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Extract from
Science of Explosives
or Gunpowder
Processing Vol 2

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SCIENCE OF EXPLOSIVES

A collection of monographs mainly on the physics and physical chemistry of explosives, being records of researches carried out during the war of 1939-1945 in Government Establishments and Universities, under the aegis of the Advisory Council on Scientific Research and Technical Development, Ministry of Supply, with contributions by Messrs. Imperial Chemical Industries Ltd.,

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14.16. Nitration Processes: The starting-material for nitration, cotton linters or cotton waste, which has already been heated with dilute sodium hydroxide under pressure to remove grease and other impurities and to reduce its viscosity to the required degree, is passed, before nitration, through several dusting and teasing plants and then through mechanical driers, after which the moisture content is less than 0.5 per cent. The oldest method of nitrating cellulose was to plunge it into mixed acid contained in earthenware pots until no more could be easily wetted with acid and to leave it immersed until nitration was complete. This process is still in use in at least one factory with cops (rejected portions of spun cotton) as the starting material, because the relatively uneven product, nitrated without any agitation, has specially valuable qualities for the production of blasting explosives, but for every other purpose has been superseded by either the mechanical or displacement process. The properties of a nitrocellulose of given nitrogen content vary appreciably with the method used to make it.

Mechanical nitration gives the most uniform product and is tending to supersede all other methods. In it cotton linters are generally used. The nitrator is usually an elliptical cylinder holding about 1,800 lb of mixed acid, with its axis vertical, in which rotate two paddle stirrers on vertical shafts. Mixed acid and linters are added concurrently, and after about 30 minutes the mixture of nitrocotton and spent acid is discharged through a bottom valve into a centrifuge in which the acid is spun off. The acid-wet nitrocotton is removed from the centrifuge basket and drowned in water. The displacement process was introduced in 1905 at Waltham Abbey as an improvement on the old rudimentary nitration in open vessels. The displacement pans are generally shallow cylinders of earthenware or stainless steel, about 3 ft. 9 in. in diameter and 12 in. in depth, with a central bottom outlet connected to a siphon pipe. A perforated false bottom, in sections of the same material as the pan, is laid down inside it. About 800 lb. of acid, cooled or heated to the required temperature, are run in to nearly fill the pan and the cotton, either waste or linters, is dipped into the acid with aluminium forks. When all the charge is in, a second layer of perforated plates is laid on top of the nitrated cotton and a layer of water is allowed to flow over the surface of the acid, just above the plates, thus preventing the escape of fumes from the acid into the air. Nitration is allowed to go on for an hour or more and the acid is then displaced from the pan by running water on to the upper layer continuously, so that the acid level falls and the acid finds its way out through the siphon. To minimise the heat of diluting the acid in contact with the nitrocotton, it is usual to cool the displacement water, to 4° C for guncotton or to 20° C for other varieties. The acid-free nitrocotton removed from the pan, is ready for stabilisation. As a consequence of the downward travel of a layer of hot diluted acid, the fibres nitrated by the displacement process are slightly denitrated on the surface and on account of this show appreciable difference from other nitrocottons in their behaviour to gelatinising agents. Table I summarises the conditions found suitable for the large scale production of the principal explosive types made from linters cotton.

TABLE I

Conditions of Nitration of Linters Cotton to Explosives Nitrocelluloses

Nitrocotton	N %	S %	R	t ° C	Time min	Acid	
						% HNO ₃	% H ₂ O
<u>Mechanical Nitration</u>							
<u>High nitrogen guncotton</u>	13.4	< 10	71.5	20-22	30	24	7
<u>'Pyro' nitrocotton</u>	12.45- 12.65	> 95	43	36-38	25	21	16.5
<u>Displacement Nitration</u>							
<u>Normal guncotton</u>	13.1	< 15	28	14-20	60	23.5	8
<u>Propulsive soluble N/C</u>	12.2	> 95	28	14-20	60	23.5	15
<u>Nitrating without stirring</u>							
<u>N/C for blasting explosives</u>	12-12.2	> 97	26	15	60	23.5	16

S = % soluble in Ether-Alcohol

R = weight ratio of mixed acid to cotton.

14.17. Stabilisation: Nitrocellulose retains after nitration certain impurities which render it liable to spontaneous decomposition, and cannot be washed out in water. These impurities are either small quantities of the nitrating acids or of cellulosic substances formed from them. Their amounts depend on the conditions of nitration. Stabilization therefore can be regarded as the completion of the nitration process.

From 1847, when a disastrous explosion took place at Faversham, where guncotton was being made under the original Schönbein patent, until about 1865 when Abel's classical researches had solved the problem, the removal of free and combined acid could not be accomplished, and the manufacture of nitrocotton in England was held back. Abel's solution was the process of long boiling in water, followed by pulping of the fibre, which is still the basis of stabilisation for all nitrocelluloses used for explosives⁵⁹. Of the many investigations published later, only those of Robertson⁶⁰ can now be regarded as important. He discovered that a preliminary acid boil of about twelve hours was effective in decomposing a cellulose compound which is in all probability an acid cellulose sulphate; alkaline treatment has a less useful effect. Other ideas were advocated: sulphonitric esters of cellulose, nitrous esters, nitric esters of hexoses or bioses, and nitrate esters of oxy- and hydrocellulose were supposed to be present, but none of these has been shown actually to exist in unstable nitrocellulose.

In modern practice all explosives nitrocelluloses are given a first boiling with acid water (about 1 per cent HNO_3) and are then boiled for various times with slightly alkaline water. Guncotton is the most difficult to treat. In proportion as the nitrogen content is reduced, stabilisation is easier to carry out. Although satisfactory methods of stabilising were worked out from 1865 onwards for all types of nitrocellulose, it is only recently that a systematic explanation of the data has been found possible as the result of work carried out on 'green' nitrocelluloses taken straight from the acid bath instead of on the stabilised samples with which former investigation was solely concerned⁶¹.

When acid-wet unpulped nitrocotton is washed in running water the acidity is reduced in a few hours to a figure which decreases only very slowly as the time is extended to 120 hours. In a series of such washed materials containing from 9.5 to 13.5 per cent of nitrogen, the total sulphate can be estimated, and the total free acidity determined by titration of the acetone solution. For the high nitrogen guncotton, total acidity stated as H_2SO_4 is the same in amount as the total sulphate; for the lower nitrogen-materials the total acidity is about half the sulphate; for the intermediate members of the series the ratio of the two varies with the nitrogen content, tending to unity as the guncotton composition is approached. Assuming that none of the acid given up to the acetone solution is nitric acid, the results can be explained only by the hypotheses that guncotton contains free sulphuric acid and hardly any other impurity, whereas the less nitrated products contain an acid ester $\text{R}.\text{SO}_3\text{H}$, the free acidity of which is one half of its total acid value. Guncotton, for instance is found in this way to hold 0.69 per cent of free sulphuric acid and practically no acid ester; a nitro-cotton of 10.2 per cent has no free acid but 0.52 per cent of acid ester. The amount of retained sulphuric acid of either kind varies in the same sense as the sulphuric acid fraction of the bath. From guncottons made in nitrating baths of low sulphuric (and consequently of high nitric) acid content, the included sulphuric acid is more readily removed and a short boil is sufficient. But if no sulphuric acid at all is used, simple washing is not quite effective. There appears to be present in such highly nitrated products a cellulose oxidation product that can be removed only by alkali and the prevalent method is appropriate. On the other hand, the first acid boil which is necessary to stabilise the less nitrated products would appear, on these grounds, unnecessary for gun-cotton, though it is always used.

In view of the fact, which has been well established, that sulphuric acid does not penetrate the ordered regions of the cellulose structure during the nitration process⁶², some explanation is needed of the presence of acid cellulose sulphate and occluded sulphuric acid. The ester is easily accounted for by the entry of the mixed acid as a whole to the intermicellar regions and

its reaction with exposed hydroxyl groups. For the sulphuric acid in guncotton, explanation is less easy. It has been suggested that the acid finds its way into parts of the structure which are expanded by the swelling action of the nitrating acid and that when the swollen product is washed with water, these elements of structure contract, and trap the sulphuric acid molecule between the nitrated chains. Nitric acid enclosed in the same way can be washed out entirely with water, but the sulphate ion, because of its bulk and tetrahedral configuration (in contrast to the nitrate ion, which is planar), remains enclosed.

STRUCTURE OF FIBROUS NITROCELLULOSE

14.18. Microscopic and optical characters of fibrous nitrocellulose: The observation of nitrocellulose fibres under the microscope, especially when the mineralogists' technique of using polarised light is employed, contributes to a certain extent to our knowledge of the molecular arrangement in the fibre but is of more importance as an aid to following the process of gelatinisation. In practically all explosives containing it the nitrocellulose exists to some extent as ungelatinised or semi-gelatinised fibre. The methods of physical chemistry appropriate to homogeneous systems cannot be used, and microscopical means are the most productive and the most readily applied.

The general microscopic characters of fibrous nitrocellulose are in general those of the original cellulose: if swelling has taken place during nitration the original features may even be enhanced. It is not difficult, for instance, to perceive the double set of spirals on the surface of some nitrated cottons and the bordered pits on coniferous woodpulp fibre are often readily seen. This likeness of nitrocellulose to the parent substance is obvious only in ordinary light; if polarised light is used the appearances are very different. The strong double refraction (positive in regard to the fibre-direction) and the brilliant colours of the first and second order which distinguish cellulose give place, to an extent depending on the degree of nitration, to much weaker double refraction and much feebler hues. In the technically useful range of 10 to 13 per cent nitrogen these hues are an indication, although not a very certain one, of the degree of nitration, and are useful in distinguishing one nitrocotton from another in a mixture of the two.

In a comprehensive paper of 1914 Ambronn⁶³ gave a full description of the observation made by him and others up to that year. His own contribution a principal and fundamental one, had been the discovery that the effect of nitration was eventually to reverse the positive optical character of cellulose. For low degrees of nitration the double refraction was positive in regard to length, as in cellulose, but as the nitrogen was increased this positive refraction decreased and became zero at 11.8 per cent of nitrogen, the fibre becoming isotropic and showing no colour in polarised light. At higher nitrogens the double refraction reappeared but was negative and increasingly so with rising nitrogen. The change can be detected quite easily with the usual device of a quartz wedge or selente plate on which the direction of slower light-vibration has been marked parallel to the long edge. Inserted along the fibre axis, the wedge raises the polarisation colour in the Newton scale for a positively refractive fibre, and lowers it for a negative one. Ramie gives the clearest evidence of change, but it is unmistakable for cotton also, despite the spiral structure. Some caution is necessary in making such observations because the colours vary with the refractive index and penetrative power of the immersion liquid. Phenol is an extreme instance; in it the negative refraction of nitrocellulose is reversed. These relations are not wholly clear. To some extent the Wiener effect, by which a double refraction originates from the parallel collocation of rod like elements surrounded by a liquid of different refractive index, even when these elements are isotropic, is responsible, but this explanation is insufficient and it is probable that an additional cause is to be found in change of crystal structure consequent on more or less penetration by the liquid.

If a representative series of nitrocottons of normal manufacture is examined in glycerine, which is free from any tendency to penetrate or swell, or in alcohol slightly diluted with water, it is seen that there are three main classes distinguished by polarisation colour⁶⁴. The less nitrated fibres

(nitrogen <11 per cent) appear steel-grey; with nitrogen between 11.4 and 11.8 per cent they are yellow to brownish-yellow, and blue with more than 11.8 per cent. The reversal of the double refraction is observed at 11.8 per cent. It is a curious fact that gradation between one nitrocotton and another of different nitrogen occurs by change in the proportion of fibres of one or other colour-class rather than by change in the colours themselves. Most nitrocottons are therefore mixtures of the three classes, although guncotton and those of 11.6 - 11.7 per cent nitrogen seem to be homogeneous. It is significant that so many specimens, nitrated under uniform conditions, should each seem to comprise more than one species. There are two reasons that may be given for this: the condition of nitration may be so irregular that identical fibres may be nitrated to different degrees (this probably applies to the products of the displacement process); or individual fibres may differ in structure, and show different optical behaviour although nitrated equally. Both reasons may be valid, the first most frequently.

This method of observation has been modified with advantage by dissolving in the immersion medium a dye that the nitrocotton adsorbs⁶⁵. Crystal violet (base) has been found suitable. By this means it is possible to follow the onset of gelatinisation, by dissolving the dye in the gelatiniser. In the absence of the dye the fibre usually becomes invisible between crossed nichol prisms as soon as it is markedly swollen. Using a mixture of 80 per cent of nitroglycerine with 20 per cent of glycol dinitrate containing 0.02 per cent of the dye, the reversal of optical sign was noticed at 11.9 per cent of nitrogen and the colours observed before appreciable swelling of the fibre had taken place were more vivid than without the dye. With nitrogen less than 11.4 per cent they were light red to grey, with 11.5 to 11.3 per cent, yellow, brown or red, and with higher nitrogen than this pale blue to grey. The dyed fibres showed no dichroism.

14.19. Molecular structure of fibrous nitrocellulose: Nitrated cellulose fibres yield only one definite X-ray diagram, that of the trinitrate. It is quite characteristic (with certain small spacing-variations dependent on nitrogen content, when 11.8 per cent or more of nitrogen is present) if the nitration process has been such that the parallelism of molecular chains has not been impaired. In the main the parallel arrangement persists in all the nitrocelluloses that are of technical use, and also in those which are too feebly nitrated to be soluble. Only in the products of nitrating acids in or near to the swelling band of Figure 6 does the arrangement seem to break down nearly entirely, but all the diagrams, with the one exception of the trinitrate, show only few spots and are diffuse.

The progressive replacement of hydroxyl by nitrate groups has more than once been investigated by X-ray methods^{66,68}. In the first investigation⁶⁶, of which the results have been confirmed by later work, nitrations of ramie were made with mixed acids of $H_2SO_4:HNO_3$ ratio 1:1, that is with compositions on a line intersecting the swelling band Figure 6 almost normally in its central part. The observed structures can be divided into three classes according to the situations in the swelling area of the acid compositions in which they are made.

1. Those containing less than 7.5 per cent nitrogen, showing unimpaired fibre character and no X-ray diffractions indicating nitration, but only the spots from mercerised cellulose.
2. Those containing more than 7.5 and less than 10.5 per cent nitrogen - materials all more or less disintegrated and yielding very diffuse diffractions apparently due in part to very small crystal elements of mercerised cellulose, and
3. The most important - those of more than 10.5 per cent nitrogen, giving diagrams, the definition of which improves as the nitrogen content increases until finally, when a critical point at 12.8 per cent is passed, a definite diagram, characteristic of cellulose trinitrate, makes its appearance.