

The development of Dynamite. From Braconnot to Nobel

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Resumen

Henry Braconnot (1780-1855), Théophile-Jules Pelouze (1807-1867) y Ascanio Sobrero (1812-1888) son las figuras centrales en el descubrimiento de la naturaleza explosiva y las propiedades de los productos de la reacción de las mezclas de ácido nítrico y ácido sulfúrico con carbohidratos (azúcares, almidones, celulosa y lignina) y polialcoholes, en el corto periodo de 1833 a 1850. Sus descubrimientos permitieron a Alfred Bernhard Nobel (1833-1896) transformar la información acerca de un producto de manejo peligroso en una realidad industrial e iniciar así la industria moderna de los explosivos. En este artículo se describe el desarrollo histórico del conocimiento científico hasta su cristalización en la dinamita de nuestros días.

Abstract

Henry Braconnot (1780-1855), Théophile-Jules Pelouze (1807-1867), and Ascanio Sobrero (1812-1888) are the central figures in discovering the explosive nature and properties of the reaction products of mixtures of nitric and sulfuric acids with carbohydrates (sugars, starches, cellulose, lignin) and polyalcohols, within the short period of 1833-1850. Their findings allowed Alfred Bernhard Nobel (1833-1896) to transform the knowledge about a product dangerous to handle, into industrial reality and thus initiate the modern industry of explosives. Here we describe the historical development of the scientific knowledge until its crystallization into dynamite.

That nitric acid reacted with organic compounds was long known before the work of Pelouze and Sobrero, though knowledge on the subject was somewhat limited, particularly on the difference between nitration and esterification. John Woulfe (1727-1803) had synthesized picric acid in 1771 by reacting indigo with nitric acid and observed that the product tinted

silk greenish yellow. The new dye was unsuccessful due to its poor light fastness, but it was still used to turn indigo to bright green and to dye silk and wool yellow. The explosive characteristics of the acid were discovered later; experiments with it were conducted in 1885 in Lydd, England, and the British adopted it as an explosive material, which they called *Lyddite*.

Giovanni Gioberti (1761-1834) had observed the strong explosion that sometimes took place when reacting nitric acid with ethanol. Others had prepared nitric derivatives of organic compounds, noting in many cases a powerful oxidation process. There was much uncertainty regarding the composition of the products obtained.

The breakthrough came in 1833 when Henry Braconnot (1780-1855), professor of botany at the University of Nancy, reported about the remarkable product obtained treating starch or ligneous materials with concentrated nitric acid (Braconnot, 1833). According to Braconnot, it was known that diluted nitric acid dissolved potato starch producing a mucilaginous liquid, very soluble in water. A completely different result was obtained when using concentrated acid. Treating the starch with several times its weight of nitric acid also yielded a mucilaginous liquid, totally transparent, but which water coagulated completely into a white casein-like mass. The solid was white, pulverulent and insipid, did not change the color of litmus, but changed the color of iodine tincture to yellow. Treated with concentrated sulfuric acid it yielded a colorless solution, which was not precipitated by water, it only became sticky. An interesting result was that the solid dissolved easily in warm acetic acid; a small amount of acid yielded a thick mucilage, from which water precipitated a varnish-like substance. This substance could be applied to paper and other materials producing a brilliant coating, much nicer than those produced by the best kind of gum or resin. Applied to fabrics it rendered them impervious, even when immersed in boiling water. The composition of the resulting product, as well as the details of its preparation, was poorly understood. Similar results were obtained when using lignin, resins, cotton and linen, different sugars, and pectin. Braconnot called the new material *xyloïdine* (nitrocellulose) to point out that it de-

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rived from wood. Although he recognized that xyloïdine caught fire easily, he did not realize its extreme detonating properties. He also attempted to make coatings, films, and shaped articles from it after finding that the nitrated derivative dissolved easily in wood vinegar.

In 1838 Pelouze took to study this substance and found that submerging paper, cotton, or linen tissues in cold concentrated nitric acid, produced a parchment that was extremely combustible (Pelouze, 1838). Pelouze expected that his detailed experiments and findings would clarify the questions left answered by Braconnot's results. His procedure was as follows: Reacting a mixture of starch and nitric acid of a density of 1.5 (about 90% weight acid) for some minutes resulted in the complete disappearance of the starch, with no disengagement of gas; the resulting liquid retained the yellowish tint characteristic of concentrated nitric acid. The ensuing solution was immediately treated with water and xyloïdine separated completely. Filtration of the liquid, followed by evaporation, left a very small amount of solid residue. If instead of precipitating the product with water, the reaction liquid was left in a closed vase, it slowly acquired the various tints of a mixture of nitric acid and nitrogen dioxide. Water now precipitated xyloïdine in decreasing amounts and the process ended in about two days. Xyloïdine had been destroyed completely and transformed into a new acid, which after evaporation had become a white non-crystalline deliquescent solid, weighing much more than the original starch. According to Pelouze, xyloïdine was starch in which one atom of water had been replaced by one atom of nitric acid. All of the starch was converted, explaining the increase in weight observed. An excess of nitric acid converted xyloïdine into a very soluble substance (the acid mentioned above), a result quite different from that of Braconnot, who had obtained from a given weight of starch the same weight of xyloïdine.

Additional findings were as follows: If instead of leaving the mixture of starch and concentrated nitric acid to react at ambient temperature, it was immediately brought to its boiling point, starch decomposed in a few minutes and became a deliquescent acid, easily obtained pure and in large quantities by evaporation in a water bath. Moderate heating converted it into another acid, black colored, soluble in water, and able to regenerate under the addition of nitric acid the white acid from which it originated. Concen-

trated boiling nitric acid attacked it with difficulty while cold acid transformed it slowly into oxalic acid, without disengagement of carbon dioxide. Thus, by slow oxidation, caused by the presence of an adequate quantity of concentrated acid, starch converted successively into xyloïdine, deliquescent acid, and oxalic acid, without carbon participating in the displacement of other elements from the materials. In this reaction starch plays the role of a base; the resulting xyloïdine is highly combustible, it catches fire at a temperature of about 180°C, burning energetically and without leaving a residue. This property led Pelouze to believe that xyloïdine might find use in artillery.

These discoveries would not have called attention had it not been by the sensational news published in 1846 in journals all over the world, that the Swiss chemist Christian Friedrich Schönbein (1799-1868, discoverer of ozone) had announced at the meeting of the Naturforschende Gesellschaft held in Basel on March 11, 1846, that he had succeeded in converting cotton into a powder more powerful than gunpowder. In his statement, Schönbein did not provide information regarding the manufacturing process.¹ As was to be found shortly thereafter, Schönbein had improved the process by immersing the cotton in a mixture of nitric and sulfuric acid and then washing the product to remove the excess acid. The news caught the immediate attention not only of chemists, but also of political and military circles. Chemists immediately related Schönbein's discovery to the findings of Braconnot and Pelouze.

This piece of news may well be considered the catalyst that precipitated the intense research in the area of nitration of organic compounds that eventually led to dynamite. The years 1846 and 1847 saw the publication of a very large number of papers and letters to the editor, particularly in *Comptes Rendus*, regarding the products obtained by the reaction of nitric acid with a variety of substances: sugars, cellulose materials, polyalcohols, etc.

The first publication was a letter addressed by Schönbein to Jean-Baptiste André Dumas (1800-

¹ The story goes that Schönbein had discovered guncotton by accident. He occasionally experimented at home in the kitchen; one day in 1845, after his wife had gone out of the house, he had spilled a mixture of nitric acid and sulfuric acid. After using his wife's cotton apron to mop it up, he hung the apron over the stove to dry, only to find it spontaneously ignited and

1884), permanent secretary of the Académie des Sciences, informing him that he had discovered a rather easy procedure for transforming ordinary cotton into a material having all the properties of gunpowder (Schönbein, 1846). The explosive power of the new material was clearly superior to gunpowder, as shown by the experiences that Schönbein had done in the mines of Cornouailles and at Bâle with cannons and mortars. One pound of explosive cotton produced the same effects as two to four pounds of common gunpowder. Contrary to ordinary gunpowder that exploded into thick smoke, fouling the cannon and small arms and obscuring the battle field, guncotton, well prepared, did not leave a residue, did not produce fumes, and its fabrication, besides being very cheap, did not involve dangers of explosion. Schönbein believed that by virtue of these properties the new material would find wide use in pyrotechnics and, particularly, in artillery shells.

The reading of the letter was accompanied by the remark made by César Despretz (1791-1863) that he believed that the cessation of flammability of the new powder under a weak compression, made it unsuitable for firearms.

Schönbein's letter was followed by a note from Dumas (Dumas, 1846a) stating that although the information about cotton powder was very vague, it should be taken seriously and related to the work done previously by Braconnot and Pelouze. Dumas reported that Friedrich Julius Otto (1809-1870) in Brunswick had confirmed Schönbein's findings: Cotton treated for a few minutes with concentrated nitric acid, followed by washing until all the acidity had disappeared, and drying, did produce a highly explosive material. The washing stage was the critical one because it was very difficult to get rid of the last traces of acid. After drying, these traces released nitric oxide and if the product was lit over a porcelain plate it also generated acid vapors. The promptness of the combustion of a ball of explosive cotton on a porcelain plate was the best sign of the quality of the product: Touching the ball with red-hot carbon it glowed like gunpowder, but without leaving a residue, if fired slowly and left cinders, then the preparation was inadequate for use in firearms. It could well be said that the best product was the one that was difficult to distinguish from pure cotton. According to Otto a well-prepared product had some remarkable properties: It was explosive at a very high temperature; bullets of a pocket pistol, having 1/3-inch diameter and charged with 1.25 to 1.5 grains

of this cotton, were capable of penetrating strong 1-inch thick plates.

Dumas' note ended with a recipe provided by Knopp, a préparateur at the University of Leipzig, for the preparation of gunpowder. The important news in this recipe was the use of a mixture of nitric and sulfuric acids, instead of nitric acid alone, for preparing cotton powder.

Pelouze promptly reacted to the news by publishing a short historical note in which he recalled the work done by Braconnot and himself and his earlier experiments on the possible detonating properties of xyloïdine. This note was published in the pages immediately following Dumas' note (Pelouze, 1846a). According to Pelouze, Schönbein had revealed neither the nature nor the method of preparation of cotton powder, but from the properties assigned to it, it seemed to correspond to xyloïdine. On the basis of this assumption, Pelouze wanted to set the historical record straight. Pelouze recalled that in 1838 he had found that instead of preparing xyloïdine from cellulose, it was simpler and more economical to impregnate paper, cotton, and hemp with concentrated nitric acid (Pelouze, 1838). The resulting material caught fire at about 180°C and burned with great energy without leaving a residue. Pelouze acknowledged that he had mentioned the possible use of xyloïdine in weapons, but not as a replacement for gunpowder. The credit for this possible application was clearly Schönbein's. He added that he had tested the possible use of xyloïdine by putting 0.1 g of it in a handgun and firing a shot against a 2-cm thick plate located 25 meters away. The plate had been pierced while the bullet flattened strongly against a wall. At his request, Prélat, the armourier, had tested the material in different weapons and concluded that the nitrated paper can replace common gunpowder without loss in efficacy and marksmanship.

Pelouze's paper ends with some remarks made by Guillaume Piobert (1793-1871) and Arthur Jules Morin (1795-1880) that the artillery people who had studied the substance claimed that contrary to what had been said, cotton powder did leave a residue of water and carbon in the weapon and its combustion did not develop enough heat (about 400°C). In addition, in several opportunities ignition of the powder in a cannon did not produce enough gas to propel the shell and the volume of the weakest charges used was, in general, considerable and exceeded the one convenient to use in firearms. After many tests done at the Central Arsenal, it had been possible to de-

velop products substantially more flammable and more combustible than the ones reported by others. Thus cotton powder prepared by immersing cotton in a mixture of equal volumes of concentrated sulfuric and nitric acids would detonate at 175°C. An important disadvantage was that in several opportunities dry cotton powder had caught fire spontaneously at about 100°C. The information available at the moment did not seem to guarantee the replacement of gunpowder by the new material.

In a following short note (Pelouze, 1846b) Pelouze remarked that Prélat claimed that xyloïdine either as guncotton or flammable paper had an explosive power four times that of common gunpowder and that Francisco Flores Domonte and Louis Menard (1822-1901) had found that xyloïdine prepared as described by Braconnot, was very soluble in ether and intended to use this property to determine the purity of the compound.

In a following publication (Pelouze, 1846c) Pelouze claimed that the material prepared by Braconnot was different from his: Xyloïdine was the product that water precipitated from a nitric solution of starch while Pelouze's product (which he called *pyroxiline*) was the result of the *action* of nitric acid on cotton. Xyloïdine was highly flammable and detonated by shock and when distilled in a retort left a considerable residue of carbon; on the other hand, pyroxilin detonated violently when heated to 175-180°C and was impossible to distill.

Pelouze took samples of cotton and paper having negligible amounts of cinder, dried them at 120°C, and then treated them with nitric acid and a mixture of equal volumes of concentrated nitric and sulfuric acids. A remarkable characteristic of the reaction was the rapidity with which it took place in spite of the insolubility of the cellulose; it simply occurred by impregnation. Admitting that nitrated cellulose was the sole product of the reaction, calculations indicated that it must result from the combination of two equivalents of nitric acid with one equivalent of cellulose, minus one equivalent of water and corresponding to the overall formula $C_{12}H_{11}O_{12}N_2$. From the properties and analysis of both materials it was clear that when the amylaceous and the ligneous substances lost their solid state and dissolved in concentrated nitric acid, one at room temperature and the other at a higher temperature, the products resulting from the action of water on the solutions were different from the ones originating from the simple impregnation of cellulose.

The presence of sulfuric acid had two advantages, first it concentrated the nitric acid by withdrawing part of its water, and second, its price was substantially lower than that of nitric acid, diminishing substantially the loss of the latter. In the impregnation process a substantial amount of nitric acid adhered to the solid material and was lost in the washing process. Using a mixture of the two acids reduced the loss significantly and, in addition, sulfuric acid retained the nitrous vapors that were usually part of concentrated nitric acid, making the operation less unpleasant.

Pelouze closed his paper with the interesting historical observation that Schönbein had indicated the ballistic properties of gunpowder but kept secret the fabrication procedure; eight years before him Pelouze had prepared cotton powder but did not recognize its explosive properties, and Braconnot, five years before Pelouze had discovered xyloïdine, without understanding its potential.

In an additional short notice (Pelouze, 1846d) Pelouze noticed that the introduction of percussion cap ammunitions based on mercury fulminant had led to a sizable development of the weapons industry. Unfortunately, use of this chemical had converted the ammunition industry into a most dangerous and polluting one. He expected that replacement of mercuric fulminant by nitrocellulose would result in a much safer and clean process since it was already known that cotton powder compressed with a few grains of common gunpowder yielded substantially improved percussion caps. Addition of common gunpowder led to the complete combustion of pyroxilin and the resulting inflammation was easily communicated to the complete charge.

In another letter from Schönbein (Dumas, 1846b), this time to Paulin Louyet and reported by Dumas, he insisted that his cotton powder was different from the one prepared by Pelouze and others: "allow me to say first that my cotton powder is not, as some French chemists and M. Pelouze believe, the substance they call xyloïdine. I add that my method of preparing this explosive substance is different from the one used by M. Pelouze to prepare his paper powder..."

After reading these lines, Dumas added his own ideas on the subject. Although cotton powder had yet to be analyzed, he had executed the analysis safely using the apparatus developed by Gay-Lussac and Thénard for the analysis of organic substances. Heating the combustion tube with an alcohol lamp

to about 200°-300°C, the balls of gunpowder burned lively, without the least danger, and produced water vapor, carbon dioxide, carbon monoxide, and large quantities of NO and NO₂. The raw gas contained very flammable products as shown by the fact that it burned in contact with a candle. From these results Dumas believed that if the explosion of cotton powder inside weapons produced these gases, then the weapons would not resist it and would oxidize promptly. Nevertheless, if the detonation took place in a small confined space and in a given period of time, it might generate other products because the gases would probably react between them. That is, it could well be that the use of cotton powder in firearms may not have the inconveniences that could originate from the acid products of its explosion in a free space. In the case of detonation caps the formation of NO₂ seemed unavoidable. Cotton powder damped with an aqueous solution of potassium nitrate and then dried, would generate a smaller amount of NO₂ and probably be more valuable. Cotton powder impregnated with potassium chlorate resulted in a fulminating product superior to cotton powder alone. Forty to fifty milligrams were enough for firing a pocket pistol and its effects did not damage the weapon.

Pelouze replied to the above comments (Pelouze, 1846e) saying that the problems raised by Dumas were easily avoided using cotton of the proper quality and taking care of the proper preparation of pyroxylin.

P. J. Vanderckroff found that cold sulfuric acid dissolved both pyroxylin and ordinary cotton (Vanderckroff, 1846). The two solutions behaved differently upon heating, the cotton one became strongly colored immediately while that of pyroxylin first generated a large amount of gas and became colored only after a long time. This simple procedure could then be used to distinguish between both materials. Pelouze added (Pelouze, 1847) that Richier had found that pyroxylin was soluble in methyl and ethyl acetates and that this property allowed a more exact chemical analysis, and that he believed that its correct empirical formula was C₂₄H₁₇O₁₇·5NO₅. This formula explained why this explosive did not leave a solid residue on burning because it burned completely into gases and water vapor.

A letter to Pelouze from J. E. de Vrij (de Vrij, 1847), professor of chemistry at Rotterdam, reported that starch treated with concentrated nitric acid swelled and became xyloïdine, but treated with a

mixture of equal volumes of nitric and sulfuric acids it did not swell but became pyroxylin, having the same properties as the product prepared from cotton. Four grains of pyroxylin charged into a pistol produced the same results as six grains of gunpowder. Adding concentrated sulfuric acid under agitation precipitated the pyroxylin completely as white flakes, without appreciable loss of weight and with all the original properties, except for their shape. De Vrij suggested to Pelouze that this flocculent form might find use in the manufacture of percussion caps. Adding to the nitric solution water instead of sulfuric acid precipitated bitter tasting flakes, which were soluble in alcohol and in a large amount of water, burned well in contact with a flame or upon heating, but at a slower rate than pyroxylin, and left a carbon residue. Another interesting finding was that acetone transformed instantly pyroxylin into a transparent gel that coagulated by addition of water into white flakes looking very much like cotton. Addition of large amounts of acetone resulted in the complete solution of pyroxylin. Pyroxylin was dissolved by caustic soda, while the cotton, which had been used for this preparation was not attacked. Water or acids did not precipitate the resulting solution. Concentrated sulfuric acid dissolved pyroxylin at room temperature without coloration. Addition of concentrated sulfuric acid to a nitric solution of cotton precipitated pyroxylin. Concentrated acetic acid dissolved xyloïdine prepared from cotton, but not pyroxylin. The acetic solution of xyloïdine prepared from starch was precipitated by water in the form of a powder, while that prepared from starch did it as a powder. For this reason de Vrij doubted that both had the same composition.

Anselme Payen (1795-1871) (Payen, 1847) recommended that in order to prepare pyroxylin with the highest combustible properties, it was necessary to use cellulose free of ligneous incrustations and purified of all the mineral, fatty materials, and nitrogenous materials, etc., that usually accompany vegetable matter. The nitric and sulfuric acids should be free of nitrous oxide because this gas impaired the quality of the product. At his request Morin had performed ballistic experiments of nitric cotton prepared either with a pure acid mixture or loaded with nitrogen monoxide, and found that the explosive product made with the pure acids sent the cannon ball 355.5 m away while the second mixture failed to expel the ball from the cannon.

In a closing note to this paper Pelouze reported

that Flores Domonte and Ménard had reacted fuming nitric acid with mannite (mannitol) and different kinds of sugars and gums, and obtained nitric derivatives similar to the ones obtained with starch and lignin.

It was Pelouze's last remark, which caused Sobrero to react. In a letter to Pelouze (Sobrero, 1847a) he mentioned that he had read his notice about the achievement of Flores Domonte and Ménard and although he was not aware how far have these two chemists had gone on the subject, he wanted to make it clear that "the idea of producing fulminant bodies by means of sugar and similar compounds has been realized by me a long time ago using cane sugar and dextrin; I have communicated a Note on these compounds to the Academy of Turin last January 31. I add that I have already analyzed fulminant sugar and although I have been unable to avoid the formation of nitrogen oxides during the combustion, the results that I have obtained thus far lead me to believe that this compound will be formed of sugar $C_{12}H_{11}O_{11}$ less two equivalents of water and plus two equivalents of nitric acid. The compound has furnished 3% of hydrogen and 27% carbon."

According to Sobrero, the composition of glycerin could no longer be represented by carbon and water and its combination with fatty acids indicated that it behaved like a base. Being somewhat analogue to sugar and lignin it could be assumed to react in a similar manner as these substances. So far, his results proved that glycerin reacted with a mixture of sulfuric and nitric acids to give a compound similar to fulminant cotton. Mixing glycerin with two volumes of sulfuric acid of 66°Bé and one volume of nitric acid of 43°Bé produced a very vigorous oxidation reaction. If the mixture of the two acids was kept in a refrigeration mixture and the glycerin added slowly to avoid an increase in temperature, it dissolved completely without apparent reaction. If the mixture was now added to water, an oily material heavier-than-water settled at the bottom. This oily layer was separated and washed with a large amount of water to eliminate completely the acids, without loss because it was insoluble in water. The washed material could be dissolved completely in alcohol and re-precipitated with water or it could be dissolved in ether and left to evaporate naturally. Complete drying was achieved by keeping the material under sulfuric acid for several days.

The dry material looked like olive oil slightly colored yellow. It was substantially heavier than

water and totally insoluble in it. It dissolved easily in alcohol and ether; it was odorless, tasted sweet, piquant and aromatic. Sobrero added another observation which would later prove to have tremendous medical importance: "This examination (taste) must be done carefully because it is enough to put a small amount (which can be taken by slightly moisturing the end of the little finger) on the tongue to experiment a strong headache during several hours. This action on the human body has been confirmed by several persons in my laboratory and I have tried it myself several times until I was sure it did not have toxic properties."

In a following publication (Sobrero, 1847b) Sobrero communicated to the Académie des Science about another very strong fulminant compound, nitromannite, prepared by the reaction between nitric acid and mannite, and having the composition reported by Flores Domonte and Ménard. In this paper, and a following one (Sobrero, 1847c), Sobrero gave a detailed description of his method of preparing nitromannite. Nitromannite detonated under a hammer blow with the same violence as mercury fulminant and its decomposition generated enough heat necessary to ignite the gunpowder in a rifle. Sobrero replaced the mercury fulminant in percussion caps by his new compound and found these new caps to fire as good as ordinary ones. A clear advantage for the substitution was that nitromannite was easier to fabricate than mercury fulminant and did not expose the workers to the serious dangers present when fabricating fulminant powder. In addition, Sobrero believed that fulminant mannite was cheaper to manufacture because mannitol was not expensive and its manufacture left a non-crystallizable residue mixed with a little of mannite, which could be used in medicine and veterinary as a purgative. In addition, the conversion of mannite to nitric mannite resulted in a substantial increase in weight (from 100 to 225).

In later publications on the subject (Sobrero, 1849, 1869) Sobrero added more information about the properties of nitromannite. The material seemed to decompose completely into carbon dioxide, nitrogen, and water, left no residue and could be stored indefinitely without decomposition. Contrary to other nitro organic products, nitromannite was obtained easily in crystalline form, very fragile and easily converted into powder. Humidified with an appropriate liquid it could be worked into a paste or granulated. The dry powder did not absorb humidity

from the air. Later experiments had shown that amorphous and crystalline nitromannite decomposed in the presence of diffuse light. With direct light the decomposition was very fast, releasing nitric vapor, water, etc. These facts made the use of nitromannite in war weapons questionable because it might decompose and make the weapon inefficient for attack or defense.

Sobrero's main contribution to the development of modern explosives was initially described in a paper read before the Academy of Sciences of Turin (Sobrero, 1847c), in which he gave a very detailed description of the manufacture of nitroglycerine by reacting glycerin with a mixture of nitric and sulfuric acids. Interesting enough, in spite of being aware of the dangers of self-detonation of the product, he kept a 300-gram sample, which much later he donated to the Academy. Sobrero's face was badly scarred as a result of an explosion in the 1840s.

The details of the discovery and fabrication process of nitroglycerine were repeated in papers published in 1848 and 1850 (Sobrero, 1848, 1850), together with a description of additional properties of nitroglycerine: "Pyroglycerin has a density of 1.60, it is odorless and slightly colored yellow, and the color seems to originate from foreign matter present in the glycerin and can be eliminated with great difficulty. It has a sweet and agreeable taste and presents toxic properties. It stains paper like oil, remains liquid at 20°C, it is insoluble in water and very soluble in alcohol and ether, and is precipitated by water from the alcoholic solution. It is not volatile and stands a temperature of 100°C. A drop of it heated slowly over a platinum plate seems to decompose generating nitrous vapors. At a higher temperature the decomposition is fast with deflagration and flame, leaving a small carbonaceous residue. A small amount heated fast to the decomposition temperature, decomposes violently. A small drop of a few decigrams can produce a detonation similar to the firing of a rifle. The glass of the vessel in which this experiment is performed will break if it is not strong enough". Pyroglycerin exerts a toxic action on animal physiology: "It is enough to put a small drop on the tongue and spit it immediately, to experience a strong headache for many hours. Four or five centigrams introduced in the stomach will kill a sucking pig. This toxic property has been observed with a mouse and a capybara (a small rodent from Brazil). Pyroglycerin acts as an oxidant on phosphorus, copper, and potassium. It dissolves in a hot aqueous

solution of potassium hydroxides and becomes brown. With hydrogen chloride it yields chlorine and a kind of aqua regia. The physiological properties of pyroglycerin are very interesting and require a careful study; they may lead to useful applications."

In a later communication to the Academy of Turin, read on 1869 (Sobrero, 1869), Sobrero recapitulated the history of the product and insisted that he had not discovered it while staying at Pelouze's laboratory but during his tenure at the Scuola di Meccanica e di Chimica Applicata alle Artes in Turin: "hence, nitroglycerine is the fruit of Italian work exclusively..." In this conference, Sobrero expressed his regrets at having discovered nitroglycerine: "...When I think of all the victims killed during nitroglycerine explosions, and the terrible havoc that has been wreaked, which in all probability will continue to occur in the future, I am almost ashamed to admit to be its discoverer."

The development of dynamite

According to Dumas (Dumas, 1870) initially gunpowder (a committee appointed by the French War Ministry in 1846 changed the name pyroxylin to guncotton) was celebrated in excess, criticized extensively, and discarded with indifference. A French-British mixed commission was assigned to test the new material in the Bréa Island. The plan was to compare the effect produced by an underwater explosion of gunpowder and cotton powder on the granite rocks. The gunpowder powder explosion hardly damaged the rocks while that of cotton powder caused the disappearance of a huge rock and reduced it to pieces. Not only that, the explosion threw a very large number of deep-dwelling fish to the surface of the sea, either dead or stunned. This surprising result was also used as a proof that the mortality of fish that accompanied maritime volcano eruptions was not necessarily due to the heating of the water or to the release of poisonous gases; it could very well be caused by the brusque movement of masses of water.

The armies did not see a menace in the fast explosion of cotton powder that pulverized granite. Artillerymen would classify cotton powder in the category of smashing powders, which should be kept away from the arsenals. Ordinary powders were different in the sense that powder cannon could catch fire while being prepared as a result of an accidental shock; experience indicated that they did not inflame spontaneously in the storage room. Once prepared,

the only dangers associated with gunpowder were the ones resulting from its mishandling. The situation with cotton powder was different, it could be prepared rather safely but its storage presented a safety risk. Not only that, degraded cotton powder lost its explosive power and converted largely into sugary material. After fourteen years, about one-half of the samples exposed to air and humidity would decompose without detonating. Thus cotton powder remained what it was from the very beginning, a material appropriate for mining more than for military uses.

In 1864, Pelouze and Maurey, one of the gunpowder commissars, reported on the use of guncotton as a war agent (Pelouze and Maurey, 1864). This paper was an extensive critical report on the new procedures developed by the Austrian general Lenk for fabricating and using guncotton. After Schönbein's discovery, the French Army had organized the large-scale manufacture of the new product at the explosives factory in Bouchet. Between 1847 and 1848 this establishment had provided about 5000 kg of the product for the many experiments done in France to substitute by guncotton the gunpowder used in mines and fire arms. Similarly, the Austrian Army had established large manufacturing facilities at Hirtenberg, under the direction of Lenk, but until 1862 their process remained a mystery, no foreigner having been admitted to the factory.

In France, two main objections had been raised against the substitution, one based on the fragility effect that the new powder imparted to the walls of weapons, and the other related to the accidents of decomposition and spontaneous explosions that had been observed in France and aboard. A strong explosion at the Austrian factory in 1862 had led to a substantial reduction of the manufacture, until Lenk had introduced some alleged improvements in the process. Although Lenk did not contest the possible exothermic reactions that could lead to the inflammation of guncotton, he believed that taking appropriate measures during the preparation process could prevent them.

The Lenk procedure was based on the same chemical reactions as the ones used at the Bouchet arsenal. The Austrian and French guncottons were a compound resulting from the immersion of cotton in a mixture of nitric and sulfuric acids. The proportions of these two acids could be varied in a wide range without modifying the quality of the product. According to Lenk, the method used at Bouchet,

where 200 g of cotton were reacted with 2 liters of acid mixture, did not yield the same product as the Austrian one, which used a substantially larger volume of acids and special equipment for mixing the reagents. Another modification introduced by Lenk was the use of soluble glass of 12°Bé to block the cotton fibers by precipitation of silicate. This action retarded the development of gases and eliminated the traces of acid they might contain.

The French researchers analyzed all the information available from Austria and compared guncotton prepared by the two methods. Their final result was that both products (Lenk's and Bouchet's), were basically the same, except for the 2% of silicate present in the Austrian product. Both had essentially the same centesimal analysis, both exploded at about 100°C; their heating to 55, 60, and 80°C caused identical decompositions, and they also had the same ballistic properties.

Nitroglycerine was the first, and is still one of the most widely produced nitrate esters. It is used in dynamites produced by absorbing nitroglycerine in fine wood meal or other powdered absorbent. This process prevents the formation of micro bubbles and stabilizes the liquid. The nitroglycerine is also thickened or gelatinized by the addition of a small percentage of nitrocellulose, a process which assists in preventing "weeping" (exuding) or settling out of the absorbent material. Because settling does occur, boxes of stored non-gelled dynamites are turned over at regular intervals to reverse the settling flow.

As will be detailed below, Alfred Nobel, another of Pelouze's students, took the knowledge back to the Nobel family's defunct armaments factory and began experimenting with the materiel around 1860; it did, indeed, prove to be very difficult to discover how to handle it safely. Throughout the 1860s Nobel received several patents around the world for mixtures, devices and manufacturing methods based on the explosive power of nitroglycerine, eventually leading to the invention of dynamite.

The development of nitroglycerine as an explosive (Bellamy and De Modica, 1988)

To Sobrero goes the credit of having discovered nitroglycerine, to Alfred Nobel and his family, of transforming it into an industrial commodity. Immanuel Nobel (1801-1872), Alfred's father, was a well-known building constructor, who during his stay in Russia became interested in explosives. In 1859 he sent his 17-year old son Alfred to Paris to

further his scientific education at Pelouze's laboratory. During this stay Alfred became acquainted with Sobrero and his discoveries and on his return to Sweden the Nobel family initiated experiments on ways of taming nitroglycerine for use in mining and quarrying. They duplicated Sobrero's methods until they were able to produce nitroglycerine in kilogram amounts. Their major problem was how to get nitroglycerine to detonate properly; sometimes it would explode without releasing all the available energy, sometimes, it would merely burn. Eventually, Alfred Nobel was able to develop a new type of detonator, which solved the problem. The detonator was placed in contact with the explosive and set off by means of a fuse passing through the wooden stopper.

After solving the problem of controlled detonation, the next obstacle was how to transport nitroglycerine without risk. Nobel's initial solution to the problem was to mix the nitroglycerine with 15-20% of methyl alcohol to give a liquid much less sensitive to mechanical shock, which could be transported relatively problem-free. The alcoholic solution was packed in hermetically sealed cans to prevent the evaporation of the solvent and sent to any distance and in any climate without the risk of explosion. At the job site the nitroglycerine was recovered by adding water to the solution. The process was still dangerous because any spilled alcohol-nitroglycerine mixture rapidly lost its methyl alcohol by evaporation leaving a dangerous coating of the explosive on the ground. George M. Mowbray developed another alternative in the USA taking advantage that nitroglycerine freezes at about 13°C, can be kept frozen by packing in ice, and in the solid state it is relatively insensitive to mechanical shock. The frozen explosive was subsequently thawed before use. Mowbray was able to manufacture and sell about 500 tons of nitroglycerine to mining and engineering firms, before closing his plant because of patent difficulties.

Despite all efforts to transport and use nitroglycerine in the safest possible way, accidents continued to occur and led some countries to either completely ban its use or severely restrict its transport. On September 3, 1864, an explosion occurred in Nobel's laboratory, which was situated in his home, on the outskirts of Stockholm. Five people were killed, including 21-year old Emil Nobel, Alfred's youngest brother. As a result of this accident the city of Stockholm enforced laws that experiments with explosives could not be made within the city limits of Stockholm. Nobel therefore temporarily contin-

ued production on a barge anchored in Lake Malaren to the west of Stockholm.

Nobel began now searching for a porous material, which would absorb nitroglycerine without diminishing its explosive capacity. Of the many materials tested (porous silica, paper, paper pulp, wood waste, brick dust, coal, dry clay, etc.), kieselguhr (a porous diatomaceous earth) turned out to be the most appropriate. It was chemically inert and would easily absorb up to three times its weight of nitroglycerine; the resulting putty-like substance could be shaped into sticks ready for the user to put straight into the borehole, and while it was sensitive to shock, a blasting cap could still detonate it. Nobel named the new product *dynamite* (from Greek *dynamis* = power) and patented it in Great Britain (1867) and the United States (1868). Dynamite established Nobel's fame worldwide and was soon put to use in blasting tunnels, cutting canals, and building railways and roads.

Although Nobel's kieselguhr dynamite removed most of the problems associated with the use of pure nitroglycerine, it was not quite the perfect solution: 25% of this composite dynamite was non-explosive, that is, the explosive effect was correspondingly less than that of pure nitroglycerine. Before very long, two groups of dynamites were being developed: (a) dynamites with an inert absorbent, e.g., kieselguhr dynamite and, (b) dynamites with an active absorbent,

The usual active absorbents are substances such as sodium, potassium, and ammonium nitrate, chlorates, and black powder, but they may also be a non-explosive material under ordinary conditions, for example, sawdust, sugar, and coal, which in the presence of a powerful explosive like nitroglycerine contributes to the energy release by converting to products like CO₂ and H₂O.

Nobel continued to experiment in search of better compositions and in 1875 he invented a more powerful form of dynamite, *blasting gelatin*, which he patented the following year. Blasting gelatin is a gel-like mixture of nitrocellulose with nitroglycerine having a consistency depending upon the amount of nitrocellulose dissolved in the nitroglycerine. Unlike many other dynamites, it does not absorb water and is almost unaffected by immersion in water. It also resists freezing better than the other dynamites. In 1887 Nobel introduced *ballistite*, one of the first nitroglycerine smokeless powders and a precursor of cordite. The original ballistite, as developed by No-

bel, contained 10% camphor and equal parts nitroglycerine and collodion. The camphor reacted with any acidic products of the chemical breakdown of the two explosives, but did tend to evaporate over time leaving a potentially unstable mixture. Nobel's patent specified that the nitrocellulose should be "of the well-known soluble kind".

Nowadays, ballistite is a double-base powder used as a rocket propellant. It is composed of two explosive substances, nitrocellulose and nitroglycerine, blended together with diphenylamine, which acts as a stabilizer. It burns with a considerable amount of flash and smoke, and generates a great volume of gas. Ballistite burns progressively, but at a rate dependent upon the composition and physical characteristics of the powder grain, the temperature of the powder grain before ignition, and the pressure during reaction.

By 1896 there were 93 Nobel factories in the world with an annual production capacity of 66,500 tons.

The physiological influence of nitroglycerine (Rossettani and Cervasel, 1988; Marsh and Marsh, 2000)

Angina pectoris is a term for chest pain due to the heart not getting enough oxygen. William Heberden (1710-1801), a British physician, explained it for the first time in 1768 in a paper presented to the College of Physicians of London. Heberden described both typical exertional angina as well as variant angina, which eventually affected a patient only when he was in bed and was relieved by sitting-up. In the late 1700s several English physicians correlated the angina suffered by living patients with the obstruction of heart blood vessels found in post mortems of the same patients. Despite this early insight, many leading physicians through much of the following century blamed the chest pain on indigestion and treated angina with soda or chalk to relieve stomach acidity.

One significant fact is that it was in Nobel's dynamite factories in the late 1860s that the antianginal effect of nitroglycerine was discovered. Two interesting observations were made. First, factory workers on Monday mornings often complained of headaches that disappeared over the weekends. Second, factory workers suffering from angina pectoris or heart failure often experienced relief from chest pain during the workweek, but which recurred on weekends. Both effects were attributed to the vasodilator action of nitroglycerine, which quickly became

apparent to the physicians and physiologists in local communities. Another significant fact is that Nobel himself suffered from angina pectoris and refused to take nitroglycerine, in spite of his doctor's advice.

Sobrero's headache caused the immediate involvement of Constantin Hering (1800-1880), professor at the Hahnemann Medical School in Philadelphia. Hering promptly repeated the observation in healthy volunteers and in 1849 reported "there is nothing known which in such small quantities and with such precision causes headache. Every substance with certain effect ought also to be considered as important to the physician" (Hering, 1849). Nitroglycerine was renamed *glonine* by Hering and became an ideal candidate for inclusion in the growing set of homeopathic remedies. Interest in glonine by the regular medical profession was limited, probably because of their skepticism of the whole homeopathic dogma.

The first British physician to experiment with nitroglycerine in 1858 was Alfred Field using it in a 68-year-old woman with intense chest pain. Another British physician, Thomas Lauder Brunton (1844-1916), introduced the first drug against angina, amyl nitrite, in 1867. Until then, only brandy and ether had been able to provide relief. The story goes that Brunton saw a medical friend use amyl nitrite to decrease blood pressure in animals and thought it might be useful with angina. Eventually he added ether, ammonia and chloroform as possible palliatives. Patients treated with chloroform stopped reporting pain temporarily but resumed when they had recovered from the "partial stupefaction" induced by the chloroform." In 1876, Brunton reported that nitroglycerine, which had a similar action to amyl nitrite, gave him 'such an awful headache' that he hesitated giving it to patients.

In 1878, William Murrell, a London physician, after trying nitroglycerine on an angina patient and observing the widely differing times of relief provided by amyl nitrite and nitroglycerine ("a few seconds' compared with nearly an hour") decided to use it more widely in the summer of that year. He recognized that the drug dilated blood vessels and reduced the workload on the heart, allowing a more effective treatment of patients with angina. After one week, "there had been a very great improvement" and "a dose of medicine taken during an attack would cut it short."

Within four years, nitroglycerine was acclaimed as the "...remedy par excellence for angina pectoris"

and the *Boston Medical and Surgical Journal* declared that it was “inhuman to allow a patient to endure the agonizing pain and sense of impending death which render angina pectoris so dire, when we can offer a form of relief in the majority of cases, nearly instantaneous.”

Thus, by the end of the 19th century, thirty-three years after its discovery by Sobrero, nitroglycerine was established as a treatment for the relief of angina pain. However, discovery of the mechanism of action was to wait for another 80 years.

Angina pectoris is usually a symptom of a condition called myocardial ischemia, occurring when the heart muscle does not get as much blood and oxygen as it needs. Although the heart may get enough blood for daily activities, the arteries may not be able to supply enough oxygen at high-demand times such as during exercise (even just walking), stress, or extreme temperatures. Nitroglycerine is used to treat the symptoms of chest pain or angina. Depending on the dosage and how it is taken, it may help prevent attacks of chest pain or relieve an attack that is occurring. It does this by increasing blood flow to the heart and by reducing the heart's workload. The principal action of nitroglycerine is vasodilatation, that is, widening of the blood vessels.

Nitrates dilate veins, arteries, and coronary arteries by relaxing vascular smooth muscle. They produce these effects by entering vascular smooth muscle cells where they are metabolized to 1,2-glyceryl dinitrate and nitrite, via mitochondrial aldehyde dehydrogenase, and then nitric oxide and S-nitrosothiols. A recent paper by Chen *et al.* (Chen *et al.*, 2002) describes in detail the role of mitochondrial aldehyde dehydrogenase, which specifically generates 1,2-glyceryl dinitrate from nitroglycerine, in the bioactivation of nitroglycerine to bring forth vasorelaxation and in the development of tolerance to the drug. ▣

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