

Ascanio Sobrero

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RESUMEN. Ascanio Sobrero (1812–1888), inicialmente educado como médico, fue uno de los más consumados químicos Italianos de su época. Se le recuerda en forma especial por haber descubierto la nitroglicerina, su poder explosivo y su uso como vaso dilatante. Alfred Nobel transformaría la nitroglicerina en dinamita y daría nacimiento a la industria moderna de los explosivos. Sobrero realizó importantes investigaciones sobre los productos obtenidos por destilación de resinas y aceites esenciales; como resultado de una de ellas, descubrió el hidrato de pirrolo (sobrerol), que sigue siendo usado hoy en día para el tratamiento de afecciones bronquiales.

ABSTRACT. Ascanio Sobrero (1812–1888), initially educated as a physician, was one of the most accomplished Italian chemists of his time. He is particularly remembered for having discovered nitroglycerin, its explosive characteristics, and its use as a vasodilant. Alfred Nobel would transform nitroglycerin into dynamite and give birth to the modern explosives industry. Sobrero did some important research on the products obtained by distillation of resins and essential oils; as a result of these he discovered pyrrole hydrate (sobrerol) that continues to be used today to treat bronchial diseases.

LIFE AND CAREER¹

Ascanio Sobrero (Fig. 1) was born on October 12, 1812 in Casale Monferrato, Alessandria, the third child of Giuseppe Gaetano Sobrero (1781-1873) and Giuseppina Demichelis (1794-1878). His father was a physician who taught at the Liceo Imperiale Napoleonico in the city. Giuseppe Gaetano was an important public person in the metropolis, serving a vicesinaco of Cavallermaggiore and had been elected Cavaliere dell'Ordine Mauriziano. The other children were Lorenzo (1807-1865) whom became a judge; Felicita; and Candido (1812-1890), Ascanio's twin brother, who became a general and served as member of the city council of Cavallermaggiore.

At that time, Casale Monferrato was the most important city of the Piedmont. With the conquest of Italy by Napoleon, Collegio Trevisio,



Fig. 1. Ascanio Sobrero (1812 - 1888).

the religious school of the city, was closed and in 1805 Napoleon ordered the transfer of the school at Alessandria to Casale Monferrato to be reopened under the name Liceo Imperiale Napoleonico. Following

the demonstrations and signs of discontent of the people at Alessandria Napoleon answered "*le rivalità tra città e città, triste seguito dell'estrema divisione dello stato, devono cessare* (the rivalry between cities, a sad consequence of the extreme division of the state, must stop). Together with the Lyceum arrived also the Courts of Justice and the Commerce Chamber. All these actions resulted in a tremendous impetus to the development of the city.

After the establishment of the Napoleonic regime, the Sobrero family moved from Murello, where it had been living for several generations, to Cavallermaggiore. Giuseppe Gaetano took a position as teacher at the Liceo and started teaching mathematics, physics, and philosophy to the fifth and sixth class. The Liceo, who was under the double academic supervision of the University of Paris and the *Università Imperiale de Genova*, was closed in 1814 after the defeat of Napoleon and substituted by the Reale Collegio di Educazione, as a state institution. The new curriculum, lasting seven years, included courses on surgery, chemistry, surveying, notary, philosophy, algebra, arithmetic, practical courses, and preparatory courses for entrance to the *Regia Università di Torino*.

Ascanio and his twin brother initiated their studies in this new school where Ascanio's abilities were promptly discovered, as illustrated by his record: "*giovane di molte speranze, ingegno eccelente e grandissimo studio*" (a young man of promising future, most talented and studious). Before the end of his

studies, his father was appointed Secretary of the *Regia Università di Torino* and the family moved to Turin, the capital city of the Savoyan kingdom and home of the Government, the Senate, the Chamber of Deputies, the different Ministries, and the *Accademia delle Scienze*.

After passing the University entrance examinations, Ascanio entered the school of medicine and in 1832 received his medical degree and the following year the degree in surgery and the right to exercise medicine. Ascanio was interested in following a teaching career and in 1835 he took the examination for obtaining the degree of *dottore aggregato all'Università* (adjunct). For this purpose he prepared a thesis written in Latin, about the nervous system in general and, in particular, the function and pathological characteristics of the neuritis in relation to human anatomy.² Political intrigues caused him to be classified as *non-idoneo* (unsuitable). The resulting disappointment led him to abandon the practice of medicine and devote himself to the study of chemistry. Politics led medicine to lose a practicing physician and chemistry to acquire a future brilliant scientist.

To fulfill his aspirations Sobrero began working as an assistant in the laboratory of general chemistry, directed by Vittorio Michelotti (1774-1842), and in the laboratory of pharmaceutical chemistry, directed by Giuseppe Lavini. He stayed for four years in this position and then, under the advice of his uncle, Baron General Carlo Raffaele Sobrero (1791-1878; graduate of the *École Polytechnique*, Paris; Member of the *Accademia delle Scienze di Torino*), he decided to continue his training in Paris, to where he moved in the fall of 1840. He was then 28 years old.

At that time his uncle was the general director of the Chemical Laboratory of the Arsenal in Torino, and also of the Real Fonderia (the cannon foundry of the arsenal). The war needs of the country had made the arsenal one of the centers of chemical activity in the Piedmont area, performing research in the manufacture of gunpowder and metallurgy applied to the manufacture of cannons. The uncle, during

his career and studies, had become acquainted with the most famous European chemists, particularly Jöns Jacob Berzelius (1779-1848) in Sweden and Théophile-Jules Pelouze (1807-1867) in France. Later on, his uncle would play an important role in Ascanio's development of nitroglycerin.

His uncle provided him with a letter of recommendation to Pelouze. Ascanio was not so much interested in obtaining a degree but in enlarging his training as much as possible. Hence he sat in the lectures given by Jean-Baptiste Dumas (1800-1884), Jean Darcet (1725-1801), Anselme Payen (1795-1871), Antoine-Jerôme Balard (1802-1876), César Despretz (1791-1863), Jean Louis Prevost (1790-1850), and others. Eventually, in 1841, Pelouze, a brilliant experimentalist who at that time was particularly interested on the action of nitric acid on organic substances, took him as his assistant, a relation, which in due course would lead Sobrero to discover nitroglycerin.

Sobrero's initial research activities were related to the distillation of several resins and essential oils and led to his first scientific publications.³⁻⁵ While at Pelouze's laboratory, Sobrero befriended Charles-Louis Barreswil (1817-1870) and together they wrote a 535-page book about analytical techniques on qualitative and quantitative chemical analysis.⁶ The authors dedicated their book to their mentor Pelouze.

Sobrero remained in Pelouze's laboratory for 31 months and on April 1843 he moved to Giessen, Germany, to pursue his studies in the new school of chemistry established by Justus von Liebig (1803-1883). He stayed with Liebig for six months and among other activities he completed a very important piece of research about pyroguaiac acid (today: *o*-hydroxyanisole; guaiacol; pyrocatechol monomethyl ether; catechol monomethyl ether; 1-hydroxy-2-methoxybenzene; methyl catechol) obtained by the dry distillation of resin of guaiac (Note 1) started in Paris with Pelouze.⁷ Guaiacol has been used since the middle of the eighteenth century as an expectorant, antiseptic, and local anesthetic.

After three years of absence from Italy, Sobrero returned to Torino where Lavini engaged him as *applicato alla chimica generale*. One of his first activities was the translation from German to Italian of Remigio Fresenius' (1818-1897) book *Guida all'Analisi Chimica Quantitativa*.⁸

In 1845 he was appointed to the chair of chemistry at the *Scuola di Meccanica e di Chimica Applicata alle Artes*, created by the Royal Chamber of Agriculture and Commerce to promote the Piedmont industry. In 1848 he was appointed Professor (*Professore Applicato*) of General Chemistry at the University of Turin and Professor (*Professore Effettivo*) of Chemistry Applied to the Manufactures.

Between 1850 and 1852 Sobrero collaborated with Francesco Selmi (1817-1881; one of the founders of colloid chemistry), describing in 1850 the preparation of lead tetrachloride. In 1859 a new law of Public Instruction divided the engineering scholastic program in two stages, the first of theoretical and propedeutic character, attached to the University of Turin, and the second, more practical, to the *Scuola di Applicazione per gli Ingegneri*, located at the Palazzo Valentino, which would become the nucleus of today's Torino's Politecnico. In 1860 Sobrero was appointed in this school to the newly created chair of *Chimica Docimastica* and served in this position until 1882. In 1877 the Municipality of Torino created the *Scuola Cavour* for the teaching of chemistry, which was organized by Sobrero who also served as its first President.

In 1844 Sobrero became member of the *Accademia delle Scienze de Torino* and eventually he was elected its Adjunct Secretary and then Permanent Secretary. He was a member of the *Accademia de Agricoltura* and President of the same in 1851. Other positions were *Consigliere Comunale and Assessore all'Igiene*; member of the *Commissioni per la Pubblica Esposizione dei Prodotti dell'Industria Nazionali* (1844); member of the committee of the Universal Exposition in London (1851), and President of the *Commissione delle Industrie Chimiche*

Note 1. Guaiac is a clinical reagent reacts with iron in blood and is commonly used for the fecal occult blood test, a noninvasive test that detects the presence of hidden (occult) blood in the stool. Hidden blood in stool is often the first, and in many cases the only warning sign that a person has colorectal disease, including colon cancer.

for the *Esposizione Nazionale di Torino* (1884). He was awarded many honors from Italian and foreign scientific Societies, among them, the cross of Merito Civile.

Ascanio married Ottavia Botteri and after her death in 1864, Giulia Routin. Three daughters and one son were born out of these marriages; unfortunately two of the daughters, Maria (1858-1867) and Candida Felicita (1857-1868) and the son (1854) died at a young age. The only survivor was the third daughter, Apollonia.

Ascanio Sobrero passed away in Torino on May 26, 1888 at the age of 76 and was buried in the family mausoleum (*Cavalier Giuseppe Sobrero e discendenti*) in *Cavaller-maggiore*. He suffered from heart and circulatory disorders.

SCIENTIFIC CONTRIBUTION

Sobrero published 28 scientific papers and several books in the areas of his expertise.⁹⁻¹² Most of his papers were related to the study or resins, essential oils, and the products of their distillation and the nitration of organic materials in general, and polyalcohols and sugars in particular.

Resins, essential oils, and their distillation products

This research activity was a natural result of Sobrero's activities during his stay with Pelouze, a well-known expert in the field.

It was known that the partial combustion of birch (*Betula alba*) bark yields a liquid tar rich in pyrogenic (fever inducers) oily products. This tar does not lose its fluidity even when cooled considerably and for this reason it is employed in Russia for lubricating the axles of vehicles and waterproofing roofs. Upon distillation the tar yields a brown oily liquid, highly fragrant, lighter than water, and having a strong acid reaction. Sobrero's first research papers^{3,4} were related to investigating the latter material.

First, the raw oil was distilled and the different fractions collected. At above 100 °C a light yellow clear liquid was obtained, having a pleasant smell reminding that of turpentine and birch. At higher temperature the distillates became denser, smelling like empyreumatic oils and their color became more and more intense as the distillation progressed.

The first fraction contained a yellow hydrocarbonic oil of acidic

nature, similar to turpentine and mixed with other products, which could not be eliminated by simple distillation. Its components were separated by repeatedly washing with aqueous potassium hydroxide to eliminate the acid substances, followed by distillation at temperatures above 100 °C, additional washings with aqueous lime, and several distillations in the presence of carbon dioxide. The final middle fraction collected was considered to be a material sufficiently pure to allow studying its properties. It is a colorless liquid smelling like turpentine and birch bark, having a specific weight of 0.847 at 20 °C and boiling at about 156 °C. The oil was found to be soluble in alcohol and ether, slightly soluble in water and to dissolve resins. Cooled to about -17 °C it became cloudy and precipitated a white solid substance probably analogue to the stearoptene (the solid crystalline component of a volatile oil) of turpentine corresponding to the formula $C_{20}H_{32}$, the same as that of the volatile oil of turpentine. Its vapor has a density of 4.7686 g/cm³ at 21 °C and 760 mmHg. The similarity of this oil with that of turpentine essence suggested the same uses as for the latter.

The oil was reacted with boiling dilute nitric acid without releasing nitrous vapors. After a long reaction time it turned into a resinous substance soluble in alcohol and ether; the alcoholic solution deposited a yellow-green substance that did not seem to be crystalline. The remaining solution retained another substance of rose color. Both substances combined with bases and seemed to form resins.

The reaction of diluted nitric acid with the volatile oil of birch produces a green oil, which can be distilled. The color is unstable that disappears at 100 °C and at the same time a flocculent resinous material precipitates that releases a little of nitrogen. During the initial distillation a large amount of hydrogen cyanide develops and remains in the alembic.

Sobrero also studied the reaction of other volatile oils and natural resins with nitric acid, for example, lemon, lavender, bigarade (Spanish bitter orange), ginger, aspic, clove, chamomile, pine resin, mastic, copal, galbanum, and colophon, and, interesting enough, he found that all of these materials also released hydrogen cyanide.

In 1843 John Dalpiaz communicated to the *Société de Pharmacie* that hydrogen cyanide was also produced during the preparation of methyl nitrate.¹³ Gustave Adolphe Chatin (1813-1901) and Bernard Derosne (1783-1855), the referees of the paper, added the comment that the acid was also produced during the reaction of nitric acid with fats. These results, coupled with Sobrero's own, and that the production of hydrogen cyanide is usually accompanied by the production of ammonia, led him to study of the reaction of nitric acid with organic substances that do not contain nitrogen.¹⁴ Sobrero's experiments led to the following additional information: (a) during the preparation of methyl nitrate by Liebig's method, if a stream of NO₂ is bubbled through the liquid, it is possible to detect in the alcohol the presence of ammonia and HCN. It is also possible to detect these two compounds in the distilled water used to keep the ester under it for several days at 15 to 21 °C; (b) decomposing the ester inside a porcelain tube full with pumice stone at high temperature, leads to the formation of both compounds; their relative proportion varies with the temperature of the process; if the pumice stone is replaced by platinum sponge, less HCN is produced with a larger amount of ammonia; if the pumice stone is replaced by carbon, very little HCN is produced together with substantial amounts of ammonia; (c) passing a current of NO₂ mixed with ethyl ether through a porcelain tube heated to white, there is production of HCN and ammonia; NO produces the same results; (d) mixtures of NO₂ and vapors of turpentine decompose in the same manner, and finally, (e) every time that sugar, a resin, or a fat oil are oxidized with nitric acid, the distillation products contain HCN and ammonia is found in the residue in the flask.

In another paper Sobrero reported on the acid product obtained by the thermal distillation of the guaiaic resin (*guaiaicum officinale*), which he named *pyroguaiac acid*.⁷ The dry distillation of the guaiaic resin gave as volatile products water and an oily substance composed of a neutral oil, lighter than water, and a denser acid oil, which were easily separated by distillation, the neutral oil passing over first. The second fraction, containing the acid oil, started boiling over at 210 °C.

The acid was purified by further distillation in a current of carbon dioxide and found to be heavier than water, having a strong smell similar to that of guaic resin burned over incandescent carbon. It has a spicy peppery taste, similar to that of clove. It is soluble in alcohol and ether and slightly soluble in water. It has a density of 1.119 at 22 °C and boils at 210 °C. It oxidizes easily in air, initially it becomes red and finally opaque. It dissolves in a caustic solution but does not decompose alkaline carbonates. An alcohol solution of pyroguaiac acid reduces gold and silver and reduces cupric and ferric salts to a lower degree of oxidation. Nitric acid reacts violently with the acid yielding oxalic acid. Chlorine reacts with the acid disengaging a large amount of hydrogen chloride and forming a crystalline product that melts easily, sublimes at a high temperature and also crystallizes as long white needles. An alcoholic solution of the acid precipitates an aqueous solution of tribasic lead acetate. The resulting salt is amorphous, flaky, white, and curds promptly like silver chloride. It melts at 100 °C, becoming transparent and fragile like a resin; it dissolves in alcohol from where it is precipitated by evaporation or addition of water.

Sobrero analyzed the acid obtained by simple distillation and from its lead salt; both gave the same empirical formula $C_{15}H_9O_4$.

The publication of this paper led to a sharp response from Henry Sainte-Claire Deville (1818-1881).¹⁵ According to Deville, he and Pierre-Joseph Pelletier (1788-1842) had investigated the same question but in more detail, and to them belonged the priority of the findings. He was surprised that Sobrero was not aware of Deville's findings, part of which had been published in his medical thesis, presented to the *Faculté de Médecine* de Paris on June 28, 1843 (*Recherches Théoriques et Expérimentales Sur les Essences et les Résines*). According to Deville, the products obtained by distillation of guaic were more numerous than those reported by Sobrero and consisted of (a) a light colorless oil of composition $C_{20}H_{16}O_2$ representing four volumes of vapor, boiling at 118 °C, with density of 0.874, and having a pleasant bitter almond odor. This oil oxidizes in contact with air and becomes a solid crystallizing in beautiful lamina; (b) a solid substance crystallizing in

pearly pallets that volatilizes without composition, containing 76.95 % carbon, 7.46 % hydrogen, and 15.59 % oxygen, and melting at about 180 °C. This substance was not mentioned by Sobrero; (c) the oily substance that Sobrero named pyroguaiac acid, is a remarkable heavy oil capable, like creosote, of reacting with caustic potassium, metallic oxides, etc. According to Deville Sobrero's pyroguaiac acid was no more an acid than creosote, and (d) empyreumatic products of particular nature.

In his answer to Deville Sobrero¹⁶ indicated that he had begun to study the distillation of the guaiac resin the last month of June while working with Liebig at Giessen and that his literature search had not indicated that the subject had already been tackled by others. He apologized for the mistake and remarked that he expected Deville's not to think that he wanted to encroach on his rights.

The unusual aspect of this usual dispute about the priority rights to a discovery is that it involved two former physicians, which had abandoned their practice to follow a career in chemistry.

Another of Sobrero's work in the field of essential oils was related to the volatile oil of turpentine and led to the discovery of an important new chemical.¹⁷ Sobrero found that the volatile oil of wet turpentine rapidly absorbed oxygen under the influence of light and deposited a crystalline material whose composition could not be represented by any of the formulas attributed to the known hydrates of turpentine. The crystals are prismatic needles, which grow as the process continues until they achieve a length of about one centimeter. They were purified by dissolution in alcohol, crystallization by evaporation, and repeated recrystallizations from alcohol and water. The purified crystals are odorless, soluble in alcohol, ether, and water, and decomposed when dissolved in boiling water slightly acidified with sulfuric acid, yielding a volatile product of spicy odor recalling that of camphor and turpentine. Sobrero reported that the composition of the hydrate corresponded to the empirical formula $C_{20}H_{16}O_2 \cdot 2H_2O$.

Sobrero also studied the action of pure oxygen on the essence of turpentine in the presence of solar light of light,¹⁷ noting the precipitation of pyrrole hydrate, $C_{10}H_{18}O_2$.

Forty years later, William Jackson Pope (1870-1939) and Henry Edward Armstrong (1848-1937) studied this reaction in detail and recommended that the new material be named *sobrerol*, in honor of its discoverer.¹⁸ Sobrerol is widely used today as a bronchio dilatant and respiratory stimulant.

Sobrero also studied in some detail olivile, the fraction of the gum of the olive tree separated by ethanol.⁷ His findings indicated that the melting point of the compound depended on its being crystalline or amorphous. In the crystalline state it melts at 120 °C, assumes a resinous aspect, does not change its weight, and on cooling recovers its transparency but cracks without retaking the crystalline structure, its fusion point now becomes 70 °C. Dissolved in alcohol and recrystallized recovers its original melting point. Olivile can be present in anhydrous form or mono- and dihydrate. The anhydrous form is obtained by crystallizing it from anhydrous alcohol. Its equivalent formula is $C_{28}H_{18}O_{10}$. Olivile crystallized from water retains two moles of water and has a composition of $C_{28}H_{20}O_{12}$.

An interesting piece of research of Sobrero and Lavini is related to the separation of the active compounds in the secretion ejected by insects of the *Meloes* genus (oil beetles).¹⁹ The material possesses an epispastics characteristic (excites inflammation and vesication) of the same intensity as that of the cantharides (*litta vesicatoria*). The insects, pressed while alive, yield a viscous liqueur, which is then mixed with any fatty material to prepare an unguent employed as epispastics, particularly for veterinary uses. This preparation acts very violently on human beings and produces strong ulceration.

Lavini had begun in 1842 research trying to discover the epispastics substance that replaces in the meloes the cantharidin of the *litta vesicatoria*. He extracted the insects with alcohol and found that the alcoholic solution had the same epispastics property as that of the insects, and that by mixing it with a fatty material he could prepare a vesicant ointment useful for therapeutic uses.

In their work Lavini and Sobrero used a mixture of different species of the meloes of the Piedmont region. The insects were first dried, ground, and then dispersed in boiling water and the residue treated

successively with ether and alcohol. They searched for the vesicant principle in the portion soluble in water. Evaporation of an ethereal extraction of the aqueous portion produced white transparent prismatic crystals of a substance, which was found to be identical as cantharidin. The substance was insoluble in water, soluble in cold ether and less soluble in warm ether, soluble in concentrated alcohol, sulfuric and nitric acids, and in potassium hydroxide, insoluble in aqueous hydrogen chloride, and melted at 210 °C. Its elemental analysis indicated 61.17 % carbon, 6.30 % hydrogen, 32.53 % oxygen, the same composition as reported by Regnault for cantharidin.

Lavini and Sobrero established that the oily substances of the meloes do not possess epispastics properties and are very similar to the oily substances of the cantharides. It seems that the vesicant action of meloes is due to cantharidin, as manifested by the vesicles that appeared in their hands during the experiments.

INORGANIC CHEMISTRY

In addition to research in organic chemistry, Sobrero also did some work on inorganic reactions in collaboration with F. Selmi. A significant one was a study of the reaction of sulfur dioxide and hydrogen sulfide in distilled water.²⁰

Simultaneous addition of sulfur dioxide and hydrogen sulfide to distilled water results in their decomposition and deposition of sulfur; the liquid becomes strongly acid and yellow as a consequence of the dissolution of sulfur. Previous work by Heinrich Wilhelm Ferdinand Wackenroeder (1773-1798)²¹ had indicated that one of the products of the reaction is pentathionic acid. Wackenroeder's procedure consisted in first saturating the water with sulfur dioxide, then bubbling hydrogen sulfide through the solution, treating the solution first with barium carbonate and then with absolute alcohol to precipitate the salt. Sobrero and Selmi thought that it would be interesting to investigate if within the series of thionic acids, only the pentathionic one could form by this reaction. To do so, they modified Wackenroeder's procedure by bubbling both gases simultaneously through the water, during several days, in order to obtain a concentrated solution in which they could identify the acids

formed. Samples were taken at several hour periods and treated as indicated by Wackenroeder. If the only product were pentathionic acid, then the analysis would have given the same results but Sobrero and Selmi found very variable results. The resulting salts were actually a mixture of barium pentathionate and tetrathionate. In several runs they also found barium tetrapentathionate as well as sulfurous and sulfuric acids.

A particular finding was that if the precipitated sulfur was filtered and mixed with water, it divided finely and formed a very stable emulsion. Addition of a potassium salt, particularly sulfate, to this emulsion precipitated sulfur, which had lost its ability to emulsify and become pasty and elastic like natural rubber.

In another work, Sobrero and Selmi studied the action of chlorine on aqueous solutions of metal chlorides.²² It was known that an aqueous solution of manganese dichloride ($MnCl_2$) did not alter when treated with pure chlorine, but if treated with an aqueous solution of chlorine that had first exposed to solar light (and hence contained hydrogen chloride and hypochlorous acid, $HClO$), it decomposed and precipitated manganese dioxide. Based on this fact, Eugène Auguste Nicolas Millon (1812-1867) suggested using manganese dichloride as an excellent reagent for detect if water saturated with chlorine had been under the action of solar light, or what is the same, if it contained traces of hypochlorous acid. Sobrero and Selmi confirmed this discovery but found it limited to the case where the chlorinated water did not contain alkaline chlorides. If it did, it would then react with manganese dichloride, even when it had not been under the action of solar light. They also found that addition of a few drops of manganese dichloride to an aqueous solution of chlorine, potassium and sodium chloride led to the immediate precipitation of manganese dioxide.

According to Millon, lead dichloride is an excellent reagent for identifying hypochlorous acid because it immediately precipitates brown oxide. Based on their experiences with manganese dichloride, Sobrero and Selmi investigated the possibility that alkaline chlorides operate on lead chloride in the same manner, but they found totally different results. Bubbling chlorine

through a cold saturated solution of sodium chloride and containing a small amount of lead dichloride, resulted in the immediate formation of a yellow tint, quite different from that produced by chlorine when dissolved in water. At the same time, the solution was able to dissolve additional lead chloride and its yellow color became more intense. Eventually a point was reached where the dissolution of the dichloride and absorption of chlorine ceased altogether. The final solution is a remarkable product that has a very strong chlorine odor and is not affected by solar light. Exposed to air it loses chlorine and deposits lead dichloride. Added drop-by-drop to a large quantity of water causes precipitation of a brown oxide mixed with lead dichloride. Addition of caustic alkali precipitates lead dioxide while addition of potassium carbonate yields a brown precipitate, accompanied sometimes with release of carbon dioxide. The strong solution acts on metals with the same strength as aqua regia: It promptly attacks copper, zinc, iron, etc., converting them into their chlorides; it rapidly dissolves gold in thin lamina and powdered platinum; it substantially modifies organic substances, precipitating lead dichloride and generating oxidized or chlorinated products, and finally, it instantly destroys urea and oxalic acid.

Sobrero and Selmi also worked on the subject of mercury fulminate²³ and found that an alcoholic solution of mercuric chloride heated to 40 °C and treated with an alcoholic solution of potassium hydroxide, formed a yellow precipitate that was not mercuric oxide but a combination of mercury with carbon, hydrogen, and oxygen. The precipitate was amorphous, insoluble in water and alcohol, and could be purified by repeated washing with water to eliminate the excess of potassium hydroxide and potassium chloride. It was stable at room temperature and could be heated to about 200 °C without decomposition. At higher temperatures it became slight orange and then decomposed suddenly with a violent explosion, yielding only gases and no solid residue. Sobrero and Selmi found that carrying the operation under cold or without too much potassium hydroxide, the precipitates were less susceptible to detonate and left a residue of mercuric oxide. The precipitate became

rapidly black when exposed to light. When still humid and heated in a glass tube, it decomposed less violently and produced metallic mercury, water, and acetic acid. It was completely soluble in aqueous hydrogen chloride generating a piquant, irritant gas that produced in the throat a sensation similar to that of hydrogen cyanide. Sobrero and Selmi did not study the composition of this gas but reported that with silver chloride it produced a soluble precipitate, which crystallized in beautiful transparent crystals. The mercuric precipitate dissolved in sulfuric and nitric acids forming crystalline compounds. Preliminary analytical results indicated that the original precipitate contains mercury, oxygen, carbon, and hydrogen and that the latter elements are in a different ratio than in alcohol. The compound behaves as a strong base and combines with many acids.

Reacting mercury with nitric acid, followed by elimination of all the nitrous products by prolonged ebullition, and addition of alcohol in the same proportions used to prepare mercury fulminate, results in no immediate reaction as long as the procedure is performed below 100 °C. Heating the solution to a higher temperature leads to the immediate precipitation of a white crystalline compound, without generation of gases. The precipitate contains mercuric oxide, nitric acid, carbon, and hydrogen. Treated with hydrogen chloride results in the formation of volatile compound having the same odor as mentioned above.

Nitroglycerine and dynamite

The author gives now only a short description of the work of Sobrero on the preparation of nitrated organic material having an explosive nature. A more detailed story of the development of dynamite is given in another paper.²⁴

At the time of Sobrero's stay, Pelouze's laboratory was centered on the study of nitric reactions on organic substances such as starch, lignin, cotton, linen, hemp, resins, gums, etc. A determinant fact took place in 1846 when Friedrich Schönbein (1799-1868, discoverer of ozone) announced that nitration of cotton in the presence of sulfuric acid, produced an explosive product, fulmicotton.²⁵ Schönbein patented his procedure and then communicated his results to the *Académie des Sciences* in Paris. Sobrero was

aware that nitric acid reacted with glycerin oxidizing it to oxalic acid and had also experimented on the action of nitric acid upon the volatile oil from birch³ and other substances.^{14,26} Sobrero's experience in the area, stimulated by the discovery of Schönbein, led him to enlarge his investigation on the nitration of glycerin, this time using nitric acid mixed with sulfuric acid. These experiments led, by the end of 1846 and the beginning of 1847, to the synthesis of nitroglycerine and a series of other explosive products such as nitromannite, nitrosugar, and nitrolactin. Sobrero communicated these findings to Pelouze in a letter which was read to the *Académie des Sciences*²⁷ and which may be considered the birth of nitroglycerin. Sobrero's merit is not only having performed the synthesis of the product, but also having determined that the derivative was an ester and not a nitro derivative, and also its physiological effects. He wrote: "*Il faut toutefois être sur ses gardes en faisant cet essai, car il suffit d'en tenir une très-petite quantité (ce qu'on peut en prendre on y mouillant légèrement le bout du petit doigt) sur la langue pour en éprouver une migraine assez forte pendant plusieurs heures. Cette action sur le corps humain a été constatée par plusieurs personnes dans mon laboratoire, et je l'ai éprouvée plusieurs fois sur moi même avant que je fusse certain qu'elle a des propriétés toxiques*" (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's strong headache during several hours. This action on the human body has been confirmed by several persons in my laboratory and I have I have tried myself several times until I was sure it did not have toxic properties). This observation was taken over by several physicians over the world and by the end of the nineteenth century nitroglycerine was firmly established as a treatment for the relief of anginal pain.

Sobrero's first communication was followed with a note published in the *Memoirs of the Accademia delle Scienze di Torino*, in which he named the new product *piroglycerina* or *glicerina fulminante* and described it with much detail.^{14,28,29} His following publications on the same subject, reported slight modi-

fications of the chemical procedure.³⁰⁻³²

Alfred Nobel (1833-1896) recognized Sobrero as the discoverer of nitroglycerin. To Nobel goes the merit of having discovered the way to stabilize nitroglycerin and thus formulating the modern explosive powder, based on dynamite.³²

Alfred Nobel's link with Sobrero and nitroglycerine also originated from the work of Pelouze. In 1850 he embarked on an extensive tour of North American and Europe and the crucial turning point was his arrival at the Pelouze laboratory. This visit came about because one of Noble's teachers was the chemist Nikolay Zinin (1812-1880), who had also studied under Pelouze. Thus when Nobel arrived in Paris, he discovered that Sobrero had manufactured nitroglycerine four years early. Nobel immediately recognized the potential in this newly discovered chemical and returned to Stockholm he and his father began experimentation. In 1863 Nobel realized his first epoch-making invention, the Nobel patent detonator that allowed the controlled detonation of nitroglycerine.³³

A suitable closing remark is that years afterwards, Sobrero expressed regrets at the results of his discovery, in the following words: "...ripensando alle vittime che la nitroglycerin ha fatte colle sue esplosione, et di tremendi danni che ne derivarono e ne deriveranno ancora, quasi mi vergogno d'aver scritte queste parole di rivendicazione della suo scoperta... (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).³¹

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