RESEÑA BIOGRAFICA

Nicolas Leblanc. Chemical revolution and social injustice

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RESUMEN. El desarrollo del carbonato de sodio como parte de la industria química pesada está intimamente ligado con la revolución química que tuvo lugar en los siglos dieciocho y diecinueve. Fuertes razones políticas y económicas llevaron a la búsqueda de procedimientos sintéticos para reemplazar las fuentes natural de carbonatos que estaban disponibles desde el siglo diecisiete. In 1789 Leblanc desarrolló un proceso sintético usando sal común como material prima y puso a disposición de Francia y del mundo entero un descubrimiento de innegable utilidad. Fuertes acontecimientos políticos impidieron a Leblanc recibir una compensación adecuada; las generaciones siguientes fueron las grandes beneficiarias de su descubrimiento.

ABSTRACT. The development of sodium carbonate as a major commodity is intimately attached to the chemical revolution that took place in the eighteenth and nineteenth century. Strong political and economical reasons led to the search of synthetic procedures to replace the natural sources of soda that were available by the seventeenth century. In 1789 Nicolas Leblanc developed a synthetic process that used common salt as raw material and thus made available to France and the world a discovery of incontestable use; political events prevented him from receiving the right compensation; the following generations were the ones to benefit from his discovery.

LIFE AND CAREER[1-3]

Nicolas Leblanc was born on December 6, 1742, at *Ivoy-le-Pré*, a small town in the present district of Sancerrois, the son of Nicolas Leblanc and Marie Berthin. When his father, manager of a forge at the local iron works passed away in 1751 Nicolas was put under the guardianship of Dr. Bien, a good friend of the family living in Bourges. From him Leblanc absorbed an interest in medicine and when his guardian died in 1759 Nicolas, only seventeen, went to Paris to study medicine and surgery at the *École de Chirurgie*, together with many other young men, such as Claude-Louis Berthollet (1748-1822), Antoine-Laurent Lavoisier (1743-1794), and Louis Nicolas Vauquelin (1763-1829), who eventually would become famous for their discoveries in the area of chemistry. After his graduation as *maitre en chirurgie* (master of surgery) he practiced his profession for several years and in 1775 he married Marie-Françoise Charpentier; they had four children: Marie-Marguerite (1779-1839), Adèlaide-Rosalie (1783-1800), César-Nicolas (1787-1835), and Charles (1791-1812). The youngest son died during the retreat from Russian during the Napoleonic wars.

Leblanc's patrimony had been consumed by his schooling, and as his family responsibilities increased he needed a more regular income than was provided by the fees from his private patients. In 1780 he accepted the post as surgeon to the household of the *Duc d'Orléans* (1747-1793; the future *Philippe Égalité*); where he had as colleague, Berthollet, serving as physician to the Duc.[2]

By the middle of the seventeenth century new discoveries were making chemistry more and more popular and important. As a result it became very common for scientists to give private courses open to a fee-paying audience composed of interested students and general public. It is of interest to note that not only these courses were attended by men that would eventually become famous scientists [for example, Jean Darcet (1725-1801), Pierre-Joseph Macquer (1718-1784), Joseph Louis Proust (1754-1784), and Nicolas Desmarest (1725-1815)], these students would also, in due time, give their own private courses. One of this was Darcet, a medical doctor turned chemist and a graduate of the private courses given by Guillaume François Rouelle (1703-1770). About 1785 Leblanc started attending Darcet's courses and there he met and became friend with noted scientists such as Berthollet, Antoine-François Fourcroy (1750-1809), René Just Haüy (1743-1822), and Vauquelin.

The patronage of the Orléans family, which lasted until the duke was guillotined in November 1793, gave Leblanc the opportunity to do research; he turned to chemical experiments as a diversion. His funds were limited, so he chose a field that required little equipment and few chemicals. In March 1786, he sent the *Académie des Sciences* the first of a series of papers on crystal growth, *Essai sur Quelques Phénomènes Relatifs à la Cristallization*. His second

memoir, entitled *Observations sur l'Alun Cubique et sur le Vitriol de Cobalt*, was presented on May 16, 1787, and on May 3, 1788, he read to the *Académie* an additional *memoir* about the crystallization of different salts.

His *memoirs* about crystallization were so well received that on July 25, 1792 the reviewing committee formed by Louis Jean-Marie Daubenton (1716-1800), Balthazar-Georges Sage (1740-1824), and Berthollet, recommended "*que l'Académie doit inviter M. Leblanc à s'occuper de fournir une collection complète de tous les sels cristallisés; nous pensons, de plus d'être favorisée par des encouragements particuliers, que M. Leblanc y a déjà employé un temps considérable, et que la constance avec laquelle il a suivi son travail lui a fait faire des sacrifices auxquels son peu d'aisance ajoute un nouveaux prix. Enfin, il serait à désirer que la collection de M. Leblanc fût placée dans un lieu où ell pût servir à l'instruction de ceux qui cultivent l'histoire naturelle, et en particulier la cristallographie, et que l'auteur se hâtât de publier les différents mémoires qu'il a composés sur ce sujet pour diriger ceux qui souhaiteraient se livrer à la pratique d'un art neuf à beaucoup d'égards, intéressant pour le progrées de la chimie, et dont on pourra même tirer des lumières pour perfectionner la théorie de la cristallisation*" (that the Academy invite M. Leblanc to consider the preparation of a complete collection of all crystallized salts, and that the execution of this project be given special support because he has already spent considerable time on it and has made sacrifices, which his limited means render all the more valuable. It should be desirable to put M. Leblanc's collection in a place were it might served for the instruction of those who are studying natural history, particularly crystallography. It is to be hoped that the author will hasten to publish the various papers he has written on this subject to guide those who wish to take up the practice of an art that is new in many aspects...).

Leblanc summarized his many works in the area of crystallization in his book *Christallotechnie*.[4]

In 1788 Leblanc read to the *Athenée des Arts* a *memoir* relative to the spontaneous combustion of piles of pit-coal and the means to prevent it. This work was a consequence of his being assigned to manage the control of the fire that had erupted on October of that year at a huge pile coal located at the Chabrely quarry. His numerous results on the subject were summarized in another unpublished memoir entitled *Analyse Comparative des Charbons de Terre de France avec les Charbons de Terre d'Angleterre*. Although these publications may be considered of minor scientific value, they are significant because they reveal Leblanc's strong interest on the application of chemistry to industrial problems.[1]

In 1751 Axel Frederik Cronsted (1722-1765) reported that the material called kupfernickel (the devil's copper, as miners of the day called it) was a metal (nickel) in its own right, rather than a combination of arsenic, iron, copper, nickel, and cobalt, as was generally believed by his contemporaries Some time later Darcet became interested on the possibility of isolating the new element from its original mineral. By successive calcinations he succeeded in eliminating most of the iron contained in the mineral, but the resulting residue still contained significant amounts of arsenic. In 1786 he suggested to Leblanc to study the problem, which he did at various opportunities. Leblanc's inconclusive results were not published until twelve years later after he had read a *memoir* to the *Lycée des Arts* (1798). According to Leblanc, he had dissolved the usual calcination residue of the mineral in sulfuric acid and found that it could be magnetized rather easily. On the other hand, Darcet's residue was not susceptible to magnetization (At that time it was not known that nickel loses its magnetic properties when heated above 250 °C). Leblanc studied the saline solutions produced by the action of sulfuric acid and found that they contained cupric and nickel sulfate, as well as arsenic sulfide. He crystallized the nickel solutions and observed that the crystals always contained arsenic; incineration of the crystals made them burn in the same manner as pyrophoric substances did. Reduction of the corresponding ashes with pulverized carbon led to the formation of arsenical vapors and a very malleable solid that was attracted by a magnet, and presented many of the properties of nickel. This *memoir* contains what is probably the first report of an experiment which has since become classic: Leblanc indicates that an infallible method to discover the presence of copper in his dissolutions is to add lamella of iron to the solution and to note the copper particles, which appear attached to the iron.

Leblanc's most important work dating from this period is the one that led him in 1789 to the discovery of his process for the artificial preparation of soda, as described below.[5,6]

During the period that Leblanc was developing his process (one of the most turbulent of the French Revolution) and bringing it into commercial production, he did not keep apart from the social and political events taking place in France, he served his country in different positions, with abnegation and devotion, giving to the public thing his honest and unselfish cooperation.[1] His industrial activities were well known and in many opportunities the authorities appointed him to serve in key public commissions and activities. In 1792 he was appointed administrator of the department of the Seine, he did such a good job that he was reappointed five times (1792-1796). He compiled excellent reports on a variety of topics, such as public health and hygienic measures, poor relief, and hospital construction, as well as military, industrial and engineering problems. For these activities he received no pay.[3] In July 1793 he was appointed *Commissaire* for the improvement of the Arsenal and sent on a mission to the *École Militaire*, he was also appointed *Commisaire* for examining the machinery for spinning cotton, *Commisaire* for the works of naval construction; *Commisaire* for the organization of the civil and military police; and *Commisaire* for the construction of a canal leading to the Arsenal. In the same year Leblanc and Bourgoin prepared a report about the integration of the confiscated bishopric buildings to the *Hôtel-Dieu* (a hospital for the poor) and recommended the need to build many more new hospitals. The report also contained many recommendations that reflect Leblanc's medical training and experience: Elimination of the 450 double beds located at the lower floors of the Hospital *Hôtel-Dieu*, which lacked air; to open four new halls for elder patients; the building of a large number of baths; separation of the halls of men from those of women; to use special rooms for treating patients requiring surgery; and to add to the *Hôtel-Dieu* all the necessary teaching facilities (an amphitheater, a library, and a cabinet for pathological

anatomy). In addition, Leblanc and Bourgoin recommended that a hospital be built in every quarter of a city.[1]

On January 4, 1794, Leblanc was appointed *Régisseur des Poudres et Salpètres* (Commissioner of gunpowder and saltpeter) at the Arsenal. This was one of the few paid jobs he held. The board had four members and had its headquarters at the Arsenal. Leblanc moved his family there after he was forced to give up their house on the grounds of the soda factory at St. Denis.

In the same year he was appointed to the *Commision des Arts*, a body adjunct to the Committee of Public Instruction.[1] The main duty of this committee was to list and collect into warehouses the scientific material coming from the religious communities, from the houses of the *émigrés*, or from those who had been executed. The Commission of Arts also requested him to visit the scientific and literary collections and to propose new ways to improve their management. Leblanc suggested several methods for speeding up the cataloging of books seized from religious communities. Volunteers were doing this work and Leblanc recommended that they be paid so that they could devote full time to the task, and thus make thousands of books and manuscripts available to the public more quickly.[3]

To Leblanc fell the unwelcome task of inventorying Lavoisier's laboratory, which had been guillotined on May 8, 1794.

A particular mission entrusted to Leblanc by the Committee of Public Health (June 1795) was to examine the mineral resources of the departments of Tarn and Aveyron and to take the necessary steps to reinitiate the exploitation of the large local alum mines.[1] For this mission the Committee appointed Leblanc *chimiste-directeur* (chemist director) to the large concession of the *copperas* and *alum* mines at St. Georges, which had been awarded to Morlhon, and ordered the *concessionaire* to pay Leblanc's salary and expenses. Nothing was paid. While serving on this mission Leblanc sent to the Agency of Mines several papers and collections of ores, crystals, and minerals.

All of these non-paid public activities put a severe strain on Leblanc's income; to try to alleviate it his two daughters opened a little dry goods store, hoping to bolster the family budget, but there was no chance of success in such times of political turn moil and monetary inflation for a small retail business run by two teen age girls.

The manufacture of sal ammoniac at St. Denis drew Leblanc's attention to the ammonia obtained by heating organic materials. Leblanc was the first to think about using animal wastes and sewages as fertilizers because they were logical, cheap sources of ammonia. He demonstrated the practicality of his ideas in a small scale apparatus, built at St. Denis, especially designed for distilling animal refuse for the manufacture of ammonium chloride. In 1804 he sent to the *Institut National* (the former *Académie des Sciences*) a long account on his method of utilizing such wastes. The committee appointed by the *Institut* to evaluate the account, consisting of Vauquelin, Fourcroy, and Nicolas Deyeux (1744-1837), wrote a very encouraging report in which they remarked that although it was well known that animal and vegetable matters decomposed by putrefaction could serve as excellent fertilizers, their way of operation and the cause of their action were unknown. Leblanc had found that the fertilizing value of animal and vegetable matter was roughly proportional to the ammonia content and that ammonia or its salts should be one of the essential bases of a fertilizer. Hence, there was a substantial practical value in Leblanc's suggestion of utilizing urines, putrid blood, and other fluids capable of releasing large amounts of ammonia, for fertilizing the land and substituting other substances, which were being used for this purpose. In addition, these liquid and semi-solid residues could be used to manufacture muriate of ammonia (ammonium chloride), a material having extended industrial use.

Encouraged by this report Leblanc sent a copy of it to the government together with a request for a grant of 1 200 to 1 500 francs to cover the cost of an improved model of his apparatus. He justified his request by pointing out that his process would allow the production of very valuable by-products from a large amount of animal refuse that went lost every day and also polluted the atmosphere. In addition, he asked *"qu'un brevet d'invention me soit délivré gratis pour quinze années en remplacement de celui que j'avais obtenu pour la fabrication de la soude, du bénéfice duquel j'ai été dépouillé par le gouvernement révolutionnaire"* (for a free fifteen year patent to compensate for the one I obtained for the manufacture of soda, and whose benefits were taken from me by the revolutionary government). Likewise he requested from the *Préfecture de la Seine* to grant him a monopoly to utilize the animal offal and liquid wastes from the cesspools of the municipal authority. All of Leblanc's requests fell into deaf ears; he did not obtain the grant, the patent, or the monopoly. Although Leblanc cannot be considered the father of the fertilizer industry, he should be given credit for being one of the pioneers in the scientific study of fertilizers and being one of the first to propose the recovery of the values in sewage and other noxious wastes.[1]

These series of disappointments was climaxed by a family tragedy. The younger daughter, Adèlaide-Rosalie, a healthy girl of sixteen, suddenly lost the use of limbs and died six months later.[3]

In December 1796, Leblanc's friends in the Department of Tarn, become aware of his critical economic conditions, were instrumental in having the *École Centrale* at Alby (the main city of Tarn) offer him the chair of *Histoire Naturelle*. Leblanc declined it saying that *"la chaire d'histoire naturelle exige des connaissances profondes qui ne sont point à ma portée"* (the chair of natural history requires a profound store of knowledge that is far beyond of me).

THE SODIUM CARBONATE PROBLEM

Up to the middle of the eighteenth century potassium carbonate (vegetable soda) and sodium carbonate (mineral carbonate) were obtained from natural deposits or from the ashes of certain plants and seaweed. Ashes were produced from wood (*potash or pearl ash*) imported from Eastern Europe and the Colonies, from seaweeds (*kelp*) growing in Scotland, Ireland, Norway, and Northern France, and from Salsola soda (*barilla*), a salty plant growing in the Mediterranean coast of Spain. The two carbonates were an essential raw material for three growing industries: it was used in the textile processing as an alkaline scour in the bleaching of linen and cotton cloth; in glassmaking as a fluxing ingredient to lower the melting point of soda lime glass compositions; and in soap-making. Since vegetable

soda was also produced from wood ashes, a timber shortage started developing, helped by the many wars that were taking place at the time and by producing countries protecting their resources. In addition, barilla supply was erratic, not only because it came only from Spain but also because of war blockades. The net result was demand growing more rapidly than supply and that these natural resources were becoming the bottleneck for industrial progress.

Thus strong incentives were established to devise new methods for the preparation of sodium carbonate and caustic soda.[7,8] The resulting development of synthetic methods for manufacturing sodium carbonate may be considered the catalyst that led to the chemical revolution that followed.

The French government, in particular, recognized this difficulty in 1775 when the King Louis XVI offered a 2 400 *livres* prize through the *Académie des Sciences* for a practical process for making artificial soda from common salt. The offer stimulated research not only in France but also in England and other countries. Although no prize was awarded, by the time Leblanc made his discovery in 1789 several establishments were manufacturing artificial soda in France, if only as a byproduct.

DEVELOPMENT OF SYNTHETIC PROCEDURES[9]

Baud has summarized the events that took place from the moment the *Académie* requested proposals for converting common salt into sodium carbonate and the development of Leblanc's procedure, as follows:[9]

(a) *1776*: Establishment of a prize by the *Académie* to reward the author of an industrial process *"en vue d'extraire l'alkali pur du sel marin, sans que la valeur de cet alkali mineral excédât le prix de celui qu'on tire des meilleures soudes étrangères."* (to extract alkali pure from marine salt such that the price of it will not exceed that paid for the best foreign sodas).

(b) *1779*: Experiments of *Athénas at Port de Croisic*, August 16, in the presence of Pierre-Clément Grignon (1723-1784), after verification during 1778 and 1779 of the experiments of *Père Malherbe by Macquer and de Montigny*.

(c) *1782*: *Memoir* sent by Guyton de Morveau on February 16 to the *Contrôleur Général des Finances*. A fifteen-year privilege granted to Athénas and associates (Jourdan and *La Bernardière*) to establish a factory for the manufacture of artificial soda near Nantes.

(d) *1783*: Establishment by Louis XVI of the *Alkali Prize* to be awarded that same year in Saint-Martin. A fifteen-year privilege granted on September 23, to Hollenweger conditioned to installing his industry near Nantes,

(e) *1784*: First experiments by Leblanc.

(f) *1788*: Decree of August 23, revoking the privileges granted to *Athénas, Guyton de Morveau*, and Hollenweger, because they had failed to establish their industry within the time allotted for this purpose. Granting of a new privilege to *Guyton de Morveau and the Marquis de Bullion* to establish artificial soda manufacturing facilities in Brittany, Poitou, Aunis, Saintonge, and maritime Flanders.

(g) *1789*: Publication of a preliminary speech by *Jean-Claude La Métherie* (1743-1817) and deposition in the hands of Berthollet, on March 4, of a *memoir by Jean-Antoine Carny* (1751-1830) and *Géraud de Fontmartin* describing two manufacturing processes, in addition to Leblanc's experiments, repeated at the request of the *Duc d'Orléans*, at the chemistry laboratory of the *Collége de France*, under the supervision of *Darcet and Jerôme Dizé* (1764-1852).

(h) *1790*: On March 27, a month after the signature of an first agreement in front of *Jacques Lutherland*, a London notary, where the *Duc d'Orléans* was staying after the October events. Leblanc deposited in the hands of the notary *Brichard* a package containing the description of two new procedures, one for the conversion of marine salt to soda and the second a personal letter to Dizé, for the manufacture of lead white (together with a favourable report by Darcet). In the following months Leblanc performed additional experiments and started the construction his industry.

Many famous chemists tried their own ways to solve the problem; as will now be described.

In 1779 Carl Wilhelm Scheele (1742-1786) proposed an alternative route for manufacturing sodium hydroxide, based on reacting sodium chloride with lime in the presence of iron.[10] In 1783 *Guyton de Morveau* and Carny implemented a modified version of Scheele's process that remained in operation until 1794. In this procedure marine salt was moistened slaked lime and the mixture allowed to stand for some time, after which the alkaline efflorescence was laboriously scrapped by hand.

The earliest practicable process presented to the *Académie* was developed by a Benedictine *abbé, Père Chrétien Guillaume de Malherbe* (1721-1794), who in 1777 succeeded in converting sodium sulfate into soda using charcoal and iron scrap. Malherbe's method was based on the reduction of sodium sulfate to sulfide by fluxing with charcoal in a reverberatory furnace. Iron scrap was added then and the final mixture consisted of a mass of ferrous sulfide and caustic soda, formed by the action of oxygen in the fire gases. The solid residue was lixiviated to extract the soda and the resulting solution sold as such or evaporated to produce impure sodium carbonate. In order to commercialise his process Malherbe entered in association with an entrepreneur and chemical artisan named Pierre-LouisAthénas (1752-1829), who performed additional research and found that the iron scrap could be replaced by ores, brought directly from the mines, or by *vitriol martial* (copperas or ferrous sulfate) obtained from the peat bogs of Brittany. Replacement of the scrap by ores had the advantage of eliminating the need for sulfuric acid, which was both expensive and likely to be unobtainable whenever the supply of saltpetre was pre-empted by military requirements.[11]

About 1777 *Jean Claude de la Méthiere* (1743-1817) proposed to fuse sodium sulfate with coal, extract the carbonate from the product, and use the sulfur dioxide released to manufacture sulfuric acid for converting the sodium chloride into sulfate. *De la Métherie*'s process was a theoretical one, about which *Louis-Jacques Thénard* (1777-1857) *et al.* made the comment that if de la Méthiere had performed the experience he proposed, he would have found that the reaction between sodium sulfate and carbon did not yield sulfur dioxide and pure sodium carbonate, the sulfate was actually converted into a sulfide. In addition, the vegetable acid he recommended as a purifying agent would be indispensable for the total soda to be obtained because the sodium sulfide produced could be converted economically into sodium carbonate

only with the help of carbon dioxide.[12]

Another privilege was granted to Hollenweger, a former artisan at the royal glass factory. Hollenweger's process first converted Glauber's salt into sodium sulfide by incineration with powdered charcoal and then derived soda from the sulfide.

One of the larger producers of artificial soda was Jean-Antoine Chaptal (1756-1832) who manufactured large amounts of artificial soda by reacting common salt and litharge (lead oxide). The method was very simple and yielded lead oxychloride and soda but because of the cost of litharge it was also very expensive. The lead oxychloride could be used for pigment, either directly as yellow lead or as white lead, after its conversion into lead sulfate by dilute sulfuric acid.

In practice, none of the plants built for the application of the various processes was successful, nor there were in a position to produce soda ash at a price that could compete with Spanish barilla, either in quality or price. Their operating cost was very high and attempts to cheapen the product by replacing salt with sodium sulfate, soap leys, or kelp liquors (both of which had a high salt content) could only be justified on the basis of lower taxes or no taxes at all. In addition, they were inappropriate for large-scale manufacture, they were hard to operate, their yield was low, generated much waste of difficult disposal, and the end product was of relatively low quality.[7,8]

Leblanc's process, though only partly original, overcame most of these defects and became the first really efficient artificial-soda process.

LEBLANC'S PROCESS[5]

Leblanc began to work on the soda problem about 1784 and by 1787 he understood that its solution lay on *La Méthiere*'s impractical process. In his own words: *"J'ai trouvé en general, que les procédés connus étaient imcomplets, insuffisants ou trop dispendieux... Le citoyen Lamétherie inséra dans le Journal de Physique des observations sur la décomposition du sulfate de soude par l'incinération avec le charbon; il ne doutoit pas que de nouvelles expériences procurassent un jour le moyen de décomposer complétement ce sulfate appelé sel de Glauber. Je m'attachai à cette idée, et la addition du carbonate de chaux remplit parfaitement mon object. J'en prévins Lamétherie; c'étoit à ses observations que je devois ce premier succès, puisqu'elles avoient été l'occasion de mon dernier travail* (I found, in general, that the known methods were incomplete, inadequate, or too expensive... The citizen *Lamétherie* published in the Journal de Physique some observations on the decomposition of the sulfate of soda by incineration with coal; he does not doubt that additional experiments will provide some day the method of completely decomposing the sulfate, known as Glauber's salt. I pursued this idea, and the addition of carbonate of lime fulfilled my object perfectly. In this, I anticipated *Lamétherie*; it was to his observation that I owed this first success, since they occasioned my final experiments.[12]

The process developed by Leblanc consisted of a first step for producing sodium sulfate by the reaction between sodium chloride and sulfuric acid. Afterwards, the sulfate was reduced with coal to the sulfide, which in turn was reacted with chalk or lime to form soda and calcium sulfide. The pertinent chemical reactions are:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl(g) \quad (9)$$

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO(g) \quad (10)$$

$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS \quad (11)$$

Successive descriptions of Leblanc's procedure make it possible to follow the development of his process in three well-defined steps from the laboratory to the industrial stage. In the beginning Leblanc carried out the transformation of sodium sulfate to soda in crucibles because he had not found yet the best proportions of sulfate, limestone, and charcoal; and had not made any progress with the preliminary conversion of sodium chloride to sodium sulfate. By the time he applied for a patent on July 15, 1791, he had already perfected a reverberatory furnace for the second reaction, converting sulfate to soda, and he had come very close to determining the optimum proportions between the reactants.

The *Duc d'Orléans* was interested in industrial investments and on hearing about Leblanc's achievements, he requested from Darcet to certify the merits of the soda process before he would make an investment. Leblanc was given laboratory space at the *Collège de France*. Darcet, who was fully occupied, asked Dizé, his assistant, to work with Leblanc.[2] When the first attempts to reproduce the results failed, Leblanc requested that a report be delayed and that Dizé continue working with him in order to find and overcome the source of the difficulty. Dizé agreed, with the concurrence of Darcet, and thus did the development of the Leblanc process began in the laboratory of the *Collège de France*.

A preliminary agreement was signed on February 12, 1790, in the presence of James Lutherland, a public London notary (Note 1); its essential points were: (a) Leblanc was to deposit a complete description of his process for making soda (which he did on March 27, 1790), (b) Dizé to do likely for his method of manufacturing white lead, (3) details of a sal ammoniac manufacture were to be given by Leblanc, who made no claims that the method was original, (d) the description of the processes for manufacturing soda and white lead were to be certified by Darcet (Note 2), and then sealed by the three principals, and not to be

1. At that time the French political situation had forced the Duc d'Orléans to move to England.

2. The undersigned, professor of chemistry at the Collège de France and of the Académie des Sciences, certifies that the procedure described below and another two places, is exactly the same as the one that has been realized under my eyes in different opportunities and with success, in my private laboratory and in large scale at the laboratory of the Collège du France, such that by this process, sea salt is decomposed and the base converted into soda of high purity; I also certify that this same process can be used to establish a manufacture of sal ammoniac. Given in Paris on March 24, 1788. Signed: Darcet.

opened except in case of death, or abandonment by the authors, In return, the Duc accepted to furnish 200 000 livres to enable Leblanc and Dizé *"to carry on the said process advantageously."* It is important to note that Dizé is not mentioned in connection with the soda process. The detailed procedures, together with Darcet's certificate (Note 2), notarized on March 24, 1790) were deposited in the hands of the notary Brichard in Paris, on March 27, 1790. All these documents remained sealed until 1856 when they were opened by court order at the request of the *Académie des Sciences*.

In addition, Leblanc and Dizé signed a private agreement on January 15, 1791 establishing that the profits from soda and sal ammoniac were to be divided three fifths to Leblanc and two fifths to Dizé; the gain from white lead (actually sulfate) was to be distributed in the reverse proportion. The right of each to his own invention was reaffirmed. The sal ammoniac manufacture was a natural *appendage* to the soda process. It made use of the hydrogen chloride obtained in the preparation of salt cake and the ammonia prrepared by distillation of animal materials. According to the report of Thenard *et al.*[12], the arrangement clearly established the existence of three different processes; that of manufacturing soda, of which Leblanc was the author, of manufacturing white lead, of which Dizé was the author, and of sal ammoniac, not attributed to any one.[2] On January 27, 1791, Leblanc, Dizé, and the *Duc d'Orléans* entered into a twenty-year definite partnership. Henri Shée (1739-1820) was to be recognized as the administrator of the Duc's interests. Leblanc's salary was fixed at 4 000 livres per year and Dizé's 2 000 livres. These were minimum payments, and were guaranteed in case their shares of the profits did not reach these amounts. The first tenth of the net return was assigned to the Duc, as interest at 10 % and to amortize his capital payment of 200 000 livres. Any remaining profits were to go nine-twentieths to the Duc, six-twentieths to Leblanc, three-twentieths to Dizé, and two-twentieths to Shée. As stated by Anastasi[1] the terms of the contract reflected the partners optimism regarding the commercial future of the project.

In 1791 the Constituent Assembly granted inventors the right to secure patents. Leblanc was one of the first to take advantage of this possibility and Darcet, Desmarest (a geologist, Inspector of Industries), and Claude Urbain de Retz de Servières (Director of Patents) were appointed to verify the accuracy of the description of his process. They reported that *"après avoir scrupuleusement examiné la méthode employée par le dit sieur Leblanc pour l'extraction de la soude par la décomposition en grand du sel marin, nous avons reconnu que l'invention était différente et très supérieure à tout ce qui, juspu'à ce jour, était parvenu à notre connaissance, tant par l'économie, la célérité et la sûreté des procédés, que para la richesse et la pureté des resultats... Nous estimons que la découverte du sieur Leblanc, par toutes les raisons politiques et commerciales, mérite les encouragements de la nation française et que le secret de sa découverte doit être soigneusemnet gardé"* (Having carefully examined the method employed by the said M. Leblanc for producing soda by the large scale decomposition of sea salt, we acknowledge that the invention is new and very superior to all that up to now have come to our knowledge as regards to economy, speed and certainty of the method as well as regards to the abundance and purity of the products...We believe that the discovery of M. Leblanc for political and economic reasons merits the encouragement of the French nation, and that the secret of the discovery should be well guarded).[2]

A patent was granted to Leblanc on September 25, 1791 giving him the exclusive right to work or license his process for a period of fifteen years. The essential features described in the patent were as follows: One part of Glauber's salt, one-half part of limestone, and one-quart part of charcoal were crushed and mixed between iron rollers. The mixture was then spread out in a reverberatory furnace, the working holes closed, fire was applied, and the mixture heated until fusion. The reaction took place only after the mixture had acquired a semi-paste consistency; after that the rate was very fast. The mixture began to froth releasing a flammable gas, and finally became converted into soda. During all these processes it was necessary to stir the mass frequently. The operation was considered finished when no more gas was released. The final fused material was called *black ash*; it had a complex composition that changed rapidly in contact with air. It was lixiviated with water yielding a solid residue and a solution of sodium carbonate. On the basis of 100 kg per part, each batch produced about 150 kg of soda.

The main components of black ash were, approximately 41.6 % weight sodium carbonate, 29.8 % calcium sulfide, 11.6 % calcium carbonate, and 4.4 % coke. In the beginning of the implementation of the process the black ash was sold as such directly to soap boilers and other users.

In the same year that Leblanc was granted a patent, and after Darcet had made a favorable report in 1790, a plant was built near *Saint-Denis*, at a place known as *Maison-de Seine*, four miles from Paris, where access would be easy for barges bringing limestone from Meudon. Very soon the plant was producing about 250 kg of soda per day, together with some lead sulfate and ammonium chloride. Because of the war with Spain, the price of barilla had gone up tremendously, and subsequently there was a large profit in the manufacture of soda from common salt.[2]

Leblanc's plant did well until 1793, when the *Duc d'Orléans* was guillotined and the plant confiscated (as explained below). The total production of Leblanc's factory amounted to only 15 t of soda. From here on disaster followed disaster.

The Committee of Public Safety, which was essentially an executive war cabinet, set up a Commission of Power and Arms to deal specifically with questions related to munitions and their manufacture. *Guyton de Morveau*, a member of the Commission, wrote to all the soda manufacturers on January 27, 1794, that the Committee was now concerned with eliminating France's dependence of foreign sources for soda and establishing enough local facilities for its manufacture. For this reason it was necessary to collect all the available technical and scientific information on the subject, as well as to carry on a survey of all the available plants. The pertinent people were ordered to appear in front of the Commission to confer on the topic and to make known to it the location of their manufacturing plants, the quantity of soda they put on the market, how much they could furnish, and the date they could start their deliveries.[2]

After all the required information was collected, a special committee that included Darcet was ap-

pointed to examine the processes and to survey the factories. Their lengthy report was published in June 1794 and a considerable part of it dealt with the Leblanc process[13]: *"Nous avons visité cet atelier naissant avec le citoyen Loyzel, députe à la Convention, et nous avons vérifié le procédé, sur lequel nous croyons pouvoir déjà prononcer avec la plus grande certitude de succès. Cette nouvel établissement a été élevé en entier sur ses propres fondemens, et avec la prudence et la circonspection qu'on pouvoit attendre de l'intelligence et du bon esprit des trois associés... Les co-associés de cette manufacture, ainsi que ceux qui, dans différens lieux de la république, on fait à la patrie le sacrifice de leurs connoissances et leurs travaux, tous également pleins de confiance en la justice du Comité, attendent, sans inquiétude, les justes dédommagements qui leur sont dus, soit pour les avances de toute espèce, ainsi que pour le tems qu'ils ont consacré à créer et former leur établissement... Le procédé du citoyen Leblanc, par l'intermède de la craie, nous paroît celui qui peut être le plus généralement adopté; parce que cette matière première est plus universellement répandue; elle a de plus cet avantage, qu'elle n'empêche pas la soude d'être mise dans le commerce, dans l'état brut; qu'elle ressemble plus particulièrement à celle que le commerce nous procure de l'étranger... qu'elle peut s'appliquer immédiatement et sans lessivage préliminaire, à la buanderie, à la verrerie commune, et à la confection du savon"* (We have inspected their establishment, we have verified their process and we believe it is certain to be successful. This new work has been established on correct principles from start to finish and has been set up with the prudence and circumspection that was to be expected from the intelligence and good sense of the three partners... The partners in this work, who, as those in other parts of the Republic, have sacrificed their knowledge and fruits of their labors to their country are uniformly filled with confidence in the justice of the Committee. They await, with no misgivings, the just compensation due to them as repayment for their advances of all kinds and for the time they have spent in planning and building their works... The process of citizen Leblanc, which uses chalk as the intermediate, appears to us to be the one that could be most generally adopted, because this raw material is most widely distributed. The process has the added advantage of supplying a product that can be marketed in the crude state; the product is quite like that which comes from abroad... it may be used directly and without preliminary purification for bleaching, for ordinary glass, and for making soap).

In spite of France being at war, the report in all its details was made public. It contained a detailed description of Leblanc's process, all the technical details about the manufacturing techniques, a detailed drawing of all the installations and equipment at Franciade (as St. Denis was now called); as well as a description of the competing processes (Alban, Malherbe and Athénas, Chaptal and Bérard, Guyton and Carny, etc., etc.). After the war the British would get hold of the report and start their own manufacturing facilities.

The soda manufacturers thus found themselves as object of considerable attention. For Leblanc and his partners the situation was particularly complicated by the fact that the *Duc d'Orléans* had been guillotined shortly before and, consequently, his property confiscated by the State: the soda factory now belonged almost entirely to the government and not Leblanc and his partners were in charge.[2] Leblanc was confident that in spite of the confiscation the factory would continue to operate under his direction for the benefit of the Nation, and that he would continue to be remunerated 4 000 francs for his efforts. This dream lasted only from October 1793, to February 1794, when the authorities closed the factory. Leblanc found himself without his patent and without the factory; all of it belonged now to the State.

Leblanc's process at that period had not had time to demonstrate its practical superiority to all others. His factory was kept closed; the money on hands and the accounts due were taken by the government, the finished products and raw materials were sold, together with the horses, carts, and part of the equipment. Leblanc was ordered to vacate the premises and was also notified that his salary will cease after April 1, 1794. Thus, within a few months, Leblanc's entire outlook was overturned; instead of running a profitable business, he found himself shut out of his own property and dependent on a small government salary to support his ailing wife and their four children. From this time on his life was an almost continuous struggle against poverty.[3]

Following the publication of Leblanc's process, other alkali works were opened in Paris, Dieuse, Chauny, Marseilles, and other French cities. These works prospered and while war lasted, the secret was held in France. After the peace of 1802, English industrialists learned the details of the Leblanc process and began to make soda in increasing amounts in England. In the beginning English soap makers accustomed to working with barilla, distrusted the new product and would have nothing to do it. Once the prejudice had been overcome and soap making recipes had been adapted to the new material, demand for Leblanc soda rose quickly.[7,8]

It took more than a generation for Leblanc's discovery to change the situation of the soda market situation. Fifty years after Leblanc's suicide, his procedure had been adopted by all the European soda manufacturers and had produced about 300 000 t/year of different alkalis.

Dumas wrote on this respect:[12] *"Depuis le commencement du siècle, toute l'industrie des produits chimiques pivote autour des manufactures de soude artificialle et s'empare de leurs procédés our de leurs produits"* (After the beginning of the century, all the chemistry industry pivoted around the fabrication of artificial soda and took shelter on its procedures or its products).

Leblanc's process remained viable during 80 years until the advent of the Solvay process in 1863.

Leblanc's development of the synthesis of sodium carbonate from common salt led eventually to a substantial decrease in the price of soda and chlorine, the latter obtained from the by-product hydrogen chloride. Not only that, the synthesis released the industrialized countries from the need to import the chemical and be a servant of other countries.

THE STRUGGLE FOR JUSTICE

Leblanc spent nearly eight years suing for ownership of his plant and petitioning incessantly for reimbursement for the losses he had incurred. His Via Dolorosa was the combined result of the tragic and strong political events taking place in France at the time, bureaucracy, and, as claimed by Gillispie,[11] Leblanc's conflicting personality. Although in 1800 he regained the tem-

porary control of the plant, pending a definite ruling on his claims, he was unable to raise the money to operate it effectively. His hope was always that the final settlement would give him the capital he needed. However, when settlement was eventually made, the award fell far short from expectations, He went into debt, grew depressed, and on January 16, 1806, committed suicide.

It is of interest to look at the chain of events that led to Leblanc's tragic decision. Being familiar with Leblanc's many unsuccessful petitions, Berthollet, in February 1795, wrote to him in the name of the Commission *d'Agriculture et des Arts* (Commission of Agriculture and Arts): *"Le Comité pense que tu dois recevoir une indemmité proportionelle au désintéressment don't tu as fait preuve, en lui communiquant ton procédé sur l'extraction de la soude"* (The Committee is of the opinion that you are entitled to compensation in proportion to the disinterestedness of which you have given proof in revealing to it your process for making soda). Similarly, the Council of Arts and Manufacturers in 1797 and 1798 recommended that something be done for Leblanc, but *François de Neufchâteau*, Minister of the Interior, postponed action. Finally in March 1799 Leblanc was granted 3 000 francs as a national compensation of which only 600 were paid. His repeated complaints for payment of the remaining sum were always rejected with the argument that the financial state of the government did not allow it.[3]

In 1800 Chaptal became Minister of the Interior. Since Chaptal was a successful chemical manufacturer Leblanc believed that he would understand better his pleas for help and justice. Fourcroy also wrote to Chaptal in Leblanc's behalf. A token grant of 300 francs resulted:[3]

Finally, in April 1801, after so many complaints, so many requests, and so many favorable reports, the Minister of Finance ordered that the works at St. Denis be provisionally handed back to Leblanc and his associates. The Minister was confident that this action represented an appropriate compensation for the losses suffered during the six years and nine months that the factory had been closed. Since the state was the owner of the facilities (in place of the *Duc d'Orléans*), they were now four partners. During the period that the factory had been closed, Dizé and Shée had taken a passive attitude regarding Leblanc's insistent fight for justice and had followed other avenues. Dizé had become Chief Pharmacist for the Military Hospitals and Shée had entered politics and was Councillor of State. Neither of them had the time or the interest to take an active role in renewing operation of a factory that was in shambles. Thus the partnership of 1791 was dissolved by mutual consent two days after the Ministry's order, Leblanc was now in sole charge, but the factory was to remain under sequestration until the claim of the State was fully paid off. The liquidation of the financial relation between the State and the other partners would have to wait until the arbitrage of Vauquelin and Deyeux, a result that would occur nine weeks before Leblanc's death.

Leblanc reinstalled himself in St. Denis to be confronted with stiff competition from other manufacturers whose plants were better situated and in good running order. They had years of valuable experience and had built good will among their customers, particularly with the soap manufacturers in Marseille. To improve his return to the market and the financial picture of his factory, Leblanc started manufacturing additional chemicals, such as white table salt, tin chloride, and mercury oxide; he also set up a cotton bleachery. Each of these enterprises brought up their own problems and increased his debts; nevertheless he did not give up and in June 1803 he appealed for help to the newly organized *Société d'Encouragement*, requesting a loan to keep his industry viable until the *Tribunal de Commerce* (see below) would reach a decision regarding the liquidation of his conflict with the State. On the recommendation of de Morveau, Mollard, and Vauquelin the *Société* awarded him a loan of 2 000 francs, a sum far from what he needed. The loan was to be repaid in one year.[3]

In the spring of 1801 the authorities of the Department of the Seine ordered the *Tribunal de Commerce* (Tribunal of Commerce) to examine Leblanc's claims and fix damages, if any. This court held the case for four years and then declared itself incapable of handling down a well-founded decision. Thereupon the Minister of Finance assigned the claim to the Prefect of the Seine and authorized him to set up a board of experts to determine the indemnity.[3]

The board appointed consisted of four members, two nominated by the Prefect (Vauquelin and Hillaire Bellacq, a businessman and member of the chamber of commerce) and two appointed by Leblanc and his former associates (Deyeux, professor of pharmacology and member of the Institut; and Louis-Cardinal Beaurepaire, who owned a Prussian blue factory). Leblanc presented to the board a long report, setting forth in detail his estimate of the losses suffered by him and his partners. The losses were discussed under five captions: loss of income caused by the divulgation of the patent (100 000 francs); unpaid salaries to Leblanc and Dizé (40 500 francs); lost profits resulting from the interruption of soda sales during six years and nine months (603 500 francs), loss of the privilege on soda during the remaining seven years of the patent (743 000 francs); and loss of benefits on the fabrication of white lead and sal ammoniac (756 000 francs). The total loss, according to Leblanc, amounted to 2 243 000 francs; *"quelque élevé que puisse paraître ce chiffre des dommages causés, it est bien au-dessous des bénefices certains qu'on pouvait attendre de cette enterprise, don't les products étaient d'un usage general, journalier et presque d'une nécessité première"* (though this figure may appear high, it is far below the profits that could have been expected from the enterprise, whose products were of general and daily use, and almost a basic need).[3]

The report of the arbitrators was handed in on November 8, 1805. In their opinion the business was entitled to 280 777 francs only. Of this the Nation was credited with 164,160 francs (resulting from the confiscation of the Duc d'Orléans share) leaving to the associates 116 608 francs. Leblanc and Dizé's share each was 52 473 francs, and 11 660 francs for Shée. Even this inadequate sum was never paid to Leblanc or his children. Anastasi writes: *"Ainsi, pour Leblanc, vingt années de travail, une des plus grandes découvertes de ce siècle, se soldaient par 52 474 francs. O justice!"* (the reward of twenty years of toil, and the founding of one of the most important industrial processes of this century were cancelled with 52 474 francs. Oh justice!).

The tribunal's decision was the final blow to Leblanc; he could not take it anymore, his fortunes had reached bottom. He became more and more introvert, slept little, stopped working in his laboratory, and spent most of the nights in his

office writing. On January 16, 1806 he sent a bullet through his head, and was dead when the family reached his study. He was buried at St. Denis and his ill fate pursued him even after death. The town grew, the cemetery was engulfed, and by 1840 his grave was lost and not even his tombstone was saved.[3]

Leblanc's family had to sell most of their personal property to pay the debts and to meet the death dues. Reduced to poverty they moved to Paris and struggled valiantly, sustained by the hope that something would be done for them eventually. Leblanc's widow appealed for help to Joséphine, the wife of the Emperor, to no avail.[3] Friends of the family used their influence to accelerate approval of the verdict of the arbitrators by the Minister of Finance. This act took place on August 1806 and its implementation represented another blow. First, the award was reduced to 110 443 francs to conform to the new rate of exchange, second, the Liquidator General (de Fermont) was entitled to issue non-redeemable five per cent bonds in this amount, but he delayed payment. In 1807 he ruled that the indemnity in no case could not exceed the value of the factory, and consequently the account had been squared when the soda works had been turned back to Leblanc and his partners.[3]

When the last appeal failed, Madame Leblanc, who had been sick for almost twenty years, collapsed and became a permanent invalid. She passed away in 1829, at the age of sixty-nine.

Towards the end of 1855, at the conclusion of the First International Exposition in Paris, and after the report of the general commission had remarked the results and progress achieved by the industries based on artificial soda, the descendants of Nicolas Leblanc addressed to the Emperor Napoleon III a petition requesting reparation for the damages caused to their grandfather: *"Le moment n'est-il pas venu, Sire, de render à la mémoire de Le Blanc un hommage qui lui est dû à tant de titres et qui serait à la fois une consolation pour sa famille et une réparation pour les souffrances que ses contemporains lui ont infligés? La France et l'Europe lui doivent une reconnaissance don't Votre Majesté seule peut trouver l'expression et don't il n'appartient qu'à elle de se faire l'interprète."* (Has not the time come, Sire, to render to the memory of Leblanc the testimonial due to him for so many reasons and which would be both a consolation to his family and reparation for the sufferings inflicted on him by his contemporaries? France and Europe owe him a recognition, which Your Majesty alone can voice and of which You alone can be the expositor). The point was made that after more than fifty years after Leblanc's death artificial soda was manufactured in France and abroad only using his process.

The Emperor instructed the Minister of Public Education to gather the data necessary for a decision and the Minister, in turn, asked the *Académie des Sciences* to emit its opinion on the legitimacy of the reclamation for aid; the widow and children of Dizé were to be included in any recommendations sent to the Emperor. The *Académie* appointed an evaluation committee consisting of the most important chemists of the time: François Ernest Ballard (1833-1894), Michel Eugéne Chevreul (1786-1889), Jean-Baptiste André Dumas (1800-1884), Théophile-Jules Pelouze (1807-1867), Victor Regnault (1810-1878), and Louis-Jacques Thénard (1777-1857).

The report was delivered on March 31, 1856, and made public the same year. It established unequivocally that the manufacturing process belonged wholly and irrevocably to Nicolas Leblanc. Its main points were the following: (1) the discovery of the process was solely due to Leblanc, (2) Dizé's collaboration was limited to helping in determining the best proportions of the raw materials and to aid in laying out and starting the factory. They recommended that any testimonial to the inventor of the process should be made to Leblanc's memory and addressed to his descendants. If any indemnities were granted to compensate for the sequestration of the factory, the divulging of the patent and its cancellation, the grant should be divided according to the partnership agreement of January 27, 1791. The report was adopted, sent to the Emperor, where it was filed, without further action.[3]

The echoes of the report caught the public attention and aroused the sympathies for this useful man that had provided his country with such an important and productive discovery and whose only award was misery and misfortune. The public opinion led to the national recognition of this achievement, Paris named one of its streets Leblanc, the cities of Marseille and Lille placed his bust in their main buildings, and eventually Lille named Leblanc one of its main roads.[1]

EPILOGUE

According to Dumas:[12] *"Ce que Leblanc a produit ne peut être égalé que par les découvertes de Watt dans la mécanique. Si deux homes ont trouvé dans le denier siècle le moyen de fournir aux autres homes le plus de bonheur, le plus de commodities pour la vie, ce sont, coup sûr, Watt et Leblanc"* (What Leblanc has produced can only be equated to the discoveries of Watt in mechanics. If two men have found in the last century the means of providing other men the maximum of happiness, the maximum of life comfort, they are, without doubt, Watt and Leblanc).

BIBLIOGRAPHY

1. Anastasi A., *Nicolas Leblanc, sa Vie, ses Travaux, et l'Histoire de la Soude Artificielle*, Paris, 1844.
2. Oesper R.E., Nicolas Leblanc (1742-1806), **J. Chem. Educ.**, 19, 567-572, 1942.
3. Oesper R.E., Nicolas Leblanc (1742-1806), **J. Chem. Educ.**, 20, 11-20, 1943.
4. Leblanc N., De la Cristallotechnie, ou Essai Sur les Phénomènes de la Cristallisation, et sur les Moyens de Conduire Cette Opération Pour en Obtenir des Cristaux Complets, et les Modifications dont Chacune des Formes est Susceptible, Conservatoire des Arts et Métiers, Paris, 1802.
5. Wisniak J., Sodium Carbonate - From natural sources to Leblanc and back, ***Indian J. Chem. Technol.***, 10, 99-112, 2003.
6. Leblanc N., Mémoires et Rapports Concernant la Fabrication du Sel Ammoniac et de la Soude, Goujon Fils, Paris, 1800.
7. Matthews M.H., The Development of the Synthetic Alkali Industry in Great Britain by 1823, **Ann. Sci.**, 33, 371-382, 1976.
8. Reilly D., Salts, Acids & Alkalis in the 19th Century, **Isis**, 42, 287-296, 1951.
9. Baud P., Les Origines de la Grande Industrie Chimique en France, **Revue Historique**, 174, 1-18, 1934.
10. Scheele C., **Kongl. Vetenskaps. Acad. Handlingar**, XI, 158, 1779.
11. Gillispie C.C., The Discovery of the Leblanc Process, **Isis**, 48, 152-170, 1957.
12. Thenard L.J., Chevreul M.E., Pelouze T.J., Regnault V., Balard F.E., Dumas J.B.A., Rapport Relatif à la Decouverte de la Soude Artificielle, **Compt. Rendu**, 42, 553-578, 1856.
13. Lelievre C., Pelletier B., Darcet, J., Giroud M., Extrait d'un Rapport sur les Divers Moyens d'Extraire avec Avantage la Soude du Sel Marin, **Ann. Chim.**, 19, 58-156, 1797.