		Observations.
	90° C.	100° C.	90° C.	100° C.	
96	48 hours	6 hours	4 hours, <i>very faint.</i>	2 hours	At 90° only faint indications of nitrous acid were obtained up to the close of experiment; at 100° the vapours were abundantly evolved after 5½ hours' exposure.
97	26 hours	26 hours	6 hours	5 hours	In both instances the coloration of the atmosphere was very faint throughout the experiment.
98	40 hours	30 hours	10 hours	45 minutes ...	The coloration by nitrous acid was only faint throughout in both instances, but the specimen exposed to 100° sustained a more considerable change than the other.
99	56 hours	20 hours	22 hours, <i>very faint.</i>	14 hours	The disengagement of nitrous acid was only very slight throughout the experiment at 90°; in the other experiment it was more copious, though not abundant at any period.
100	42 hours	10 hours	None observed	50 minutes ...	The specimen heated to 100° was decomposing rapidly after the lapse of 9½ hours; the other specimen exhibited no sign of change beyond a slight acidity.
101	46 hours	6 hours	None observed	2 hours, <i>very faint.</i>	The specimen heated to 100° commenced to evolve nitrous acid abundantly at the expiration of 6 hours, the other specimen showing no sign of change beyond a slight acidity.

It will be observed from these experiments, which are quoted as representing numerous others of a similar description, that in most instances the decomposition of the gun-cotton was not only slower but also much less serious at 90° than at 100°. Exceptional specimens, exhibiting either a very unusual want of stability (*e.g.* some of the specimens from Hirtenberg and Stowmarket which have already been referred to), or a remarkable power of resisting decomposition at 100°, generally showed but little difference in behaviour when subject to the influences of the two temperatures.

EXPOSURE OF GUN-COTTON TO TEMPERATURES RANGING FROM 50° TO 60° C.

Several experiments, corresponding in their nature to those described in the first part of the account of the action of light upon gun-cotton, have been instituted for the purpose of obtaining data regarding the influence upon the material of very long-continued exposure to the above-named temperatures. The air-dry gun-cotton was introduced into large bulbs blown at the extremities of barometer-tubes, the latter being placed with

their openings over mercury and exhausted in the manner already described, so that the height of the mercury-column in these tubes, at the commencement of the experiments, was very nearly that of the barometer at the time. Sufficient gun-cotton was employed to fill the globes pretty compactly. The bulbs were enclosed in metal water-baths, in which they were always perfectly surrounded by water maintained for definite daily periods at a constant temperature by gas-flames, accurately adjusted by self-acting regulators. Daily observations were made, before heat was again applied, of the height of mercury in the tube (with the necessary corrections), of the appearance of the gun-cotton through the glass, and of any other points worthy of note.

Experiment 102.—18 grms. of air-dry gun-cotton, manufactured at Waltham Abbey in 1863, were heated for six days, seven hours daily, to a temperature ranging between 36° and 38° C. The column of mercury was not permanently affected to the slightest extent during this period. It was afterwards intended to maintain the temperature for a long period at 49° , but upon the second day of this treatment, the heat was accidentally raised to 55° , it was therefore afterwards maintained at that point for a considerable period. After the first day of this treatment, the column of mercury continued to fall daily, to an extent ranging between 8 and 16 millims., during nine days' further exposure for six hours daily to 55° . For three subsequent days the column fell 18, 20, and 18 millims.; on the thirteenth day the fall amounted only to 11 millims. On the fourteenth day the temperature rose accidentally to 60° , and remained at that point about thirty minutes; on that day the fall of the mercury-column amounted to 23 millims. The temperature was afterwards maintained at 55° , but the daily depression of mercury did not correspond with the observations made before the temperature had accidentally reached 60° ; on three successive days it was 43 millims., 24 millims., and 37 millims. It appeared from these results that the increase of temperature to 60° had established a greater tendency to change in the gun-cotton, which afterwards continued, although the temperature was reduced to 55° .

After this exposure of the gun-cotton to heat, from six to seven hours daily, for twenty-four days, during seventeen of which the heat applied was 55° , and for a short time 60° , the specimen was removed from the globe. It had not altered in appearance, but was found to be strongly acid to test-paper; it had a peculiar pungent odour, the fibre had become tender, and its explosiveness had diminished somewhat. A portion of the specimen was washed thoroughly, first in distilled water and afterwards in slightly alkaline water, then dried and placed in a bottle, in which it has been exposed to diffused light for three years without undergoing further change. Nitrous acid vapours could not be distinguished in the globe or tube at any time during the experiment, but soon after the temperature was raised to 55° , a few small yellowish crystals of mercury-salt (mercurous nitrite) appeared upon the surface of mercury in the tube, and were added to a little as the experiment proceeded.

Experiment 103.—16 grms. of the sample of gun-cotton used in the preceding experiment, and 14.75 grms. of another sample, were exposed side by side, in one and the

same water-bath, in the manner already described, to 55° C. for six to seven hours daily, during seventy days. After the first day's heating, the column of mercury in each tube was slowly and uniformly depressed, the volume of gas evolved being somewhat greater from the second, smaller sample. At the conclusion of the seventy days' treatment it was calculated, from the capacity of the tubes and the amount of total displacement, that the larger sample had evolved 172.88 cub. centims., and the other sample 189.1 cub. centims. of gas; as, however, a few small crystals of mercury-salt had been produced in each tube by the action of nitrous acid disengaged, those quantities are of course only proximate. Upon removal from the bulbs, the colour of both specimens was unchanged; their odour was decidedly less pungent than that of the preceding specimen; both were acid to test-paper, the smaller sample being the most strongly so; in neither instance was the strength of fibre impaired, the explosiveness diminished, or the solubility in ether and alcohol appreciably increased. The specimens were divided, put into stoppered bottles without any previous purification, and one bottle of each was preserved in the dark, the other being exposed to diffused light. None of the specimens have up to the present time (a period of $3\frac{1}{2}$ years) undergone any further change.

Experiment 104.—13.8 grms. of gun-cotton were exposed in an exhausted bulb-tube, as already described, to 65° for six to seven hours daily, during a period of three months (eighty-four days). The depression of the mercury proceeded uniformly, but much more rapidly than in the preceding experiment. After several days' exposure, a notable quantity of mercurous salt was deposited in crystals within the tube. At the termination of the experiment the gun-cotton was not altered in colour and appearance, but upon removal from the bulb the fibre was found to be considerably weakened; a pungent odour and strong acidity were exhibited by the specimen, its explosive properties were notably reduced, and it dissolved to a large extent in ether and alcohol, the solution furnishing a collodion-film. A portion of the same gun-cotton enclosed in a smaller bulb-tube, sealed at both extremities, was exposed to heat for an equal period in the same water-bath. There was some pressure of gas upon opening the tube, and the gun-cotton exhibited the same appearance and properties as the sample heated over mercury. Both samples were placed in closed glass vessels, and have since been exposed to light for upwards of three years, without undergoing any further change.

Experiments 105–108.—Four specimens of gun-cotton, each weighing 19.5 grms., taken from different samples, were introduced into bulb-tubes of almost the same capacity and with stems of equal length. The bulbs were all enclosed in one water-bath, and the open extremities of the tubes were immersed in a mercury-bath, over which they were exhausted as in the preceding experiments. The water-bath was maintained at 65° seven hours daily, the uniformity of the temperature being ensured by the employment of a self-acting gas-regulator. Before commencing the application of heat each morning, the extent of depression of the mercury in the tubes was noted; and the volume of gas contained in each at stated periods was calculated from the observations made. The following Table shows the effects of uniform exposure to 65° upon these samples:—

TABLE VI.

Description of gun-cotton.	Volume of gas evolved.			Gas escaped from the tube on	Condition of the gun-cotton after 3 months' exposure 7 hours daily to 65° C.
	5th day.	12th day.	28th day.		
No. 1. Fine yarn, Waltham.	cub. centims. 57·6	cub. centims. 213·3	cub. centims.	13th day	Strong acid reaction; strength of fibre and explosiveness diminished. Aqueous extract contained nitric and oxalic acids, and reduced cupric salts readily. Proportion of matter soluble in ether and alcohol=15 per cent.
No. 2. Coarse yarn, Waltham.	9·6	16·1	47·3	65th day	Acid reaction; strength of fibre and explosiveness not appreciably diminished. Aqueous extract contained nitric acid and a trace of oxalic acid; reduced cupric salts to a very slight extent. Matter soluble in ether and alcohol=49·1 per cent. (2 per cent. in original sample).
No. 3. Fine yarn, Waltham, washed and impregnated with 0·4 per cent. of sodic carbonate.	27·3	67·7	221·7	30th day	Strongly acid reaction; strength of fibre and explosiveness only slightly reduced. Aqueous solution contained nitric acid and a small quantity of oxalic acid; reduced cupric salts slightly. Soluble matter=10 per cent.
No. 4. Coarse yarn, Stowmarket.	192·2	6th day	Acid, friable; explosiveness very much diminished. Large proportion soluble in water. Solution contained a very small quantity of nitric acid, but a large proportion of oxalic acid; reduced cupric salt very abundantly. Portion insoluble in water; dissolved in ether and alcohol.

The sample of Stowmarket gun-cotton which decomposed so readily at 65°, was an early specimen of manufacture from that establishment; it had evidently been prepared from inferior or very imperfectly purified cotton, and contained a considerable proportion of foreign matter extractable by alcohol. The two specimens of fine yarn (Nos. 1 and 3) were portions of the lowest class of products obtained at Waltham Abbey. Its impregnation with a small proportion of sodic carbonate imparted to it greater power of resisting the effects of heat; this result was not demonstrated, however, to its full extent, because the sample of the gun-cotton (No. 1) in its original condition contained some earthy carbonates, which had been at any rate partially separated from the sample impregnated with sodic carbonate.

The specimen of coarse yarn (No. 2), which was found to be but little changed by the three months' exposure to 65°, was an average specimen of the products obtained at Waltham Abbey.

Specimens 1, 2, and 3 have been preserved in stoppered bottles in the condition in which they were removed from the bulbs, and have been exposed to strong daylight for two years. They have not undergone further change.

Experiment 109.—A sample (20 grms.) of perfectly dry Waltham Abbey gun-cotton, representing the ordinary product of manufacture, was exposed in a bulb-tube exhausted over mercury to 65° C., for seven hours daily. The mercury-column was very gradually depressed, as in the preceding experiments with gun-cotton of this kind, and after the experiment had continued for ten weeks, the gas escaped from the opening of the tube. In about one week more, sufficient gas was collected for examination; it was found to consist of—

Carbonic acid	45·6 per cent.
Nitric oxide	10·8 „
Nitrogen	43·5 „

Some water had become deposited in the sides of the tube, and a small quantity of mercury-salt had formed. The application of heat to the tube was continued with the view of collecting a further quantity of gas, but the experiment was carried on uninterruptedly for a further period of nearly twelve months before a sufficient amount of gas (about 150 cub. centims.) could be collected for analysis. This second product contained—

Carbonic acid	55·7 per cent.
Hydrogen	6·4 „
Carbohydrogen [.	traces
Nitric oxide	2·1 „
Nitrogen	35·7 „

The total volume of gas evolved during fourteen months' exposure of the gun-cotton to 65° C., for seven hours daily, was about 660 cub. centims.

On removing the specimen from the bulb-tube, it exhibited no alteration in colour, appearance, or explosiveness; the strength of fibre had slightly diminished; nitric acid was detected in small quantity in the aqueous extract, but no oxalic acid. A very slight reducing action was exerted upon cupric salts, but the proportion of matter soluble in ether and alcohol had not appreciably increased. At the conclusion of the experiment the specimen was washed in slightly alkaline water, dried, and exposed to strong daylight and occasional sunlight, in a stoppered bottle. Up to the present time (after nine months' exposure) the specimen has suffered no change whatever.

It would appear from these experiments, which were always commenced *in vacuo*, but continued after a short time in an atmosphere of the gaseous and volatile products formed, that gun-cotton, prepared and purified according to the system now in use, manifests some slight but undoubted symptoms of gradual change, if maintained for several hours at as low a temperature as 55° C. in a confined space;—that a very long-continued exposure to that temperature does in some instances produce a notable alteration in the composition and explosive properties of the substance;—that a similar change is somewhat more rapidly developed if the gun-cotton be exposed to temperatures of 60° and 65°; but that the exposure of the substance several hours daily, even for months, to the highest of those temperatures does not so seriously affect the ordinary products of manufacture as to prevent their being afterwards restored, by the ordinary process of purification from acid, to a condition differing but little, practically, from that of the original material. Although these experiments were instituted with comparatively considerable quantities of gun-cotton (14–20 grms.), it must be at once admitted that, if the material were exposed in large compactly packed masses (5–10 kilos.) to the temperatures ranging between 55° and 65° for the periods given in the preceding experiments,

it would be more seriously affected, and that the changes which would ultimately be developed by the free acid accumulating in the gun-cotton might give rise to spontaneous heating of the mass. On the other hand, it must be borne in mind that even the lowest of those temperatures occurs in nature only under exceptional circumstances, *and for brief periods*.

It may perhaps be considered that the arrangement of heating the gun-cotton over a column of mercury, adopted in the foregoing experiments with the view of obtaining continuous records of the progress of change, was of a nature somewhat favourable to the material operated upon, because a small surface of mercury was exposed in direct contact with the gases or vapours evolved, and might, by its own oxidation, remove a portion of the generated acid which would otherwise have reacted injuriously upon the gun-cotton. It has indeed been stated, in the description of the experiments, that a few crystals of mercurous salt were always formed upon the exposed surface of the mercury, the production of the salt being favoured by the condensation over the metal of a small quantity of water, produced as the experiment proceeded. But it must be borne in mind that the surface of mercury exposed was always very small (only from 78–100 sq. millims.), while the quantity of cotton operated upon was considerable, and that, between each consecutive period of exposure to heat, the gun-cotton absorbed, as it cooled during the night, the water impregnated with acid which had been previously expelled from it. Experimental proof was, however, obtained that ordinary gun-cotton, when exposed to 65° in vessels not closed by mercury, and so arranged that any liberated acid would not escape from contact with the material, was more rapidly and seriously affected than was the case in the globe-experiments.

Experiment 110.—Four specimens taken from different samples of gun-cotton, exposed in a dry state to 65° in very long and narrow-necked flasks, seven hours daily for seven days, sustained no loss of weight. From the tenth to the fourteenth day after the first exposure all showed slight signs of decomposition, which proceeded with somewhat different rapidity in the several samples; two of them were completely decomposed in three weeks after first exposure, the other two resisted for very considerably longer periods.

Experiment 111.—Two other samples were similarly exposed to heat side by side; nitrous vapours became distinctly apparent six days after first exposure to 65°, and continued visible until the twelfth day's exposure. After three weeks' exposure, the specimens had lost 30 per cent. in weight, and were converted chiefly into soluble gun-cotton.

Experiment 112.—The protracted exposure of air-dry gun-cotton to a temperature ranging between 60° and 55° in a vessel *to which air had access*, did not effect any greater alteration in the material than was observed in the globe-experiments. Thus 53·968 grms. of air-dry gun-cotton, after exposure to heat seven hours daily for ten days, weighed 53·902 grms.; after a further exposure for seven days it weighed 53·882 grms., and after a third exposure for five days it weighed 53·881 grms. The sample had therefore only sustained a loss of 0·10 per cent.

Experiment 113.—Two other specimens, weighing 44 and 34 grms., were exposed day and night in a hot-air chamber, to a temperature ranging between 35° and 50°. The specimens were weighed periodically, in an air-dry condition. After the lapse of ten weeks one sample had lost 1.18 per cent., and the other 1.56 per cent.

In conducting these quantitative experiments, it was observed that the exposure of gun-cotton for a protracted period to a moderately elevated temperature had the effect of reducing the hygroscopic power of the fibre, so that upon exposure of gun-cotton which had been thus heated to the atmosphere, the maximum proportion of moisture absorbed by it was very notably lower than that contained in the original sample. The actual loss sustained by the above samples, which were always weighed after exposure to air for definite periods, was therefore somewhat less than indicated by the numbers given.

PART III.—INFLUENCE EXERTED UPON THE STABILITY OF GUN-COTTON BY SPECIAL MODES OF PREPARING AND PRESERVING IT.

I. *Reduction of gun-cotton fibre to a fine state of division.*—Abundant proofs have been obtained that the long-continued washing and the treatment with an alkaline liquid to which gun-cotton is submitted, do not completely separate from it products of the partial oxidation of organic impurities retained by the cotton up to the time of its conversion. This is unquestionably due in great measure to the tubular structure of the fibre. If the impurities were merely upon the surface of the fibre, their perfect removal by the action of solvents should be accomplished without difficulty, but it does not appear that even long-continued digestion of gun-cotton in alcohol has the effect of completely freeing it of the impurities soluble in that liquid which are locked within the fibre. The action of a warm or cold alkaline liquid upon the material might perhaps eventually result in the complete removal of these bodies, but the loss of product and destructive effect upon the fibre, resulting from any other than a brief digestion in a very dilute alkaline bath, are too considerable to admit of such a treatment. The following experiments may be quoted in illustration of this.

Experiment 114.—A quantity of gun-cotton which had already been submitted to the usual purification with water and a hot alkaline bath, was boiled for ten minutes in a solution of potassic carbonate of the strength usually employed (of specific gravity 1.02). By this treatment the material sustained a loss of 3.7 per cent., the bath having assumed an amber colour. Upon being again boiled for twenty minutes in the same alkaline bath, which thereby became considerably deepened in colour, the sample sustained a further loss of 12.09 per cent. The strength of the fibre had been considerably reduced by this treatment.

Experiment 115.—6.5 grms. of gun-cotton and 0.4 gm. of sodic carbonate were placed together with 50 cub. centims. of water in a flask to which a vertical condenser was attached, and were heated to 100° for twelve hours. The alkali was then found to have become nearly neutralized, and the dark brown liquid contained sodic nitrate in abun-

dance. The gun-cotton was washed and twice treated in the same manner, the alkali being neutralized on each occasion, as in the first instance.

But though it is evident that the treatment of gun-cotton with warm alkaline baths cannot be advantageously extended, satisfactory proof has been obtained that the stability of gun-cotton which has been purified as far as is possible by the present system, may be importantly increased by submitting the material to a special process of washing.

In the experiments instituted upon the application of gun-cotton as a substitute for gunpowder, some very advantageous results have attended the conversion of the material into homogeneous masses of any desirable form or density, by preparing it according to the method commonly employed for converting rags into paper. In reducing the material to a very fine state of division by means of the ordinary beating- and pulping-machines, the capillary power of the fibres is nearly destroyed, and the gun-cotton is, for a considerable period, very violently agitated in a large volume of water. It would be very difficult to devise a more perfect cleansing process than that to which the gun-cotton is thus submitted; and the natural result of its application is that the material thus additionally purified acquires considerably increased powers of resisting the destructive effects of heat. Samples of the pulped gun-cotton even in the most porous condition have been found to resist change perfectly upon long-continued exposure to temperatures which developed marked symptoms of decomposition in the gun-cotton purified only as usual (experiments 94 and 95 may be referred to in illustration of this).

The pulping process applied to gun-cotton affords therefore important additional means of purifying the material, the value of which may be further enhanced by employing a slightly alkaline water in the pulping-machine.

II. *Impregnation of gun-cotton with substances capable of neutralizing free acid.*—The slightest change sustained by gun-cotton is attended by the development of free acid, which, if it accumulates in the material, even to a very trifling extent, greatly promotes decomposition. Numerous experimental data have been collected with respect to the establishment and acceleration of decomposition in gun-cotton exposed to light or elevated temperature by free acid, which either is present in the imperfectly purified material, or has been developed by decomposition of gun-cotton or its organic impurities.

Experiment 116.—Samples of gun-cotton which, by exposure to elevated temperatures or for considerable periods to strong daylight, had sustained changes resulting in a considerable development of acid, have afterwards been thoroughly purified by washing and exposed to light for months, and in some instances for two and three years (up to the present time) without undergoing further change, while corresponding samples, confined in closed vessels without being purified, have continued, in some instances, to undergo decomposition, and the original substance has been completely transformed into the products repeatedly spoken of. Instances have, however, occurred in these experiments (and have already been quoted) in which gun-cotton has resisted further change, even under these circumstances.

Experiment 117.—Gun-cotton, purified as usual, has been confined in stoppered glass bottles, having previously been rendered slightly acid with nitric acid. In these instances the gun-cotton has always undergone decomposition upon exposure to light, the rapidity of its change varying with the quality of the material.

Experiment 118.—Two specimens of Waltham Abbey gun-cotton (coarse and fine yarn) were introduced into well-stoppered bottles, and pernitric oxide was then passed into those for a short time. The bottles were then tightly closed and placed in a dark cupboard, being inspected from time to time. The gas was rapidly absorbed by the gun-cotton, which assumed a green tinge and gradually contracted, the colour of the vapours in the bottles slowly becoming deeper again. After the lapse of two months both samples had contracted into compact masses, occupying less than one-fourth the original volume. Both were coloured green, and dark orange vapours filled the vessels. From this period the pernitric oxide diminished in quantity very gradually, until, about eighteen months after commencing the experiment, the atmosphere in the bottles was perfectly colourless. The coarse gun-cotton had passed into a viscid mass, exhibiting the usual characters; the fine gun-cotton, though it contracted to about one-tenth of its original volume, still retained to some extent its original appearance; crystals of oxalic acid were dispersed through the mass.

Experiment 119.—Two other samples of gun-cotton employed in the preceding experiment were placed in bottles into which nitrous acid, produced by means of starch, was passed. These bottles were afterwards also placed in the dark. The gas was gradually absorbed by the gun-cotton, the atmosphere in the bottles became colourless, and both samples were highly bleached. After the lapse of two months, a faint orange colour was exhibited, but the specimens of gun-cotton had undergone no apparent change whatever. Three months later, the bottle containing the coarse yarn exhibited deep orange vapours, the gun-cotton had contracted somewhat and assumed a green tinge. The other sample exhibited no signs of change, but a faint orange tinge was manifest in the bottle, which did not increase afterwards. Twenty-eight months after the commencement of the experiment this sample exhibits no signs of change beyond a very slight contraction. The coarse yarn has contracted to about one-third its original volume, is friable, and partly soluble in water.

Pernitric oxide, if left in contact with gun-cotton, is therefore much more rapid in its destructive action than nitrous acid; gun-cotton when confined together with either of them, undergoes gradual decomposition even in the dark.

Experiment 120.—A sample of gun-cotton which had been found to decompose very readily at 100° , was placed in a retort suitably fitted with a delivery-tube, and the gases disengaged from it were passed into four bottles containing different samples of gun-cotton. These were then perfectly closed and exposed to strong daylight.

The first sample soon began to exhibit signs of change. The colour of the vapours increased in depth, and in one month's time had become very deep-coloured, the gun-cotton having assumed a greenish tinge from absorption of gas. The sample was then placed in the dark, after which it underwent further change very gradually, first con-

tracting considerably and afterwards, after the lapse of upwards of one year, becoming converted into a somewhat hard gum-like mass.

In the case of the second and third samples, the coloured vapours disappeared at first almost entirely, but the atmosphere in the bottles became coloured again after one month's exposure to light. The depth of colour increased so rapidly in one instance that two months after first exposure to light the bottle was placed in the dark. The change in the two bottles then proceeded at about the same rate. The specimens contracted very slowly, and the nitrous vapours disappeared gradually. At present, $2\frac{1}{4}$ years after commencement of the experiment, the specimen which has been exposed to light is scarcely as much changed as the one which after a time was placed in the dark; both have contracted to about one-half their original volumes, but have preserved their normal appearance; a few very minute crystals (probably oxalic acid) are perceptible upon the sides of the bottle which has been kept in the dark.

The fourth sample (prepared at Waltham Abbey in 1863) has resisted change to a remarkable extent. The vapours were at first entirely absorbed, and the gun-cotton has become slightly bleached. A faint orange tinge was first observable in the bottle after it had been exposed to strong daylight for six months. Nitrous vapours were then slowly evolved until the depth of colour was somewhat considerable. After the lapse of several months they gradually diminished again, and ultimately disappeared once more, after about eighteen months' exposure. After the lapse of $2\frac{1}{4}$ years the gun-cotton has contracted only slightly, but exhibits no other signs of change. There can be no doubt, however, judging from this contraction and from the evolution of vapours at one period of exposure, that this sample has suffered change which would not have occurred had it been exposed to light under ordinary conditions.

The experiments in sealed tubes which have been described,—the results of examination of gases collected from gun-cotton which has been exposed to heat for long periods in contact with them,—and the general existence of nitric acid in samples of decomposed gun-cotton, appear to show that the first effect of exposure of the ordinary material to sufficient heat is the disengagement of pernitric oxide and the production of water, by which the former is converted into the nitric and nitrous acids; the latter, if allowed to remain in contact with the heated gun-cotton, is gradually reduced to nitric oxide, and finally the nitrogen becomes deoxidized at the expense of hydrogen and carbon, oxalic and carbonic acids being eventually furnished by the latter. The nitric acid produced attacks the gun-cotton at the same time; the presence of very small quantities of this substance in gun-cotton greatly accelerates the decomposition of the material by heat.

Experiment 121.—One drop of concentrated nitric acid introduced into vessels containing 2 or 3 grms. of gun-cotton, invariably brought about rapid decomposition at comparatively low temperatures (55° to 65°); and by operating at temperatures between 70° and 100° with small samples of gun-cotton to which as small a quantity as possible of dilute nitric acid was added, they were in this way generally converted into the gum-

like product, in a few hours, though instances occurred occasionally in which, even under these severe conditions, the material resisted decomposition to a remarkable extent.

In many experiments instituted with ordinary gun-cotton at 90° and 100° it was found that, if the mode of operating were such as to facilitate the escape from the apparatus of any acid vapours evolved, the gun-cotton would frequently resist decomposition in a remarkable manner, being only very gradually converted into the final products; the two following experiments demonstrate how greatly decomposition at 100° C. can be retarded by impeding the destructive action of acid generated by the exposure to a high temperature.

Experiment 121^a.—Weighed quantities (about 1.5 grm.) of dry gun-cotton were loosely packed into two narrow U-tubes, which were immersed in a water-bath and connected with an aspirator. The gun-cotton was in both instances maintained during the day at 100° C. A moderately rapid current of air was passed through one tube, and air was allowed to circulate very slowly through the other. At night both tubes were closed up with corks. Their weight was determined at intervals; the following were the results obtained:—

Duration of exposure.	Loss sustained by gun-cotton exposed to	
	slow current.	rapid current.
24 hours (4 days)	17.47 per cent.	4.8 per cent.
40 hours additional (7 days) .	32.43 „	4.12 „
196 hours additional (28 days). ———	—	5.04 „
Total loss of weight, in 11 days	50.90 „	In 39 days 13.96 „

The results of these and the preceding experiment warrant the conclusion, that as soon as acid becomes liberated in gun-cotton changes are developed in the material which would not be brought about by its simple exposure to heat, provided no free acid were present in it. If therefore it be possible to neutralize, at the instant of its liberation, any acid which may be produced by the effect of elevated temperatures upon the comparatively unstable impurities contained in small quantities in gun-cotton, the latter might be expected to resist alteration under circumstances which, if the first acidity were not counteracted, must determine the decomposition of the material.

Reference has been made in this paper, on more than one occasion, to the influence which certain mineral impurities of general occurrence in gun-cotton (earthy carbonates) were observed to exert upon the rapidity with which the substance sustained alteration, upon exposure to heat. Some samples, which were heated for comparatively considerable periods without exhibiting signs of change, were found to contain much larger proportions of calcic and magnesian carbonates than specimens with which, in other respects, they were identical.

This observation led, at an early stage of these investigations, to careful observations of the comparative effects of high temperatures (100° and 90° C.) upon a variety of samples, which were known to vary as regards the proportions of earthy and alkaline carbonates distributed through them. Some specimens were repeatedly rinsed in distilled

water (whereby the larger proportion of earthy carbonates attached to the fibre was removed) and exposed to heat in comparison with corresponding specimens not thus treated. Some other samples were extracted with dilute acid and washed; but as acetic acid was used in most of those experiments, the results of their exposure to heat (experiments 90-93) were not of the nature anticipated, for the reason, as already explained, that the treatment in question removed not merely carbonates but also a proportion of the organic impurities. The extraction of the gun-cotton with dilute hydrochloric acid does not remove organic impurities; and, as has already been shown, this treatment has the effect of rendering ordinary gun-cotton more susceptible to the destructive effects of high temperatures.

A considerable quantity of Waltham gun-cotton, after having been purified in the usual way, was saturated with a solution of sodic carbonate of sufficient strength to deposit from 0.4 to 0.5 per cent. of the salt in the gun-cotton, after the latter had been expressed in the hydro-extractor and dried. Portions of the material thus prepared were carefully washed out in distilled water and submitted to heat in comparison with corresponding samples of the "alkalized" gun-cotton. The washing process did not merely extract the sodic carbonate, it also effected the mechanical removal of a large proportion of the earthy carbonates deposited upon the gun-cotton during the long-continued washing in spring- or river-water.

The results observed in this series of experiments are given in the two following Tables.

TABLE VII.

No. of experiment.	Description of gun-cotton.	Quantity employed.	Total exposure to 100° C.	Interval between first exposure and first signs of decomposition.	Loss of weight sustained by the gun-cotton.	Temperature observations.	Other observations.
122	Fine yarn, Waltham, impregnated with 0.4 per cent. of sodic carbonate.	grms. 22	11 hours in 3 days (1½ hour on the 3rd day).	7 hours	Not observed.	During 4½ hours' heating on the 1st day no indications of a rise of temperature were obtained. After 2 hours' heating on the 2nd day, the temperature rose very slowly, reaching 106° C. by the close of the day's experiment; an interval of 1 day elapsed before the experiment was resumed. Upon exposure to heat on the 3rd day, the temperature speedily exceeded 100°; in 1½ hour it had reached 113° C., and soon afterwards the gun-cotton <i>exploded</i> .	The coloration of the atmosphere in the vessel was only very faint until after 3 hours' treatment on the 2nd day, and the decomposition was very gradual when compared with that in experiments made with corresponding quantities of ordinary gun-cotton.
123	The same description as used in experiment 122.	22	16½ hours in 3 days (2½ hours on 3rd day).	8 hours	2.6 per cent. in 14 hours (2 days).	At the close of the 1st day (after 6½ hours) the temperature rose slowly to 102° C.; on the 2nd day it rose gradually to the same temperature and remained stationary during 6 hours. On the 3rd day it rose gradually to 104°·5, and remained stationary for 1½ hour; the thermometer then rose somewhat rapidly to 113° C., and the gun-cotton <i>exploded</i> almost immediately afterwards.	The coloration of the atmosphere in the flask was very faint on the first day, and there was only a slight increase in colour until the thermometer passed 104° C. on the 3rd day.

TABLE VII. (continued.)

No. of experiment.	Description of gun-cotton.	Quantity employed.	Total exposure to 100° C.	Interval between first exposure and first signs of decomposition.	Loss of weight sustained by the gun-cotton.	Temperature observations.	Other observations.
124*	The same as in experiment 122.	grms. 6.5	16 hours in 3 days.	None observed	None sustained.	No increase of temperature indicated.	It was observed about 1 hour after commencing the experiment that a very small quantity of water had penetrated into the flask through the cork, which had been accidentally immersed in the water of the bath for a short time. The gun-cotton remained perfectly unchanged; it was dried at the close of the experiment, and found to have sustained no loss in weight.
125	The same as in experiment 122.	6.5	22 hours in 4 days.	7 hours	14 per c. after 3rd day, 4.5 per c. after 4th day, total loss 18.5 per c.	No rise of temperature on the 1st day. After 1 hour's heating on the 2nd day, the thermometer indicated 101°, and remained stationary throughout the day. On the 3rd day the thermometer rose to 104° in 1 hour, but had fallen again to 100° in 15 minutes; no further change occurred up to termination of the experiment.	The nitrous-acid vapours were only faint up to the rise of temperature on the 3rd day, and were never abundant. The colour of the gun-cotton was not altered. It had an acid reaction and slightly pungent odour after the treatment; its explosiveness did not appear diminished. The aqueous extract gave a faint indication of nitric acid, did not reduce cupric salts, nor furnish a precipitate with calcic chloride. The solubility of the gun-cotton in ether and alcohol had notably increased.
126	The same as experiment 122, but washed repeatedly in distilled water. This treatment not only extracted the alkali, but separated much of the earthy carbonates attached to the fibre.	6.5	1 ^h 10 ^m	50 minutes ..	Not observed.	After 45 minutes' heating the temperature rose rapidly; 116° was indicated shortly before the sample exploded.	The results of these two experiments should be compared with those obtained in the preceding experiment, and with those furnished in experiment 29 Table I. by 6.5 grms. of the same sample of gun-cotton, which had not been impregnated with alkali, nor submitted to the extra-washing process.
127†		6.5	1 ^h 15 ^m	1 hour	" "	At the close of the 1st hour's heating the temperature rose rapidly. In 10 minutes it had reached 113°, and in 5 minutes more it was 118°; the gun-cotton exploded almost immediately afterwards.	
128	Coarse yarn, Waltham, impregnated with 0.5 per cent. of sodic carbonate.	6.5	22 hours in 4 days.	10 hours	" "	The first rise in temperature was observed after 3 hours' heating on the 3rd day. The thermometer rose gradually to 110°, but soon began to fall again, and had returned to 100° before the close of the 3rd day. No change occurred on the 4th day.	Nitrous acid was abundantly evolved for a short time on the 3rd day. The gun-cotton after the experiment had a pale brownish colour, but the small portion surrounding the upper part of the thermometer had become blackened and hard, in consequence of the destructive action exerted by the moisture charged with acid, which condensed upon the thermometer-stem and fell upon that part of the sample. The aqueous extract contained nitric acid, no oxalic acid, and reduced cupric salts slightly. The gun-cotton dissolved to a large extent in ether and alcohol.

* This experiment furnished an important indication of the preservative effect of moisture. The gun-cotton was not wet but only thoroughly damp.

† A third experiment, corresponding to these two, furnished precisely similar results.

TABLE VII. (continued.)

No. of experiment.	Description of gun-cotton.	Quantity employed.	Total exposure to 100° C.	Interval between first exposure and first signs of decomposition.	Loss of weight sustained by the gun-cotton.	Temperature observations.	Other observations.
129	The same as experiment 128, but washed repeatedly in distilled water.	grms. 6.5	20 hours in 3 days.	4 hours	Not observed..	The temperature began to rise on the 1st day after 4 hours' heating. It rose to 109° in 30 minutes, and remained stationary till the close of the day. On the 2nd day it rose gradually to 104°, and after remaining stationary for some time, gradually returned to 100°. No change observed on the 3rd day.	Nitrous vapours were very abundant after 5 hours' heating during 1 hour. The gun-cotton assumed a brown colour. The aqueous extract contained nitric acid, a little oxalic acid, and reduced cupric salts abundantly. The insoluble portion was feebly explosive, and almost perfectly soluble in ether and alcohol.
130	The same as experiment 129, but very carefully washed in distilled water.	6.5	22 hours in 4 days.	2 ^h 30 ^m	„ „	After 2 hours' heating the temperature rose, and had reached 103° by the close of the 3rd hour, and 109° in another hour. On the 2nd day the thermometer rose to 102° in 30 minutes after commencing, and reached 106° in 15 minutes more. It soon afterwards began to fall, and had returned to 100° by the close of the 6th hour. No rise of temperature occurred on the 3rd and 4th days.	The substance had contracted considerably, was brown and pulverulent, soluble to a considerable extent in water, the solution exhibiting the usual reactions.
131	Medium-size yarn, Waltham.	6.5	21 hours in 3 days.	3 hours	20 per cent....	The temperature began to increase slightly at the close of the 3rd hour; the maximum temperature 110° was reached in 3 ^h 50 ^m . The thermometer then soon began to fall, and after nearly 7 hours' total heating, had returned to 100°. No change of temperature on the 2nd and 3rd days.	The gun-cotton became dissolved on the 2nd day. At the conclusion it was brown and pulverulent, partially soluble in water; the solution contained a minute quantity of oxalic acid, and reduced cupric salts abundantly. The residue dissolved in ether and alcohol, furnishing a horny brittle substance, which deflagrated when heated.
132	Same as experiment 131, but carefully washed in distilled water.	6.5	21 hours in 3 days.	1 ^h 30 ^m	31 per cent....	The temperature rose gradually above 100° after 1½ hour's heating. In 2 ^h 50 ^m it had reached 111°; the thermometer fell slowly soon afterwards; in 3 ^h 30 ^m from the commencement it had returned to 105°, and indicated 100° in 6 hours after commencement. No change on the 2nd and 3rd days.	The substance had sustained the same alteration as in the preceding experiment, but was soluble to a larger extent in water.
133	Same as experiment 131, but extracted with dilute acid and afterwards carefully washed.	6.5	21 hours in 3 days.	1 hour	34.6 per cent..	The temperature began to rise before expiration of the 1st hour. In 2 ^h 15 ^m it had reached 110°; the thermometer then fell and returned to 100° by the close of the 1st day's experiment.	The colour of the product was deeper than the two preceding, and a very large proportion was soluble in water.
134	Medium-size yarn, another sample.	6.5	20 hours in 3 days.	2 hours	20.3 per cent..	After 2 hours' heating the temperature rose gradually and reached 111°·5 at the expiration of the 3rd hour. It then returned slowly to 100° by the close of the 1st day's heating. No change on the 2nd and 3rd day.	Both samples had assumed a buff colour, were strongly acid and friable. The unwashed gun-cotton furnished the largest proportion soluble in water. The aqueous solutions furnished the usual reactions.
135	Same as experiment 134, but repeatedly soaked and washed in distilled water.	6.5	20 hours in 3 days.	1 ^h 45 ^m	Not recorded..	The temperature began to rise after the lapse of 1 ^h 40 ^m ; in 3 ^h 7 ^m it had reached 118°·5. In another hour it had fallen to 103°·5, and it returned to 100° by the close of the 1st day. No subsequent rise.	

TABLE VII. (continued.)

No. of experiment.	Description of gun-cotton.	Quantity employed.	Total exposure to 100° C.	Interval between first exposure and first signs of decomposition.	Loss of weight sustained by the gun-cotton.	Temperature observations.	Other observations.
136	Coarse yarn, "silicated".	grms. 6.5	22 hours in 4 days.	3 ^h 25 ^m	24 per cent....	After 3 ^h 30 ^m the thermometer began to rise. In 4 hours it indicated 107°, and in 4½ hours 110°. It soon afterwards began to fall, returning to 107° by the close of the 5th hour. On the 2nd day it rose to 104°·5 in 30 minutes, but soon fell again slowly to 100° after the lapse of 4 hours. No further change.	The sample had sustained the usual changes, but did not yield a very large proportion of soluble matter to water.
137	Coarse yarn, "not silicated".	6.5	1 hour, exploded.	30 minutes ...	Not observed..	The temperature began to rise in 35 minutes; it reached 107° in 55 minutes, rising very rapidly.	This sample was of the same date of manufacture as the silicated specimen used in experiment 15.

TABLE VIII.

No. of experiment.	Nature of gun-cotton.	Quantity employed.	Duration of exposure to 90° C.	First indication of decomposition after commencement of experiment.	Loss of weight.	Other observations.
138	Fine yarn, Waltham, impregnated with 0.5 per cent. of sodic carbonate.	grms. 8.5	36 hours in 6 days.	26 hours; 6th day.	In 6 days; 2.22 per c.	A very small quantity of carbonic acid escaped from the flask on the 2nd day; on the 3rd day the quantity was a little more considerable. The temperature having accidentally risen to 95° on the 6th day, nitrous acid was for the first time disengaged. At close of the experiment, the gun-cotton was perfectly white; it had an acid reaction, but the strength of fibre and explosiveness were scarcely affected.
139	Coarse yarn, Waltham, impregnated with 0.4 per cent. of sodic carbonate.	3	77 hours in 12 days.	9 hours; <i>very faint</i> .	In 6 days; 3.9 per cent.	The nitrous vapours were never disengaged abundantly. The gun-cotton became of a buff colour by the close of the experiment; it was friable and soluble to a considerable extent in water, and in ether and alcohol.
140	Fine yarn, containing 0.5 per cent. of sodic carbonate.	2	32 hours in 6 days.	30 hours; 6th day, <i>very faint</i> .	In 6 days; 2.73 per c.	The nitrous vapours were never more than faint. The gun-cotton furnished a slightly acid aqueous extract, in which neither nitric nor oxalic acids could be detected, and which did not reduce cupric salts. The solubility in ether and alcohol was scarcely affected.
141	Coarse yarn, containing 0.4 per cent. of sodic carbonate.	2	32 hours in 6 days.	15 hours; 3rd day, <i>very faint</i> .	In 6 days; 1.17 per c.	The gun-cotton was almost odourless, only very faintly acid, and exhibited no change in explosiveness or other properties.
142	Same as experiment 4, but repeatedly washed in distilled water.	4.5	32 hours in 6 days.	1 hour.....	In 6 days; 40.6 per c.	Nitrous acid was abundantly evolved 1 hour after commencement of experiment. The gun-cotton became brown, friable, soluble to a considerable extent in water, and in ether and alcohol.
143	Same as experiment 3, but repeatedly washed in distilled water.	2	32 hours in 6 days.	3 hours.	In 6 days; 10.5 per c.	The gun-cotton was strongly acid, and a small proportion was dissolved in water, the solution reducing cupric salts; the proportion soluble in ether and alcohol had considerably increased.

It will be seen that, in the experiments instituted at 100° C., with very considerable quantities of the "alkalized" gun-cotton (experiments 122 and 123) seven and eight hours elapsed before any symptom of decomposition was observed, while in operating with similar quantities of ordinary gun-cotton (experiments 26 and 27) decomposition became manifest in two hours and four hours. A comparison of experiment 27 with experiments 122 and 123, also shows that when once the gun-cotton began to undergo

considerable change, the decomposition proceeded much more rapidly in that material than in the alkalized samples.

The influence of the small proportion of alkaline carbonate in retarding the decomposition of the gun-cotton becomes still more evident when smaller quantities of the material are experimented with. It is well illustrated by the results of experiment 29 (Table I.), and those furnished by an equal quantity of the same gun-cotton impregnated with 0.4 per cent. of sodic carbonate. The former exhibited the first indications of change in three hours, the latter in seven hours, after first exposure. The temperature of the ordinary gun-cotton afterwards rose much more rapidly and considerably, and the loss of weight sustained by it in three days' exposure was nearly double that which the "alkalized" sample suffered in four days' treatment, and the alteration sustained by the latter specimen was comparatively slight.

But the protective power exerted by small proportions of carbonates is even more strikingly demonstrated by a comparison of experiment 125 with experiments 126 and 127. While the "alkalized" sample exhibited no signs of change until after the lapse of seven hours, equal quantities of the same sample, purified from carbonates by washing, exploded after exposure to 100° for 1.25 hour. Experiment 128, made with another description of gun-cotton, also impregnated with a small proportion of sodic carbonate, is similarly illustrative of this protective power when compared with experiment 28, Table I., and with experiments 129 and 130, conducted with equal quantities of the original gun-cotton and with the same material freed from carbonates by washing. The comparison of experiment 131 with 132, and of 134 with 135, affords proof that the small proportion of earthy carbonates ordinarily existing in gun-cotton exert a decided protective action, and experiment 133, conducted with a specimen from which these carbonates had been completely extracted by acid treatment, furnished further confirmation of this point.

In the experiments instituted at 90° C., Nos. 138–141, conducted with samples of "alkalized" gun-cotton, also afford important proof of the protective effect of small quantities of carbonates, upon comparing the results with those furnished by experiments 142 and 143. The first of these samples scarcely sustained any alteration by exposure for thirty-two to thirty-six hours to 90° C. during six days, while the specimens of ordinary gun-cotton were considerably altered by similar treatment.

Experiments 136 and 137 afforded a very decided proof that the silicating process prescribed by Von LENK exerts some amount of protective influence upon gun-cotton when exposed to heat, though this result is not due, as supposed by him, to the closing up of the fibre by an insoluble silicate, but simply to the deposition of a small quantity of earthy (and possibly of alkaline) carbonate upon the fibre when the silicate undergoes decomposition during the drying and the subsequent washing process. The amount of protection thus afforded to the gun-cotton is, however, obviously as liable to variation as that resulting from the deposition of calcic and magnesian carbonates upon the material during the long-continued immersion in flowing water. Numerous specimens of gun-

cotton which had been silicated, varied greatly in their powers of resisting change at high temperatures, but they were invariably rendered decidedly more prone to change if thoroughly washed in distilled water previous to their exposure to heat.

It is remarkable how very small a proportion of a carbonate deposited upon the fibre of gun-cotton, exerts a notable influence upon its power of resisting the effects of heat. Thus, a portion of a sample of gun-cotton which had been carefully freed from carbonates, was saturated with perfectly clear lime-water, wrung out and dried. Upon exposure to 100° in comparison with an equal weight of the sample purified from carbonates, the very small quantity of calcic carbonate which had been deposited upon the gun-cotton proved sufficient to delay to a notable extent the period of first decomposition, and to modify somewhat the results of change produced by exposure for a definite period at 100° C.

In experiment 138, conducted at 90° C., the alkalized gun-cotton was heated in a flask to which a delivery-tube was attached, and the gas which escaped was examined. It was then observed that, upon the second day's exposure, a very small quantity of carbonic acid was continuously evolved; that the quantity increased somewhat upon the third day; and that no nitrous vapours escaped until the sixth day, when the temperature was accidentally raised to 95° . Carbonic acid was then still evolved in small quantity. Similar evidence of the slow decomposition of the carbonate, which always preceded any disengagement of nitrous acid, was obtained in other experiments.

Some experiments were instituted in *sealed tubes* with the gun-cotton impregnated with 0.4 per cent. of sodic carbonate.

Experiment 144.—A specimen was enclosed in a tube with air at the atmospheric pressure, and exposed to 100° C. for $3\frac{3}{4}$ hours, on the first day, during which period no trace of nitrous vapour was visible. It was afterwards heated to 100° six hours daily for thirteen days, and no coloration of the air in the tube was observed at any time during this treatment. After four days' exposure, the tube was opened and gas escaped under somewhat considerable pressure. The tube was sealed up again, and at the close of the experiment it was opened once more, when gas escaped only under slight pressure. The specimen became discoloured in a few places after some time (which is invariably the case when gun-cotton containing alkaline matter is exposed to a high temperature), but exhibited no other signs of change. In similar experiments conducted with ordinary gun-cotton, deep nitrous vapours were observed in the tubes within three hours from the commencement of the experiment, and the material was always converted into a gum-like mass; in some instances the tube exploded violently after a time.

Experiment 145.—An experiment similar to the preceding was instituted with alkalized gun-cotton in a more closely packed condition, the tube being exhausted, filled with nitrogen, and re-exhausted before sealing. This tube was heated to 100° for ten hours (in two days), and afterwards left exposed to light for twenty-four hours, without the slightest coloration by nitrous vapours being observed. On being again heated,

very faint nitrous vapours were observed after two hours' exposure; these did not increase at all, but disappeared entirely after continuation of the heating for four hours longer. When the tube had been heated for six days the point was opened, and gas escaped under considerable pressure. The tube was again closed and heated for nine days, six hours daily; upon afterwards opening it, gas escaped only under slight pressure. It was again heated to 100° for seven days, when the tube was accidentally fractured by the effects of a neighbouring explosion. At this time the gun-cotton had become darkened in some places and had an acid reaction, but exhibited little other signs of change.

Several experiments were conducted with gun-cotton containing considerably larger proportions of sodic carbonate than the samples previously employed, for the purpose of obtaining data with regard to the progressive changes resulting from the protracted exposure of "alkalized" gun-cotton to heat. The results obtained are fairly represented by the following selected experiments.

Experiment 146.—6.5 grms. of Waltham Abbey gun-cotton were impregnated with 0.45 gm. of sodic carbonate. The air-dry specimen was exposed to 100° (for five to six hours daily), being loosely packed in a narrow-necked flask. Small weighed quantities of the sample (from 0.07 to 0.1 gm.) were removed from the flask for examination each morning before heat was again applied. The darkening, always produced by heating gun-cotton with an alkali substance, commenced upon the first day's exposure to heat, but no other effect was noticed; after six days' exposure the gun-cotton was still slightly alkaline, the coloration having gradually increased, until some parts exhibited a brown tint. In other respects the substance was unchanged. After the ninth day's heating the gun-cotton was found to be quite neutral. About one-fifth of the specimen was then removed for examination. Water extracted the colouring-matter entirely, and a brown solution was obtained, in which sodic nitrate and nitrite were readily detected. The liquid also reduced cupric salts slightly. The gun-cotton itself had not suffered any change in explosiveness or strength of fibre, nor had the solubility in ether and alcohol increased appreciably.

The exposure of the sample to 100° C. was continued for seven days longer. On the sixth day a small portion was examined and found still to be neutral. On the seventh day, the atmosphere in the flask was found to have an acid reaction, though no nitrous vapours were perceptible.

Upon determining the weight of the gun-cotton (with deduction of the portions used during the experiment), it was found by calculation that the loss which it had sustained during exposure to heat for 100 hours (in sixteen days) was greater than would have been caused by the complete expulsion of carbonic acid from the carbonate employed. The aqueous extract was highly coloured, the gun-cotton being left almost colourless. Sodic nitrate and nitrite existed plentifully in the liquid, and the latter reduced cupric oxide in an alkaline solution. The washed gun-cotton was found, as might have been anti-

ipated, to have sustained a greater loss than would have been caused by the extraction of the alkaline base entirely in the form of nitrate. The gun-cotton soluble in ether and alcohol now contained in the specimen amounted to 6.98 per cent.; the material originally contained 2.3 per cent., the increase amounted therefore only to 4.68 per cent. The proportion of nitrogen-oxides which would have been liberated by the reduction to that extent of trinitrocellulose even to the lowest of the substitution-products would not have sufficed to decompose the sodic carbonate present. It would appear from these results that the principal effect of the very long-continued exposure of this "alkalized" gun-cotton was to establish a very gradual action of the alkaline carbonate upon the gun-cotton (resulting in the production of glucic acid, &c.), and that even the *first* stage of decomposition (consisting in the reduction to soluble gun-cotton) caused simply by the action of heat upon the ordinary material, only proceeded to a very slight extent during the sixteen days' treatment.

Experiment 147.—6.5 grms. of gun-cotton were impregnated with 0.38 grm. of sodic carbonate. The sample was thoroughly dried and exposed to 100°, as in the preceding experiment. After the lapse of three days a weighed sample of the gun-cotton was examined. It had darkened somewhat, was alkaline, and exhibited no change of properties. After six days' exposure it was still alkaline, and its solubility in ether and alcohol had not increased appreciably; upon the ninth day the sample was found to be neutral. The experiment was then stopped, the gun-cotton was extracted with water, and the proportion of nitrogen-acids existing in it as sodium-salts was determined by means of nascent hydrogen. The result showed that less than four-tenths of the sodic carbonate employed had been neutralized by those acids, the remainder existing in combination with organic acids. Traces of ammonia were evolved during the treatment of the gun-cotton in this and the preceding experiment, and the loss in weight sustained by the material was greater than would have been occasioned by the simple expulsion of carbonic acid from the carbonate. The solubility in ether and alcohol of the sample had only increased to about double the original proportion.

It was of course impossible actually to demonstrate by experiment whether the small proportion of organic acid produced in these experiments, which exhibited the properties of reducing cupric oxide in an alkaline solution, was glucic acid, resulting from the action of the alkali upon the gun-cotton, or whether it consisted of the pectic acids found in the products of spontaneous decomposition; but as abundant proof exists that the latter are only the products of a *secondary* change resulting from the action upon gun-cotton of liberated nitrogen acids (see especially experiments 155 and 156), there appear to be very good grounds for the conclusion that the results observed in these experiments were mainly ascribable to the action of the alkaline carbonate upon the gun-cotton and the organic impurities present, and that the effects exclusively due to the protracted exposure of the substance to 100° were limited to the liberation of a very small proportion of nitrogen-acid, which was at once neutralized, the only change produced in the gun-cotton consisting therefore in the decomposition of the small quantities of compara-

tively unstable organic impurities, and in a slight increase of the proportion of soluble gun-cotton*.

The power possessed by carbonates to prevent or arrest the decomposition of gun-cotton when exposed to high temperatures, has been demonstrated in a striking manner by some experiments which have, at the same time, furnished evidence in support of the conclusion that the organic impurities contained in gun-cotton constitute the primary cause of its susceptibility to change under the influence of heat and light.

Experiment 148.—Specimens of gun-cotton were exposed in flasks to 90° and 100° until decomposition was established to such an extent that the vessels were filled with deep-coloured vapours; a small quantity of calcic or magnesian carbonate was then introduced into the flask, or the gun-cotton was removed from the vessel, dusted over with a carbonate, and immediately replaced. Decomposition was at once arrested by these means; moreover, the gun-cotton no longer exhibited any susceptibility of decomposition even if exposed to 90° and 100° for several successive days.

Experiment 149.—About 5 grms. of ordinary gun-cotton were dusted over with finely pulverized potassic bicarbonate† and exposed to about 95° in a long-necked flask, side by side with a corresponding quantity of the same specimen of gun-cotton in its ordinary condition. The “alkalized” gun-cotton gradually darkened upon the second day’s exposure, eventually assuming a brown colour. After exposure to the above temperature during five days for seven hours daily, the unprepared gun-cotton began to evolve nitrous vapours abundantly. The examination of a small specimen showed that the sample had undergone very little change, the solubility in ether and alcohol having slightly increased.

It was now removed from the flask, dusted over with the powdered carbonate, and immediately re-exposed to heat. All decomposition ceased, the gun-cotton behaving exactly like the specimen which was originally alkalinized, except that the usual darkening took place very slowly indeed. When it had been maintained at 95° – 100° , seven hours daily for eight days, it was still alkaline; after treatment with water, it exhibited all the original properties of the gun-cotton; the solubility in ether and alcohol had undergone no increase since the alkaline salt was applied‡.

The other specimen to which the carbonate had been applied in the first instance, was examined after exposure to 95° for seven days. The aqueous extract had a brownish colour, and reduced cupric salt to a very slight extent. The extracted gun-cotton was perfectly white; the strength of fibre, explosiveness, and solubility in ether and alcohol had undergone no change. It was now dried and again exposed in a clean flask to 95° –

* The analysis of a specimen of soluble gun-cotton into which the ordinary material had been entirely converted by the gradual action of heat, has furnished results which appear to indicate that trinitrocellulose may become soluble in ether and alcohol without undergoing any modification in its ultimate composition. This point is now being made the subject of further investigation.

† The object of employing this salt was to exclude any protective effect which might be exerted in the course of the experiment by the absorption of moisture, if a calcic, magnesian, or sodic carbonate were employed, and a small quantity of the corresponding nitrate were produced.

‡ The exposure of this sample to 100° was afterwards continued for three weeks without any effect.—*June 1867.*

100°. During six days it has not exhibited the slightest indication of decomposition; no acidity has yet been developed in it, and it is still unchanged in all its properties*.

It would appear from these experiments that a carbonate applied in the most simple manner to gun-cotton in which decomposition has been established, will effectually arrest the change; and that if gun-cotton containing a carbonate be exposed for some time to heat, the latter promotes the transformation of the unstable organic impurities into products fixed by the base, the result being that the gun-cotton undergoes a searching purification from these substances, and afterwards exhibits, in consequence, remarkable stability under very severe conditions of exposure to heat.

A number of experiments has been instituted on the comparative effects of exposure to 90° and 60° C. of samples of gun-cotton impregnated with different proportions of alkaline carbonates ranging from 1 to 10 per cent., the object being to ascertain whether the first-named proportion would suffice to afford security against the development of free acid in the gun-cotton, even under conditions of exposure to heat much more severe than could ever be met with in actual practice, or to determine what proportion might be necessary for that purpose. The results of these experiments showed that 1 per cent. of sodic carbonate, uniformly distributed through gun-cotton, produced but very little darkening effect upon the material, even when the latter was exposed seven hours daily for several weeks (three weeks and upwards) to 95° or 100°, and that no free acid was developed by a continuation of exposure to 95°–100° for three weeks. Gun-cotton containing 2 per cent. of the carbonate did not change colour to a much greater extent, and exhibited still a distinct alkaline reaction after exposure to 95°–100° for four weeks. Samples containing from 4 per cent. upwards of alkaline carbonate darkened very considerably upon long-continued exposure to heat; and a trifling loss in weight was sustained by them, in instances when the treatment was continued between four and five months. This loss somewhat exceeded that which would have been simply occasioned by expulsion of the entire carbonic acid contained in the sodic salt, and furnished evidence of the escape of small proportions of volatile matter. The strength of the fibre was not appreciably affected even in the experiments continued for a considerable period at 90°–100° with the samples containing the highest proportion of carbonates. The colouring matter produced by the action of the alkali was entirely extracted by water; and the properties of the gun-cotton were unchanged.

It therefore appears that, although the presence of somewhat considerable proportions of alkaline carbonate (even as much as 10 per cent.) in gun-cotton does not exert any important action which can be pronounced prejudicial even under very severe conditions of exposure to heat, a proportion as low as 1 per cent. suffices to protect the material, for a longer period than ever could occur in actual practice, from the destructive action of such acid as may be liberated by the decomposition of the organic impurities or by

* The exposure of this sample to 100° was continued for a total period of thirty days, after extraction of the carbonate, without any change resulting. A portion of the specimen was then exposed, seven hours daily for three days, to 115°, and it did not exhibit any symptom of change until the close of the third day.—*June 1867.*

the very gradual effect of a high temperatures (90° – 100°) upon the pure gun-cotton. The introduction of considerable quantities of saline matter into gun-cotton necessarily gives rise to the production of smoke and to some deposition of solid residue, upon the explosion of the substance, and although the amount of both these products would then still be very trifling as compared with those of a corresponding character resulting from the explosion of gunpowder, it is inadvisable that they should be unnecessarily increased. It therefore appears preferable to limit the extent of impregnation of gun-cotton with sodic carbonate to 1 per cent.* It has been abundantly demonstrated by the experiments detailed and by one instituted upon a more considerable scale, to be presently described, that even the introduction of one-half that proportion of sodic carbonate into gun-cotton serves to afford it sufficient protection under conditions of exposure to heat exceeding in severity and duration any which the material would have to encounter if substituted for gunpowder in all directions.

III. *Protective action of Water.*—In one of the earlier experiments on the effects of exposure of gun-cotton to 100° (experiment 124, Table VII.), it was found that the accidental introduction of a very small quantity of water into the vessel containing the gun-cotton, afforded most perfect protection to the material, which exhibited no signs of change during sixteen hours' exposure to 100° , and had not sustained any loss in weight at the close of the experiment. This power possessed by water (or aqueous vapour) of preserving gun-cotton from decomposition at high temperatures† is remarkably at variance with the influence exerted by moisture, if confined together with gun-cotton under protracted exposure to bright daylight and sunlight, in which case there appears no doubt, from the results which have been described, that the aqueous vapour operates in determining to a slight extent the decomposition of the material.

Further illustrations, though less striking than the one above quoted, were furnished of the protective effect of aqueous vapour, by the comparative tardiness with which certain samples of gun-cotton containing more than the ordinary proportion of hygroscopic moisture underwent change by exposure to high temperatures (*vide* experiments 38, 39, and 40). This preservative power of water has received the fullest demonstration from the results of a considerable number of experiments, the nature of which is fairly represented by the following examples.

Experiment 150.—A hank of gun-cotton was suspended in the upper part of a capacious flask containing distilled water tinted with litmus. The water was maintained in rapid ebullition for several hours, the greater portion of the steam condensed in the neck of the flask and upon the gun-cotton, returning to the body of water. At the conclusion of the experiment the tint of the litmus (compared with a standard) had not been affected in the slightest, and the gun-cotton was perfectly neutral and unaltered.

* It is scarcely necessary to observe that this carbonate is selected for introduction into the gun-cotton because, while its solubility affords the means of its uniform distribution through a mass of material, it possesses no tendency to increase the hygroscopic properties of the latter.

† See also pp. 199 and 200.

Experiment 151.—A long wide glass tube was loosely filled with gun-cotton. One extremity was drawn out to a beak which was immersed in water tinted with litmus, the other end was connected with a small boiler from which a rapid current of steam was passed over the gun-cotton, uninterruptedly, seven hours daily for three days. Not the slightest alteration was produced in the colour of the litmus, and the gun-cotton was unchanged.

Experiment 152.—A stout glass tube, closed at one end, was partly filled with gun-cotton; sufficient water was introduced to cover the latter, and the tube was then sealed and exposed to 100° seven hours daily for six days. When the tube was opened no gas escaped, the water was not acid, and the gun-cotton exhibited no signs of alteration. The open tube was afterwards exposed to strong daylight and sunlight; after the lapse of eight months the gun-cotton was found to have a very faint acid reaction, and a minute trace of nitric acid was detected in the water. The proportion of matter soluble in ether and alcohol had very slightly increased.

Experiment 153.—Some gun-cotton was saturated with water, which was afterwards expressed to such an extent that the specimen was difficultly combustible when held in a flame. In this condition the sample was exposed in a sealed tube to 100° seven hours daily for twenty-four days. When the tube was opened, no gas issued from it; the gun-cotton exhibited a very faint acid reaction, but no other signs of change. The open tube containing the moist specimen was afterwards exposed to strong daylight and sunlight for six months; the gun-cotton was then found to have a decided acid reaction. It was digested with a small quantity of water; the aqueous extract was acid to test-paper but not to the taste; nitric acid was detected in it, but no oxalic acid; potassic hydrate imparted to it a faint yellowish tinge, and the alkaline liquid reduced cupric salts to a slight extent. The proportion of matter extracted by ether and alcohol was about double the amount originally existing in the sample. The strength of fibre was unaltered, and there was no appreciable diminution in the explosiveness of the gun-cotton.

Experiment 154.—7 grms. of gun-cotton were thoroughly moistened by being suspended for some time in an atmosphere of steam; the sample was then placed in a flask the sides of which were previously moistened. This flask was connected by a delivery-tube with another containing water, and was also fitted with a straight narrow glass tube. A small quantity of steam was passed into the flask from time to time as the moisture became partially expelled during the experiment. After three days' exposure to 100° (six hours daily), a weighed sample was removed for examination. The gun-cotton had become slightly discoloured in a few places, where it was in immediate contact with the sides of the flask. Water extracted a minute quantity of colouring-matter; no other effect of the exposure to heat was observed. The gun-cotton was again heated to 100° for five days (six hours daily); it was then removed, the flask dried and weighed. By these eight days' exposure to 100° in a moist atmosphere it had sustained a loss of only 1.7 per cent. A weighed sample was again examined, it furnished a very faint indication of acidity. The reactions of nitric acid could not be

obtained with the aqueous extract; the proportion of matter extractable by ether and alcohol had very slightly increased.

The sample was again moistened, and exposed to 100° , as before, for nine days; at the expiration of this period it had sustained a further loss of 1.01 per cent. The total loss during the seventeen days' treatment amounted therefore to 2.71 per cent. The condition of the sample was now as follows:—it had darkened in a few places where in close contact with the glass, and possessed a faint odour, such as is always observed in gun-cotton which has been stored for some time in a warm locality; its acidity had not increased, but a faint reaction of nitric acid was obtained in the aqueous extract after concentration to a small bulk. A trace of lime was also found in solution (evidently as calcic nitrate produced from carbonate in the sample). The proportion of matter extracted by ether and alcohol amounted to 4.1 per cent.; in its original condition the sample contained 2.3 per cent.

Experiment 155.—6.5 grms. of gun-cotton were saturated with moisture and placed in a flask fitted with a straight narrow glass tube of considerable length, for the purpose of rendering the expulsion of water very gradual. After exposure to 100° six hours daily, for three days, the specimen was still moist. The examination of a weighed sample did not furnish the slightest indications of change. The same negative result attended the examination of a second sample after further exposure of the gun-cotton to 100° for three days. The apparatus now contained but very little moisture; after a renewed exposure for three hours to 100° , a very faint coloration by nitrous vapours was observed in the flask; a sample was examined, but beyond a faint acidity no signs of change were detected. The heat was continued for four hours more on the same day, at the expiration of which the coloration in the flask was somewhat more distinct; but there were no signs of nitrous vapours on the following morning. The indication of change in the gun-cotton was still limited to a very faint acidity. The sample was once more heated for six hours, during which period no trace of moisture was deposited upon the cool portions of the glass. Nitrous vapours appeared again in very small quantity, and did not increase up to the termination of the experiment; but on the following morning the apparatus contained deep-coloured vapours. The gun-cotton was now extracted with water; the liquid contained a small quantity of nitric acid, but did not reduce cupric salt. The washed gun-cotton was almost perfectly soluble in ether and alcohol; the insoluble portion amounted only to 1.25 per cent.

Experiment 156.—6.5 grms. of gun-cotton in an air-dry condition were placed in a capacious flask (the interior surface of which had been previously moistened) fitted with a long narrow glass tube. A piece of litmus was suspended in the neck of the flask. Shortly after the gun-cotton had been first exposed to 100° the litmus gradually assumed a wine-red tint, and when the heating had been continued for five hours, the paper had become bleached. There was no other indication of change. At the expiration of the second day's heating, the small quantity of water which had condensed in the neck of the flask exhibited an acid reaction, and the gun-cotton possessed the peculiar odour

which has repeatedly been referred to. Towards the close of the third day no trace of moisture was visible in the cool portion of the flask; a very small quantity was deposited some distance up the quill-tube. Soon afterwards a faint coloration by nitrous vapours was observed, which had very considerably increased by the following morning. The gun-cotton was then found to be acid, the strength of fibre and explosiveness had both diminished; the aqueous extract contained nitric acid, but not oxalic acid, nor did it reduce cupric salt even when highly concentrated. About three-fourths of the washed gun-cotton dissolved in ether and alcohol, a portion being rapidly dissolved, the remainder more slowly; the more soluble part yielded a tough collodion film*.

The following points of interest and importance are established by the results of these and other similar experiments.

(1) Gun-cotton immersed in water perfectly resists decomposition when exposed for long-continued periods to $100^{\circ}\text{C}.$; and this severe treatment has no effect upon the material, even if it is only in a moist condition, or confined in an atmosphere of aqueous vapour. But if the moist specimens are exposed to bright daylight and sunlight for a considerable period, the water or aqueous vapour does not exert the same protective power (see experiments 2 and 4, and p. 192).

(2) If the water or aqueous vapour is allowed to escape during exposure to 100° until the gun-cotton and the atmosphere surrounding it have become almost dry, decomposition commences very gradually; and by arresting the change at a particular period the material is found to be completely reduced to soluble gun-cotton, without the formation of any appreciable amount of the secondary products which result from the action of liberated acid upon the cellulose-products (see experiments 155 and 156).

The perfect protection afforded by moisture to gun-cotton at $100^{\circ}\text{C}.$, under severe conditions, rendered any experiments in this direction at somewhat lower temperatures unnecessary. The following experiment furnishes, however, interesting confirmation of the results obtained by operating at higher temperatures.

Experiment 157.—69.706 grms. of gun-cotton, in an air-dry condition, and 52.196 grms. of the same sample, soaked in distilled water, which was afterwards expressed as completely as possible, were introduced into large bottles, into which the stoppers were loosely inserted. These were then placed in a water-oven, the temperature of which was continually maintained at 60° – 65° day and night. At the expiration of two months both samples were weighed in an air-dry condition. The results indicated a loss of weight of 12.8 per cent. in the dry sample, and of only 0.13 per cent. in the other. After further exposure of the samples as before, for five weeks, the vessel containing the dry one was filled with very deep-coloured vapours, and the experiment was

* This product was submitted to analysis. The proportion of carbon found corresponded more nearly to that contained in trinitrocellulose than to that required by the formula of the next lower cellulose-product (dinitrocellulose). It would appear as though the former had been rendered soluble in ether and alcohol, only a small proportion having suffered reduction. This point is still under investigation.

therefore interrupted, and the samples were again weighed. The dry specimen had sustained a loss of 34 per cent., was quite friable, and had become converted partly into soluble gun-cotton and partly into the products soluble in water. The sample which had been exposed in a moist condition had sustained a total loss of 0.89 per cent., and did not exhibit the slightest signs of acidity. This sample was again submitted in a moist state to a warm atmosphere, ranging from 55° to 65°, day and night for four calendar months. The total loss which it had then sustained after continuous exposure to heat for between seven and eight months, amounted to 1.47 per cent. The gun-cotton exhibited no acid reaction, and the moisture condensed upon the sides of the bottle gave only a faint indication with litmus paper.

Careful observations have been instituted upon the storage of considerable quantities of the material in a wet or merely moist condition. Ordinary gun-cotton has been immersed in sufficient distilled water just to cover it, and has been kept in that condition in closed vessels, with light excluded, for $2\frac{1}{2}$ years. It is perhaps scarcely necessary to state that the material has not sustained the slightest change, and that the distilled water in which it has been preserved is perfectly neutral, the only impurity found in the latter being a small quantity of saline matter extracted from the gun-cotton. A portion of this sample was transferred to a large glass bottle twelve months ago, and has been left exposed to diffused daylight. This difference in the mode of preservation has been quite without effect upon the gun-cotton.

The principal stock of gun-cotton manufactured at Waltham Abbey for experimental purposes, amounting to about 3000 lbs., has been preserved in a moist condition (just as obtained from the centrifugal hydro-extractor) in closed cases until required for use, some of the packages having been kept for about two years; a few, specially set apart for periodical examination, have been preserved for about three years. I have to record no indications of the slightest change except in instances where the gun-cotton had been preserved in close contact with the tinned-copper linings of some gunpowder cases used for its storage. It was found, after some time, that the surfaces of these became oxidized where they were in contact with the moist material, and that this oxidation determined the development of an acid reaction in the gun-cotton, which, however, was, and has continued to be, confined to the portions in immediate contact with the surface of metal*.

Gun-cotton in the condition above referred to contains sufficient water to render it quite unflammable, it may therefore be preserved with perfect safety in this convenient condition, and may be at any time prepared for use by desiccation. As far as can be

* The readily oxidizable character of tin and the tendency of a metal to establish, by its own oxidation, that of readily oxidizable substances which are in contact with it, are well known. If gunpowder containing even the ordinary proportion of moisture remain in contact with a surface of tin, the metal becomes oxidized and the gunpowder acquires an acid reaction, sulphuric acid being detected after some time. Similarly, some remarkable instances of the oxidation of iron by contact with somewhat damp gunpowder, attended by the production of sulphuric acid, have come under my notice.

concluded from three years' experience, the close packing of gun-cotton in this damp state is not even in the slightest degree injurious to the structure of the fibre, no tendency whatever of the material to become rotten when thus preserved has yet been discovered. On the contrary, most decided evidence has been obtained that gun-cotton when kept in a damp condition is very considerably more permanent than ordinary cotton, or vegetable substances of similar nature. Thus, many hanks of the gun-cotton stored in the damp state were tied with tape and string for purposes of distinction. Upon examining these hanks ten months after they had been packed, the tape was in all instances found to be almost if not entirely destroyed, crumbling away when touched, and being transformed principally into fungoid bodies; the strings were also quite rotten and covered with vegetable growth, but the gun-cotton even in close proximity to them was unaffected. Similar results were observed in the case of a number of samples of gun-cotton which had been packed in a dry condition in paper envelopes and placed in a small very damp chamber. About twelve months after they were stored the paper wrappings and strings were found to be covered with vegetable growth and partly destroyed, while no vestiges of similar growth or other signs of change were detected in the gun-cotton. A wooden reel having some gun-cotton yarn wound upon it which had been kept in the same locality was also found to be covered in all exposed parts with fungoid growth, but the gun-cotton in immediate contact with the latter upon the wood was unaffected and perfectly free from mildew. This specimen has been preserved for another year in a damp atmosphere upon the reel and exposed to light. In some parts the mildew has extended to the gun-cotton immediately in contact with the wood, but the rest of the material is unaffected.

PART IV.—OTHER OBSERVATIONS, INSTITUTED UPON LARGE QUANTITIES OF GUN-COTTON.

A series of observations has been conducted for about three years under my direction and in accordance with a programme approved of by the Committee on Gun-cotton, for the purpose of ascertaining the effects of storage in considerable quantities, under the ordinary atmospheric conditions of this country, and under conditions, as regards temperature, representing the extremes likely to be met with in tropical climates or in warm localities (*e. g.* the magazines of ships). The gun-cotton, which, with these objects in view, was closely packed in large ammunition-boxes, comprised not simply parcels of the material as obtained by following the present system of manufacture, but also others in the production of which modifications had purposely been introduced with the view of determining the influence which might be exerted, by possible accidental departure from one or other of the fixed regulations of manufacture, upon the stability of the material. The following is a summary of the observations made up to the present time.

I. Storage of Gun-cotton under ordinary conditions of temperature.

(a) *The gun-cotton being closely packed in a damp condition.*—Attempts have been made to ascertain whether the close packing of gun-cotton in a damp condition would

render it liable to spontaneous heating. Comparative experiments were instituted with gun-cotton, and with cotton-wool in its original unpurified condition. The materials were prepared in two ways; in one experiment they were exposed to an atmosphere saturated with moisture until about 5 or 6 per cent. of water had been absorbed; they were then closely packed in boxes; in another a small portion was moistened (the excess of water being expressed) and packed in the centre of a considerable quantity of dry material. These packages were first occasionally exposed to the sun, they were afterwards preserved for several weeks in a chamber, the atmosphere of which was artificially heated; but in neither instance could any indication of the development of heat be obtained, although the external temperature frequently reached and sometimes exceeded 50° . The inference drawn from these negative results is that gun-cotton is not more liable to spontaneous heating than ordinary cotton-wool. The latter was exposed in a damp and very closely packed condition, in quantities of from ten to thirty pounds, to a heated atmosphere for several months, in order, if possible, to establish spontaneous heating under conditions to which gun-cotton might afterwards be submitted, but the experiments were without result.

The important evidence which has been collected regarding the perfect preservation of damp gun-cotton, when stored under ordinary conditions of temperature, has already been referred to.

(b) *The gun-cotton being closely packed in an ordinarily dry condition.*—Large ammunition-boxes were closely packed with gun-cotton of the following kinds:—

(1) Prepared strictly in accordance with the directions laid down by Von LENK (*i. e.* including the “silicating” treatment).

(2) The same, made up into cartridges.

(3) Prepared in the ordinary manner, but not “silicated.”

(4) Not “silicated,” and packed together with a few skeins ($1\frac{1}{4}$ lb.) of gun-cotton which had only been purified by washing in water (the treatment with alkaline water having been omitted).

(5) Not “silicated,” and packed together with some gun-cotton soluble in ether and alcohol.

(6) Ordinary gun-cotton impregnated with about 0.3 per cent. of sodic carbonate.

Pieces of litmus paper were placed in different parts of the various packages.

Cases containing Nos. 1, 3, and 6 were packed in July and September 1864, and stored in a dry locality. During the summer months the maximum temperatures recorded in this store room ranged from $16^{\circ}5$ to 24° . About six months after the boxes were packed, one of each kind was opened for examination. All the samples had a faint peculiar odour like that of pine-wood, which is always developed in the closely packed material, and was most marked in the unsilicated gun-cotton. Some parts of the litmus paper enclosed in the latter had assumed a pink tinge, and where it had been placed between the gun-cotton and the metal surface of the packing case, it was decidedly

reddened in spots; the tin surface, moreover, exhibited slight signs of oxidation in some places where it was in very close contact with the gun-cotton*.

The litmus in the "silicated" and "alkalized" gun-cotton was unaffected except, again, in one or two small places where it had been interposed between the gun-cotton and the metal surfaces. The boxes were closed immediately after inspection and examined eight months afterwards, when they were found quite unaltered; the litmus paper in the centre of the unsilicated gun-cotton had not been at all affected, but, as before, it was slightly reddened when it had been in contact with the metal.

After further preservation for eighteen months the boxes have recently been again inspected; their condition is precisely what it was on the previous examination. The metal surfaces in the boxes containing the gun-cotton not silicated, exhibited more decided indications of oxidation where they have been in close contact with the gun-cotton than in the other boxes.

Storage in a closely packed condition for nearly three years has therefore not at all affected the gun-cotton in these three states. The material which was not silicated has affected, to a slightly greater extent than the others, the metal surfaces with which it has been in close contact.

Some other cases containing portions of the stock of gun-cotton, "silicated" and not silicated, manufactured in the summer of 1863, and preserved since that time ($3\frac{3}{4}$ years) in a closely packed and ordinarily dry condition, have also been recently inspected, and their contents have been found to be as perfect as those of the cases just described.

The cartridges enclosed in serge bags were packed and stored about $2\frac{1}{4}$ years ago. Their condition is unaltered, and the metal cases containing them are perfectly bright.

The cases containing a proportion of imperfectly purified gun-cotton and of soluble gun-cotton (Nos. 1 and 5) were packed early in January 1866. After storage for fifteen months their contents have been examined and found to present no points of difference from the other packages of gun-cotton above described, the only indications of acidity being discovered where the metal surfaces and the gun-cotton were in very close contact.

Steps are now being taken to substitute simple wooden boxes, rendered impervious to moisture, for the metal-lined ammunition cases in which these stores of gun-cotton are now packed, and which have evidently, in all the experiments with large quantities of gun-cotton, constituted an element unfavourable to the stability of the material, the influence of which it is, however, important to have determined. In storing gun-cotton it is obviously as unnecessary as it is inadvisable to employ receptacles of metal.

II. *Exposure of large packages of gun-cotton, in different conditions, to heat.*

(a) *Preliminary experiment.*—A wooden box holding $4\frac{1}{4}$ lbs. of gun-cotton when closely packed, was fitted with a gutta-percha tube intended to receive a thermometer.

* A piece of bright sheet tin which was packed on this occasion in the centre of the gun-cotton was examined after a period of one year and found to have become corroded in spots, the gun-cotton having a slight acid reaction at the places where this effect was produced.

The sides of the tube were perforated in several places, and it passed horizontally through the centre of the box, the openings being closed with corks. The box was painted black, and having been tightly filled with skeins of gun-cotton, amounting to about 4 lbs., it was placed in the open air throughout each day in the month of August 1864, in a position where it would be most frequently exposed to the sun's rays, and would also receive the heat radiated from a brick wall*. A registering thermometer was enclosed in the tube of the box, and another was placed on the outside, readings being taken of both twice daily. The highest temperature indicated upon the exterior of the box was generally about 6° or 7° above that of the centre of the gun-cotton. The temperature of the latter ranged from 14° (early in the morning) to 38° , while the temperature-indications on the exterior of the box ranged between 15° and 47° . The average temperature in the centre of the box at 5 o'clock in the afternoon was 32° . At the close of the month the box was opened, the gun-cotton possessed the faint odour peculiar to the material when closely packed, but exhibited no signs of change.

The box was immediately reclosed (some litmus paper being introduced) and placed in a chamber artificially heated. The temperature in this chamber was maintained as constantly as possible at 50° , but fluctuating a few degrees on either side. During one month's exposure in this chamber the temperature of the centre was stationary at about 49° for some time on four occasions; but the maximum temperature attained during the day ranged, with those exceptions, between 43° and 47° . At the expiration of the month, the litmus paper was found to be reddened, and the gun-cotton had a somewhat pungent odour. A portion of it, extracted with a small quantity of cold water, furnished a very faintly acid liquid, which, upon being kept in a covered vessel for some hours, was found upon the following day to be distinctly alkaline. No nitric acid could be detected, and with the exception of the peculiar odour the gun-cotton gave no indication of change. It was returned to the box together with litmus paper, and exposed again to heat in the chamber for a few days. The litmus had then changed as before. The gun-cotton was now removed from the box and fully exposed to air for an hour, when it was repacked together with litmus paper and placed in an apartment at the ordinary atmospheric temperature. The contents of the box were inspected weekly; a very trifling reaction was produced upon the litmus in some parts only, and this effect did not increase.

The gun-cotton was afterwards repacked, a very imperfectly purified skein being placed in the centre. It was then kept in the warm chamber for seven months, during which period the temperature of the air surrounding the box ranged between 30° and 50° . When the box was afterwards opened the litmus paper was red and rotten, and the material possessed a pungent odour, but no nitrous vapours were perceptible. One of the skeins in immediate contact with the imperfectly purified gun-cotton was extracted with water, but furnished only a very faintly acid liquid. The box was repacked as quickly as possible, all apertures were perfectly closed up, and it was placed in a

* The box was removed indoors late in the afternoon and replaced at nine in the morning. It was also placed under shelter when rain fell.

magazine. After the lapse of $1\frac{3}{4}$ year it was examined, and its contents were found unchanged, except that the odour was decidedly less pungent than before.

The data furnished by this preliminary experiment appeared to warrant the conclusion that further and more extensive trials of the effects of heat upon gun-cotton might be safely instituted. The following experiments were therefore made.

b. *Exposure of a large case of gun-cotton to the sun's rays.*—A large wooden box with blackened exterior, and fitted with a central tube to receive the recording thermometer, was compactly filled with rather more than 36 lbs. of gun-cotton, *not* silicated, which had been manufactured two years previously. This box was exposed to the open air on all bright sunny days between the middle of April and 1st of October last year; it was placed at a short distance from the brick wall of a hot-air chamber, in a position where it would be exposed to the maximum available amount of sunlight. At night and during wet weather it was placed under shelter. Readings were taken every two hours of the thermometer in the central tube, and of one exposed upon the outside of the box. The extreme temperature attained by the centre of the gun-cotton was 35° , the thermometer upon the box having indicated 49° on that day. Upon several occasions the thermometer in the centre of the box recorded $32^{\circ}5$. The latter generally attained its maximum temperature from four to six hours after the highest external temperature had been registered. The following are some of the highest readings recorded during the $5\frac{1}{2}$ months' exposure of the box.

	Inside the box.	Outside the box.		Inside the box.	Outside the box.
April	$18^{\circ}5$	$27^{\circ}5$	July	$26^{\circ}5$	$32^{\circ}5$
	20	27.5		35	49
	21.5	30.5		31.5	40.5
	26.5	40		31.5	40
May	19	27		25.5	37
	20	35.5		32.5	45
	22.5	37.5		26.5	36
	20.5	29		28.5	43
	29	44	August . . .	22.5	40.5
	26.5	39		24	39.5
	25	42.5		22.5	39
June	20.5	43.5		22.5	43.5
	20.5	43.5		24	41
	19.5	27.5		23	30.5
	26.5	36.5		23	36.5
	32.5	46.5	September . .	16.5–27	20–31
	25.5	34.5			
	25	37			
	33	47.5			

When the box was opened, the litmus paper was found to have assumed a pink tinge, and the usual faint odour of confined gun-cotton was somewhat more manifest than if the box had been preserved under ordinary atmospheric conditions, but the material itself was quite unchanged.

c. *Exposure of gun-cotton in different conditions to a heated atmosphere in a confined space.*—A chamber was constructed of brickwork, and suitably fitted for the reception of a number of large ammunition-boxes. A system of iron pipes, standing in the centre of the chambers, was supplied with hot water from a boiler placed in a shed distinct from the chamber and heated with gas. By this arrangement, the atmosphere in the room could be maintained at artificial temperatures without risk of accident.

The boxes in which the gun-cotton was packed were the large ammunition-cases employed in military service, and consisted of thin tinned-copper cases enclosed in stout wooden boxes and very tightly closed with double lids. Experience showed, some time after the experiment was set on foot, that the employment of these metal-lined cases was unquestionably prejudicial to the gun-cotton, as the very slightest development of acid in the latter, where it was in actual contact with the sides of the case, established oxidation of the metal surfaces, whereby in turn the alteration of the gun-cotton at those parts was considerably promoted.

Each case was fitted with a central tube to receive a registering thermometer, in the same way as the black boxes already described. The gun-cotton was closely packed, and the description of material placed in the several boxes was varied (as shown in the following Table) with the view of examining the effects of different modifications in the manufacture upon the power of gun-cotton to resist the effects of heat.

In the first instance, the temperature of the hot-air chamber was raised as rapidly as possible to between 49° and 50° , and then maintained at that temperature (within narrow limits on either side) for several hours daily, periodical readings of a thermometer exposed in the room and of those enclosed in the central tubes of the boxes were recorded. The heating of the chamber was commenced at six in the morning; the maximum temperature was generally attained at about eleven o'clock, and it was maintained (for seven hours) until six in the afternoon.

After the first day of the experiment the temperature of the air in the chamber at six in the morning was always from 8° to 11° lower than the temperatures recorded in the boxes, excepting on the Monday morning, when the difference amounted only to between 1° and 3° . The rapidity with which the temperature rose in the interior of the boxes varied somewhat; the thermometers were stationary, or fell slightly for about two hours after the heating was commenced; at the close of that period the air in the chamber was generally (except on Mondays) 10° or 12° higher than that of the centre of the gun-cotton, the latter then rose gradually, almost reaching the maximum in ten hours, but still rising 2° or 3° in the last two hours. Even after seven hours' exposure to air at the maximum temperature, the contents of the case were, in the centre, from 5° to 9° cooler than the external air. The daily records of temperature obtained from the different

boxes during three months' exposure to a maximum temperature of 50° were very uniform, and not the slightest indication of any development of heat in the mass of the gun-cotton was obtained in any one instance. The maximum temperatures within the boxes were always considerably below the temperatures of the air in the chamber at the time, the difference ranging between 6° and 11° , excepting on Mondays, when the boxes never reached so high a temperature as on other days.

At the termination of three months it was decided to raise the temperature of the chamber to between 54° and 55° . The experiment was conducted as before, and readings of the thermometers were taken every two hours. The temperature of the chamber was generally raised to 54° by about eleven in the morning (sometimes earlier), and was maintained as constantly as possible at that temperature for seven hours. On 79 days out of 195, the temperature of the room reached $55^{\circ}\cdot 5$, and continued so from two to four hours. During three months no indication of development of heat was obtained in any one of the boxes; the temperature-records within these at the close of the day were during this period (excluding Mondays) from 6° to 11° below that in the chamber itself, and the highest maximum temperature attained by the boxes up to the termination of that period was 49° . One of the boxes then furnished indications of some development of heat in its contents; it was therefore removed, and the experiment was continued with the remainder of the boxes. During the last three months the maximum temperatures recorded in the several boxes confined in the chamber, more nearly approached that of the air surrounding them; the differences between the readings of thermometers within and outside the boxes at six in the evening ranged between $5^{\circ}\cdot 5$ and 1° .

The following is a tabulated statement of the descriptions of gun-cotton operated upon, and the duration and results of their exposure to heat. In the statements given in this Table, of the lowest and the mean of the temperatures recorded in the several packages, the readings obtained on Mondays have not been included, as they were considerably below those of the other five days in the week, in consequence of the chamber and boxes having cooled down during Sundays.

TABLE IX.

Description of gun-cotton employed.	Quantity contained in one box.	Exposure to 49°-50°.		Exposure to 54°-55°.		Causes of removal from the hot-air chamber.	Condition of the gun-cotton when removed from the chamber, and other remarks.
		Duration of exposure to a maximum temperature of 49°-50° C.	Lowest and highest temperatures recorded in the interior of the boxes at 6 a.m. 6 p.m.	Duration of exposure to a maximum temperature of 54°-55°.	Lowest and highest temperatures recorded in the interior of the boxes at 6 a.m. 6 p.m.		
1. Made at Waltham Abbey, 1863, <i>not silicated</i> .	lbs. 11½	3 months....	21 31 39 44 6 a.m. 6 p.m.	3 months....	24.5 34.5 44 49 (39.5 when removed from the chamber). (52.5 the night before removal).	During the last two hours' heating the temperature in this box rose 4° higher than in all the other boxes (being 52.5 at 6 p.m.). At 6 the following morning it had fallen to 39.5. At 6 a.m. the temperature within this box was 44°, in the other box was only 34°.	Upon opening the box, the gun-cotton was found to be impregnated to a large extent with nitric oxide, and the metal of the case was much corroded. An acid extract was obtained with water, in which only nitric acid was detected. The soluble matter in ether and alcohol amounted to 6.8 per cent. (the original gun-cotton contained 2 per cent.). Nitric oxide escaped abundantly from this gun-cotton, when it was removed from the box, and the metal lining of the latter was considerably corroded. The change produced in the gun-cotton was confined to a slight increase in the proportion of matter dissolved by ether and alcohol (which amounted to 3.5 per cent.).
2. <i>Silicated</i> gun-cotton (manufactured in 1863) with 1 lb. of <i>imperfectly purified</i> gun-cotton (not treated with the alkaline bath) packed in the centre.	11½	3 months....	21.5 31 37.5 42.5	3½ months....	24.5 35.5 44.5 50 (44° on the morning of its removal).		
3. <i>Silicated</i> , with 12 ozs. of imperfectly converted (<i>soluble</i>) gun-cotton, <i>not silicated</i> , packed in the centre.	11½	3 months....	22.5 31 39 44	4 months....	24.5 35.5 43.5 51 (58.5 on the morning of its removal).	On the evening preceding its removal the temperature within this box was 51°; but after the next morning it was 58.5°, the temperatures in other boxes being 31.5-39.5.	The gun-cotton and the case were in the same condition as the two preceding; but the proportion of matter dissolved by ether and alcohol was somewhat higher (8 per cent.).
4. <i>Silicated</i> , manufactured at Waltham Abbey, 1863.	11½	3 months....	21 31 38.5 43.5	5 months....	24.5 39 43.5 51 (40° on the morning of its removal).	The temperature within this box was 40° at 6 a.m., while in the other boxes it was 34.5.	Nitrous vapours escaped less abundantly from this gun-cotton than from the other, and the metal case was decidedly less corroded. The matter extracted by ether and alcohol amounted to 6.5 per cent.
5. <i>Not silicated</i> , but impregnated with 0.3 per ct. of <i>sodic carbonate</i> .	13	3 months....	21 31 37.5 43.5	7 months....	24.5 39.5 43.5 51	No indication of development of heat up to the conclusion of the experiment.
6. Same gun-cotton as No. 1, having been freed from acid by digestion in alkaline water and subsequent washing in distilled water.	11	3 months....	29 39 50.5 52.5	
7. Same gun-cotton as No. 2, having been freed from acid by digestion in alkaline water, and subsequent washing in distilled water.	11	3 months....	30.5 39 49.5 52	No decided indication of development of heat was recorded in either of these packages, up to the termination of the experiment.

Note.—The above samples of gun-cotton which had been exposed to heat for 6, 6½, 7, and 8 months, had not altered appreciably in strength of fibre or explosiveness. After having been thoroughly purified from acid, they could not be distinguished from the original gun-cotton, except that they were somewhat whiter, as though prepared from a superior quality of cotton-wool.

The results of these experiments were as follows:—

(1) Gun-cotton closely packed in metal-lined cases, of considerable size, in two of which some imperfectly prepared gun-cotton was purposely included, sustained uniformly a daily exposure for twelve hours during three months to a heated atmosphere, the temperature of which generally ranged from 49° to 51° for a period of seven hours, without furnishing any indication of the development of heat within the mass of the gun-cotton, consequent upon chemical change.

(2) The further exposure of these packages for another period of three months to a heated atmosphere, the temperature of which generally ranged during seven hours daily between 54° and 55° , resulted only in *one* instance in the development of heat in the gun-cotton; and the particular box which, at the expiration of the six months' treatment, furnished this indication that its contents were undergoing decomposition, was filled with gun-cotton in the condition which all previous experiments had indicated as least capable of resisting the effects of prolonged exposure to heat; being, namely, almost free from substances (carbonates) which would exert a neutralizing action upon any acid generated by decomposition of the comparatively unstable impurities existing in the gun-cotton.

(3) The box which next furnished very slight indications of the development of heat, after exposure for $6\frac{1}{2}$ months, contained gun-cotton through which a small proportion of earthy carbonates had been distributed by its submission to the so-called "silicating process," but in the centre of which a specimen of imperfectly purified gun-cotton had been packed. There is no question that this box would have furnished much earlier indications of the occurrence of chemical change in its contents, if the gun-cotton principally composing the latter had not been protected for a considerable period by the presence of carbonates from the destructive effects of acid liberated from the imperfectly purified gun-cotton which was packed in the centre of the box.

(4) A box of "silicated" gun-cotton containing a small quantity of soluble gun-cotton not silicated, was the next to exhibit symptoms of decomposition, after having been exposed to heat for seven months. Numerous experiments have shown that the soluble gun-cotton is not more prone to decomposition than the most perfectly converted material; but the sample packed in the centre of this box was not protected by carbonates, and therefore doubtless sustained change considerably sooner than the chief portion of the contents of this box, promoting an alteration in the latter, after the lapse of some time, when the protective effect of the carbonate had become neutralized.

(5) The box which was entirely filled with gun-cotton, prepared strictly according to Von LENK'S system, including its submission to the "silicating" process, only exhibited a slight indication of internal development of heat after having been exposed for eight months to a heated atmosphere. The protective effect exerted by the small proportion of earthy carbonate deposited in the gun-cotton as a result of the "silicating" treatment was, in this instance, not diminished by the presence of any gun-cotton not thus treated, and consequently the contents of this box resisted change for a longer period than the

“silicated” gun-cotton in the two other boxes (2 and 3). Moreover, this gun-cotton, though exposed to heat for two months longer than the unsilicated gun-cotton (in No. 1 box), was found upon examination to have evolved considerably less acid.

(6) The gun-cotton which had been uniformly impregnated with only 0·3 per cent. of sodic carbonate furnished no signs whatever of development of heat up to the period when the experiment was interrupted, having been, at that time, exposed for ten months to a heated atmosphere, the temperature of which ranged, for seven hours daily during seven months, between 54° and 55° . It is much to be regretted that a careful examination of the contents of this box after so prolonged and severe an exposure to heat was prevented by an accident.

(7) The condition of the gun-cotton after exposure to heat in the three boxes first removed was very similar. Although the material was found to be highly impregnated with nitric oxide and nitrous acid (the development of which there is every reason to believe had been very considerably promoted by the large metal surfaces of the boxes which were in close contact with the gun-cotton), the decomposition had not proceeded in any one of the boxes to such an extent as to produce an alteration in the explosive and other properties of the gun-cotton. When the latter had been purified from the free acid developed in it, no difference could be discovered between it and the original material, except that it had become slightly bleached. The gun-cotton from boxes 1 and 2, after being purified by digestion in alkaline water and subsequent repeated washing in distilled water, was dried, repacked and returned to the hot-air chamber. It now contained no carbonates whatever by which the destructive effect of acid, if developed, could be retarded or prevented; but the boxes, each containing eleven pounds of this gun-cotton, were exposed to heat for three months, the temperature of the air ranging from 54° to $55^{\circ}\cdot5$ for seven hours daily, and no indication whatever of development of heat was obtained in either instance. (The purified gun-cotton from boxes 3 and 4 was also repacked and returned to the chamber at later periods.)

After the heat-experiments described above had been continued between eight and nine months, two barrels, fitted with tubes for thermometers, each containing about twenty-three pounds of gun-cotton which was neither “silicated” nor impregnated with sodic carbonate, were placed in the chamber, the object being to obtain direct proof of the extent of influence exerted by the metal surfaces in the cases employed in the other experiments, upon the behaviour of the gun-cotton itself.

Two other much smaller metal-lined cases, each containing about five pounds of gun-cotton, were also placed in the chamber at this time; one of them was filled with a sample which had already been subjected to severe exposure to heat and had subsequently been purified from acid, and the other was filled with disks prepared by compressing gun-cotton which had been reduced to pulp. Lastly, an ammunition case containing twenty-three pounds of gun-cotton, which was impregnated with a more considerable quantity of sodic carbonate than employed in the first experiment, was added to the contents of the chamber. The heating of the latter to 54° – 55° was continued

for about six weeks, when an explosion occurred, which destroyed the chamber and the whole of the samples, excepting some of the compressed gun-cotton.

As is generally the case in accidents of this kind, the immediate cause of the explosion could not be traced with certainty. The usual periodical readings of the thermometers enclosed in the packages had been taken shortly before the explosion occurred, and all the temperatures last recorded were below that of the air in the chamber, which had been at $55^{\circ}\cdot 5$ from two till six o'clock; not one of the packages had furnished any indication that heat was developed, but the temperature in the two small boxes was considerably higher than in the larger packages; the comparatively small volume of gun-cotton became much more rapidly heated throughout, so that the temperature recorded in these instances at the close of the day's heating was generally within 2° of the maximum external temperature. It appears most probable, therefore, that the small parcel of gun-cotton which had already suffered some change by exposure to heat, and which had since been exposed for six weeks to a heated atmosphere ranging between 54° and $55^{\circ}\cdot 5$ for seven hours daily, eventually sustained further alteration, which, though very gradual for a time, at length increased to such an extent that heat was very rapidly developed, raising the gun-cotton to the temperature required for its explosion within a comparatively brief period. The experiments made at 100° C. with small quantities of gun-cotton which have been described in an early part of this paper (p. 197), demonstrated that, when once a considerable decomposition of the substance had set in, the development of heat was very rapid indeed. It was believed, however, that the *first* establishment of decomposition would in all instances be indicated by so gradual a rise of temperature that frequent periodical observations of a thermometer placed in the centre of packages of heated gun-cotton would always afford the means of carrying on experiments of this class with security, a belief which was strongly supported by the results of the experiments carried on for periods of five, six, and ten months with the five large packages of gun-cotton. The power to resist serious decomposition upon continued exposure to a highly heated atmosphere had proved so unexpectedly great in the case of every one of those experiments, that it was considered important to ascertain, if possible, the full extent of those powers; and hence, with what proved to be undue reliance upon the infallibility of the measures adopted to guard against accident, the experiments were protracted and the variety of the tests increased, far beyond the extreme limits necessary for the attainment of their original object, which was to ascertain how far gun-cotton, either of ordinary manufacture, or accidentally defective, or protected by special preparation, would resist change under conditions representing the extremes, both in extent and duration, of heat to which it might be exposed if stored, or used in active military service, in tropical climates.

The Committee on Gun-cotton has endeavoured to collect reliable data with reference to the average and extreme temperatures to which gun-cotton might be exposed in ships' magazines, during the passage of vessels through tropical regions, or to which it might be subject in India if directly exposed to the sun in ammunition-boxes; these being

the most severe natural conditions of exposure to heat which would ever be likely to occur.

A statement was furnished to General SABINE, by the late Admiral FITZROY, of the maximum and minimum temperatures recorded monthly in the chronometer room of Her Majesty's Ship 'Odin' between September 1861 and September 1863, this vessel having been during that period at Japan, in the China Sea, Malacca Strait, Indian Ocean, Bengal Bay, North and South Atlantic, &c. The highest temperatures recorded were in May 1862 and April 1863 (in the Indian Ocean), being 31° (88° F.) on both occasions; the minimum temperature in those months were 29° (84° F.) and $26^{\circ}\cdot8$ (80° F.). Between February 1862 and August 1863 the registered maximum temperatures ranged between $25^{\circ}\cdot3$ and 31° , and the minimum temperatures between $14^{\circ}\cdot7$ and 29° . Admiral FITZROY considered that, except at times when men were continuously at work in a ship's magazine, the temperature within the latter would be regulated by that of the surrounding water, which, at a few feet below the surface, is never warmer than from 26° to 30° . If this is the case, the temperature-records obtained from the 'Odin' afford a fair representation of the maximum and minimum temperatures of the atmosphere in magazines where gun-cotton might be stored on board ship. Steps have, however, been taken to obtain records of the maximum and minimum temperatures actually experienced in ships' magazines.

At the request of General SABINE, Mr. POGSON, the Astronomer at Madras, took daily readings, from May 1 to June 30, 1866, of thermometers placed in boxes, the one painted black and the other white, and both exposed to the sun. The complete account of the observations made by that gentleman have not yet been received, but, in a letter to General SABINE, he states that during the above-named period, which occurred in the hottest and driest season ever experienced at Madras, the highest temperature registered inside the black box was $51^{\circ}\cdot2$ ($124^{\circ}\cdot4$ F.), that in the white box being 44° ($111^{\circ}\cdot2$ F.), whilst the lowest minimum readings recorded were $26^{\circ}\cdot8$ (80° F.) in the black box, and $26^{\circ}\cdot1$ C. (79° F.) in the white box*. The maximum temperature recorded *in the empty black box*, exposed to the sun at Madras, was therefore about 5° C. below the average temperature to which closely packed gun-cotton, in a condition most favourable to change, was exposed for about seven hours daily, during three months (having previously been similarly exposed to an atmosphere at 50° for an equal period), before there was any indication of development of heat, while gun-cotton prepared according to Von LENK's directions resisted a similar exposure for five months, and ordinary gun-cotton containing a small proportion of sodic carbonate furnished no indication of change when it had been stored under the same circumstances for seven months.

General MORIN†, in some observations upon the recent report of PÉLOUZE and MAURY on gun-cotton, referred to the existence of instances in which the atmosphere in the interior of buildings had been raised to a temperature of 38° , 40° , or 42° (the external

* The difference between the maximum records in the black and white boxes is reported as ranging between 3° and 7° .

† Comptes Rendus, vol. lix. p. 374.

atmosphere being only 21°) by the passage of solar heat through glass windows or roofs, and also stated that it was not uncommon to find the interior of powder-wagons, covered with metal, at a temperature of 50° – 60° , while the external temperature was only 24° . It is evident from the nature of this statement that the elevation of temperature to this extent in the localities described was only transient; but even if the atmosphere in magazines or ammunition-wagons were occasionally at such temperatures for several consecutive hours during a considerable period, it may be confidently maintained that gun-cotton properly purified and impregnated with a small proportion of sodic carbonate, as has been described, may be preserved in such localities with perfect safety, even in a closely packed condition. It has been shown that gun-cotton, even without the aid of the very decided though variable protection afforded to it by the "silicating" process, sustained no change whatever by continuous exposure to the sun's rays in a black box between April and September, the temperature of the external surface of the box having frequently exceeded 40° , and that the same kind of gun-cotton sustained, without any change, three months' exposure for several hours to an atmosphere of 50° , and did not exhibit any indication of change until after further exposure for nearly three months to an atmosphere maintained for several hours daily at $54^{\circ}\cdot 5$ – $55^{\circ}\cdot 5$. In both these instances the gun-cotton was as closely packed as possible, in one mass* (and in the latter it was contained in a case lined with tinned copper, which seriously influenced the effect of heat upon the gun-cotton).

It is therefore considered that the extent and circumstances of exposure to heat which even this perfectly unprotected gun-cotton resisted, may be regarded as exceeding in severity such as it would have to encounter in the actual employment of the material in naval and military service.

The following are some of the principal conclusions which may be drawn from the results of observations and investigations described in the foregoing pages:—

1. Gun-cotton produced from properly purified cotton, according to the directions given by Von LENK, may be exposed to diffused daylight, either in open air or in closed vessels, for very long periods without undergoing any change. The preservation of the material for $3\frac{1}{2}$ years under those conditions has been perfect.

2. Long-continued exposure of the substance, in a condition of ordinary dryness, to strong daylight and sunlight produces a very gradual change in gun-cotton of the description defined above; and the statements which have been published regarding the very rapid decomposition of gun-cotton when exposed to sunlight do not therefore apply to the nearly pure trinitrocellulose obtained by strictly following the system of manufacture now adopted.

* In ammunition-wagons, the gun-cotton would be packed in the form of cartridges, enclosed in serge, and with intervening air-spaces. It would therefore be in a condition much less favourable to the accumulation of heat, than the gun-cotton was, in the experimental cases.

3. If gun-cotton in closed vessels is left for protracted periods exposed to strong daylight and sunlight in a moist or damp condition, it is affected to a somewhat greater extent; but even under these circumstances the change produced in the gun-cotton by several months' exposure, is of a very trifling nature.

4. Gun-cotton which is exposed to sunlight until a faint acid reaction has become developed, and is then immediately afterwards packed into boxes which are tightly closed, does not undergo any change during subsequent preservation in ordinary store-houses (as far as the experience of $3\frac{1}{2}$ years has shown).

5. Gun-cotton prepared and purified according to the prescribed system, and stored in the ordinarily dry condition, does not furnish any indication of alteration, beyond the development, shortly after it is first packed, of a slight peculiar odour, and the power of gradually imparting to litmus, when packed with it, a pink tinge.

6. The influence exercised upon the stability of gun-cotton of average quality, as obtained by strict adherence to Von LENK's system of manufacture, by prolonged exposure to temperatures considerably exceeding those which are experienced in tropical climates, is very trifling in comparison with the results recently published by continental experimenters relating to the effects of heat upon gun-cotton; *and it may be so perfectly counteracted* by very simple means, which in no way interfere with the essential qualities of the material, that the storage and transport of gun-cotton presents no greater danger, and is, under some circumstances, attended with much less risk of accident, than is the case with gunpowder.

7. Perfectly pure gun-cotton, or trinitrocellulose, resists to a remarkable extent the destructive effects of temperatures even approaching 100° C.; and the lower nitro-products of cellulose (soluble gun-cotton) are at any rate not more prone to alteration, when pure. The incomplete conversion of cotton into the most explosive product does, therefore, not of necessity result in the production of a less perfectly permanent compound than that obtained by the most perfect action of the acid-mixture.

8. But all ordinary products of manufacture contain small proportions of organic nitrogenized impurities, of comparatively unstable properties, which have been formed by the action of nitric acid upon foreign matters retained by the cotton fibre, and which are not completely separated by the ordinary or even a more searching process of purification.

It is the presence of this class of impurity in gun-cotton which first gives rise to the development of free acid, when the substance is exposed to the action of heat; and it is the acid thus generated which eventually exerts a destructive action upon the cellulose-products, and thus establishes decomposition which heat materially accelerates. If the small quantity of acid developed from the impurity in question be neutralized as it becomes nascent, no injurious action upon the gun-cotton results, and the great promoting cause of the decomposition of gun-cotton by heat is removed. This result is readily attained by uniformly distributing through gun-cotton a small proportion of a carbonate, the sodic carbonate, applied in the form of solution, being best adapted to this purpose.

9. The introduction into the finished gun-cotton of one per cent. of sodic carbonate affords to the material the power of resisting any serious change, even when exposed to such elevated temperatures as would induce some decomposition in the perfectly pure cellulose-products. That proportion affords, therefore, security to gun-cotton against any destructive effects of the highest temperatures to which it is likely to be exposed, even under very exceptional climatic conditions. The only influences which the addition of that amount of carbonate to gun-cotton might exert upon its properties as an explosive, would consist in a trifling addition to the small amount of smoke attending its combustion, and in a slight retardation of its explosion, neither of which could be regarded as results detrimental to the probable value of the material.

10. Water acts as a most perfect protective to gun-cotton (except when it is exposed to sunlight), even under extremely severe conditions of exposure to heat. An atmosphere saturated with aqueous vapour suffices to protect it from change at elevated temperatures, and wet or damp gun-cotton may be exposed for long periods in confined spaces to 100° without sustaining any change.

Actual immersion in water is not necessary for the most perfect preservation of gun-cotton; the material, if only damp to the touch, sustains not the slightest change, even if closely packed in large quantities. The organic impurities, which doubtless give rise to the very slight development of acid observed when gun-cotton is closely packed in the dry condition, appear equally protected by the water; for damp and wet gun-cotton which has been preserved for three years has not exhibited the faintest acidity. If as much water as possible be expelled from wet gun-cotton by the centrifugal extractor, it is obtained in a condition in which, though only damp to the touch, it is perfectly non-explosive; the water thus left in the material is sufficient not only to act as a perfect protective, but also to guard against all risk of accident. It is therefore in this condition that all reserve stores of the substance should be preserved, or that it should be transported in large quantities. If the proper proportion of sodic carbonate be dissolved in the water with which the gun-cotton is originally saturated for the purpose of obtaining it in this non-explosive form, the material, whenever it is dried for conversion into cartridges, or employment in other ways, will contain the alkaline matter required for its safe storage and use in the dry condition in all climates.

Although some experiments bearing upon the different branches of inquiry included in this Memoir are still in progress, with a view to the attainment of additional knowledge of the conditions which regulate the stability of gun-cotton, it is confidently believed that the results which have been described amply demonstrate that the objections which have been of late revived, especially in France, against the employment of gun-cotton, on the ground of its instability, apply only in a comparatively slight degree to the material produced by strictly pursuing the system of manufacture perfected by Von LENK; that, as far as they do exist, they have been definitely traced to certain

difficulties in the manufacture of *pure* gun-cotton which further experimental research may overcome; but that, in the mean time, these objections are *entirely set aside* by the adoption of two very simple measures, against the employment of which no practical difficulties can be raised, and which there is every reason to believe must secure for this material the confidence of those who desire to avail themselves of the special advantages which it presents as an explosive agent.

The nature of the decomposition of gun-cotton, when exploded under different conditions, is now under investigation by me, and the results arrived at will I trust be communicated before long to the Royal Society.

NOTE.—Since this Memoir was communicated to the Royal Society, a circumstance of a very unexpected nature has been observed, accidentally in the first instance, which appears to have an important bearing upon the question of the stability of gun-cotton.

A skein of Waltham Abbey gun-cotton has been suspended upon a line in the upper part of my laboratory for about twelve months. It has therefore been freely exposed to air and diffused daylight during that period. A portion of this sample was recently employed in a comparative heat-experiment, with some specially prepared samples, and was found to resist exposure to 100° C. in a very remarkable manner. Several portions have been maintained for many hours at 100°, upon consecutive days, without undergoing the slightest change, although originally a brief exposure to that temperature sufficed to develop symptoms of decomposition in this gun-cotton.

The behaviour of this specimen led to an examination of several samples of Stowmarket gun-cotton, portions of which had been employed in the heat-experiments described in Table III. of this Memoir, and which have since been exposed to diffused daylight, in loosely stoppered bottles, for about 2½ years. Three among them which, when first examined, were found to undergo decomposition after exposure for a few minutes to 100° C., were selected for re-examination, and they all perfectly resisted decomposition upon long-continued exposure to that temperature.

It thus appears definitely established that the stability of gun-cotton is importantly increased by long-continued exposure to diffused daylight. An examination into the cause of this interesting fact is now being prosecuted, and the results promise importantly to strengthen the confidence which is already placed in the permanence of gun-cotton.—*June* 1867.