

Michel Jean Jérôme Dizé. Chemical revolution and social injustice

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RESUMEN. El nombre de Michel Jean Jérôme Dizé (1764-1852) está entrelazado con el de Nicolas Le Blanc (1742-1806) en la tragedia Griega acerca del nacimiento e infancia de la industria del carbonato de sodio sintético. Tuvo una parte importante en la mayor parte de los intentos fallidos para obtener una indemnización por la fuertes pérdidas sufridas a consecuencia de la expropiación de la fábrica por el gobierno de la Revolución Francesa. Contrariamente a Le Blanc, que se suicidó, Dizé consiguió desenredarse de la tragedia y vivir luego una vida profesional. No fue un científico destacado, pero su nombre está asociado con la cuestión de paternidad del proceso químico que condujo al carbonato sintético y a sus reclamaciones por una parte de los beneficios.

ABSTRACT. The name of Michel Jean Jérôme Dizé (1764-1852) is intertwined with that of Nicolas Le Blanc (1742-1806) in the Greek tragedy about the birth and infancy of the industry of synthetic sodium carbonate. He was actively involved in most of the failed intents to obtain an indemnification for the heavy losses incurred as a consequence of the expropriation of the factory by the Revolutionary French government. Contrary to Le Blanc, who committed suicide, Dizé succeeded in extricating himself from the tragedy and live a full professional life thereafter. He was not an outstanding scientific figure, but his name is associated with the question of paternity of the chemical process that led to synthetic carbonate, and his claims for part of the benefits.

LIFE AND CAREER^{1,2}

Michel-Jean-Jérôme Dizé was born on September 29, 1764, at Aire, in the department of Les Landes, the eldest son of the apothecary Michel Dizé (1735-1792) and his first wife, Marie Despaignet. There were two additional children from this marriage: François (1766-1811) and Marie-Anne (1768-). After the passing away of his wife Michel Dizé married Jean Cadry, on November 17, 1773.

Michel-Jean-Jérôme Dizé was married three times; first with

Adélaïde Berthélemi (1797), then with Rose-Agathe Daumont (1813), and finally with Louise-Clotilde Françoise Mondet (1825). From the first marriage he had two sons, Jean (1798-1820) and Emile, from the second, one daughter, Rose-Agathe-Caroline, and from the third marriage another daughter, Antoinette-Rose.

During his classical studies Dizé felt attracted by natural sciences and at the age of 16, after finishing school and by recommendation of

Jean Darcet (1725-1801), a friend of his father and professor of chemistry at the *Collège de France*, he moved to Paris to work under Darcet and be a pharmacy apprentice. Three years later Darcet appointed him as *préparateur* of the course in chemistry he was dictating. From 1784 to 1791 Darcet's laboratory was put under Dizé's responsibility and in this same period he also became *préparateur* of the course on experimental physics dictated by Louis Lefèvre Gineau* (1751-1829). It is at this time that Lavoisier published his famous memoirs on the decomposition and recombination of water, which proved definitely the proportions of oxygen and hydrogen that entered in its composition.^{3,4} The double functions served by the young scientist did not impair him from publishing in the *Journal de Physique* the results of his researches and experience.¹

In 1792 Dizé joined the Army ambulatory hospital at Camp-sours-Paris, as a pharmacy student, in order to escape the consequences of being under suspicion because of his relations with the Duc de Orléans (1747-1793), later Phillippe Égalité (see below). In 1793 he was appointed Pharmacien aide-major principal at the central store of the army pharmacies and on September 1795, after passing all the required examinations, he was granted the degree

*Chemist, physicist, and teacher at the *Collège de France*, who participated in the establishment of the kilogram as the unit of mass and studied with Lavoisier the composition of water.

of *maître en pharmacie*. A few months later, thanks to his solid knowledge of chemistry and chemical technology, he was charged with the administration of the *Magasin Générale des Pharmacies* of the Army, established at *Champ-de-Mars*. This institution had been created in 1792 by the Convention “pour assurer aux armées des médicaments du premier choix” (to insure that the armies get medicines of the best class). The appointment letter recognized the organization capabilities of Dizé and proposed for him the rank of *Pharmacien en Chef*. He fulfilled his job with such a success that two years later the *Journal de la Société de Pharmaciens de Paris* wrote:² “Le citoyen Dizé, placé à la tête d’un des plus magnifiques établissements de pharmacie qui ait jamais existé, celui de l’Ecole militaire à Paris, destiné à fournir les médicaments chimiques aux hôpitaux militaires de la République, a porté dans cet établissement les lumières d’un habile chimiste, en même temps que les soins, l’attention, l’ordre sévère d’un administrateur zélé” (Citizen Dizé, heading one of the most magnificent pharmacy establishments ever created, that of the Military School in Paris, charged with providing the medicines to the military hospitals of the Republic, has contributed to this institution the intelligence of a clever chemist, together with the care, attention, and severe discipline of an enthusiast administrator).²

Dizé received many honours for his contributions to science, industry, and the Nation. He was elected member of the *Société des Inventions et Découvertes* (1792), of the *Société des Arts* and the *Société de Médecine* (1795), of the *Société Libre des Pharmaciens de Paris* (1795), of the *Société de Santé de Paris* (1796), of the *Société Académique des Sciences* (1801), of the *Académie Royal de Médecine* (1823), and of the *Société d’Encouragement pour l’Industrie Nationale*.

On October 16, 1796, he was appointed professor of Natural History at the *École Gratuite de Pharmacie*; in 1798 he was appointed National Refiner of the Mint, a position he held until 1813, and in 1837 he was elected President of the *Société de Pharmacie*.

In 1801, at the request of the *Lycée des Arts*, he pronounced the tribute during the funeral of Darcet¹.

In 1788 Dizé reported the presence of calcium carbonate in the

sugar present in the clarification of sugar juices, as well as in other operations during the refining of sugar.^{5,6} He experimented in the large-scale production of citric acid for the use in army hospitals. Solid citric acid was prepared by neutralizing lemon juice with calcium carbonate, followed by treatment with an excess of diluted sulfuric acid. The sulfuric acid was needed in excess in order to destroy the mucilage the citric acid retained stubbornly when reacting with the carbonate, and which prevented its subsequent crystallization. The resulting solution was concentrated by evaporation at the temperature of boiling water; yielding a clear liquor, lemon color and slightly acid. Repeated evaporation-crystallization sequences produced white crystals of very pure citric acid of regular shape. According to Dizé, Carl Wilhelm Scheele (1742-1786) had also prepared citric acid but in very little amounts of very small crystals, which did not allowed determining their shape. Dizé found that his solid citric acid, dissolved in water, followed by addition of sugar and the oil extracted from the peelings of lemon, produced excellent lemonade for hospital use.⁶

In 1789 he published his comparative experiments on the dyes extracted from clover seeds and woad (*Isatis tinctoria*)⁷. Woad imparts to wool and silk a beautiful lemon tint while the seeds of clover stain wool yellow and silk pistachio color. The lemon color can be changed to the same yellow of the clover by adding a little of madder to the dyeing bath. The resultant yellow tint is very stable because a shade of a delicate and unstable color that has been toned down by another color of good dyeing properties resists very well the influence of light. The yellow produced by the seeds of clover and woad on wool and silk are affected by the presence of nitric acid. The yellow color of the seeds of clover and by woad cannot be applied without first sizing the base material. Applying a blue dye over the yellow of the clover seeds gives a green less beautiful, and less satisfactory to the eye than the green produced in the same manner by woad.⁷

In 1790 he analyzed the coppers of old medals and weapons and found that the brass alloy used by Greeks and Romans contained a very variable amount of tin, while in those made by the Gauls the

amount was constant and in the same proportion that the French used presently for making church bells.⁸ Shortly thereafter, he reported on a method for the immediate preparation of gallic acid and pure tannin from gallnuts and the complete analysis of the products. The extraction procedure was based on treating the groundnuts with ether, followed by drying, washing with distilled water, and treatment with sulfuric acid.⁹ The analysis of the nuts was not printed but was included in a report read to the Institute by Louis Nicolas Vauquelin (1763-1829) and Louis-Bernard Guyton de Morveau (1737-1816).

Dizé was in charge of the composition of the safety inks used for the printing of the tickets for the royal lottery during 25 years. While in this position he invented a solid and indelible safety ink, about which Vauquelin and Claude-Louis Berthollet (1748-1822) made a report to the Institute. The manufacture of this ink involved a first step of preparing, separately, a pasty aqueous solution of printing ink and crystalline sodium bicarbonate and a solution of melted red lacquer and crystalline sodium bicarbonate. The two preparations were mixed with glue of Givet and the blend evaporated until it acquired a pasty state that did not adhere to the hands. The paste was then poured into molds shaped as rectangular parallelograms, and exposed to a stream of air until the sticks achieved the desired solidity. They were then wrapped in tin sheets and ready for use. The ink thus prepared resisted the action of all chemical agents that destroy common inks and could be transported and used everywhere.¹⁰

While being National Refiner of the Mint, Dizé simplified the method by which gold was separated from its alloys with silver, by substituting the nitric acid used in the old method with concentrated sulfuric acid. This new procedure not only was cheaper but allowed for a more complete separation of the two metals.¹¹ In 1823 Dizé used his new method to build in Brussels a plant for the refining of small-value copper-silver coins and replace them by the silver florin. The method was based on refining the alloy with sulfuric acid, which left the silver undissolved.¹

Dizé also developed a very simple wet process that allowed the complete separation of the alloys of zinc with copper. The procedure was very appropriate for determining the

amount of zinc present in common brass (also known as *cuivre jaune* or *similor*), including those compositions used in the fabrication of utensils for the preparation of different foods, where it was necessary to dosage it in order to determine in a sure and safe way the poisonous quality of pure copper. In his publication he also reported own on the use of the novel method for analyzing old Greeks and Roman copper coins. The results indicated that the cadmia (a mineral containing cobalt, zinc and zinc oxide) used by the ancients to prepare brass, did not originate from a copper mine containing zinc. The three classes of cadmia, called furnace cadmia, with which the ancients prepared their brass, was actually zinc oxide, which had volatilized as a result of the strong heat used in the furnace in which they cemented or melted their calamine ore. It was not different from the cadmias and impure zinc oxides that are present at different heights in the present furnaces in which copper is cemented with zinc ores to make brass, *cuivre jaune*, or *similor*.¹¹

Dizé developed a new method for preparing sal ammoniac (ammonium chloride) based on reacting calcium sulfate with ammonium carbonate obtained from animal sources, followed by boiling the resulting ammonium sulfate with sodium chloride, leading to the double decomposition that produced sodium sulfate and ammonium chloride. The resulting ammonium chloride was purified by neutralizing with ammonium hydroxide the excess acid produced. If the salt contained ammonium sulfate, it was decomposed with calcium chloride. The resulting liquid was filtered and then crystallized.¹²

Dizé developed a very important process for the drying and preservation of beef meat, lamb, and poultry^{13,14} (see below) and afterwards published the following piece of news in the *Moniteur* (or *Gazette Nationale*) of February 22, 1794: "*La conservation des viandes par le muriate de soude (sel marin) est...un objet essentiel en ce moment...Tout le monde sait que le muriate de soude...imprime tellement le gout salé...qu'on ne peut le lui enlever que par...lavages répétés...J'ai des viandes conservées depuis un an qui sont en très bon état. Le procédé auquel je les soumetts est très simple et sans nul inconvénient pour la santé...J'invite mes confrères chimistes, qui auraient*

travaillé sur cette partie, à se présenter d'ici à un mois au Comité de Salut Public, pour déposer leurs travaux; car, à cette époque, j'y déposerai mes résultats" (the conservation of meat by the use of salt is...an important objective at this time... Everyone is aware that salt... imparts a salty taste... that can be removed... only after several washes. I possess preserved meat prepared more than a year ago that is in a very good state. The treatment procedure is very simple and without health inconveniences... I invite my fellow chemists that have worked on the subject to appear in front of the Committee of Public Health within one month, to deposit their results, because by then I will present mine).

Dizé passed away on August 21, 1852, at the age of eighty-eight years. His death was noted in many scientific journals of the time and his work praised very warmly. For example, A. Chevalier wrote in the *Journal de Chimie Médicale* (p. 667, 1855): "*Dizé... est un des homes qui a rendu à son pays le plus grands services; on lui doit la découverte, de concert avec Le Blanc, de la fabrication de la soude artificielle, découverte qui, au dire de Liebig, peut être considérée comme la principale cause de l'essor extraordinaire de l'industrie moderne...*" (Dizé is one of the men that has rendered to his country the largest service; to him we owe, together with Le Blanc, the discovery of the fabrication of artificial soda, a discovery that according to Liebig can be considered the main cause for the extraordinary development of modern industry).¹

SCIENTIFIC CONTRIBUTION

Dizé published near thirty papers and scientific reports on his activities, as well as on those of others. Many of his publications are related in one way or another to his activities as assistant to Darcet and as Chief Pharmacist of the Army. Here we describe the most significant ones particularly that derived from his relation with Le Blanc and the manufacture of synthetic sodium carbonate.

Coloration of bread by melampyrum¹³

Melampyrum is a wild perennial plant belonging to the *Scrophulariaceae* figwort family, known to grow together with wheat and its seeds to communicate to wheat flour a black or reddish-violet color and a bad

taste to the bread baked from it. There are several varieties of the plant, which are usually eaten eagerly by cows, for this reason the plant is commonly called cow's wheat.

At Dizé's time there had been many publications detailing the characteristics of the seeds of the plant, but none on the components that communicate the undesirable color and taste to wheat flour. De Bertelmy, comptroller of the flour wholesale market in Paris and in charge of litigations regarding the quality of the flour, requested from Dizé to address the subject and develop a procedure for detecting the presence of the melampyrum variety field cow-wheat (*melampyrum arvense*) in wheat flour (This variety was also called poverty weed, as its seeds devalued the value of corn).¹

In the introduction to his paper on the subject¹³ Dizé summarized all the known facts about the properties of melampyrum seeds. The fresh seeds have a weak mahogany color that turns black upon drying. Pressing the grains strongly between two pieces of glue-less paper leaves a permanent oily stain. The grains have an herbaceous and unpleasant taste, their husk is very hard, ligneous, hard to crack, and yields a white amygdalate, which can be flattened in the pestle in the same way as milky seeds. Infused in cold distilled water they communicate to the water a light tawny greenish color; in boiling water they swells and whiten. This concoction does not change the color of red or blue litmus paper. Addition of a few drops of aluminum sulfate separates a greenish starch; addition of potassium bicarbonate precipitates a yellow-green lac. Ammonia in contact with the seed acquires a yellow color; saturated with a solution of aluminum sulfate results in a lemon color precipitate. An interesting finding was that the grains of melampyrum did not contain the violet dye naturally but developed it artificially, as in the case of indigo, after fermentation. The coloration appears when fermentation takes place in the presence of a cereal. The dye diffuses very easily and a few grains of the seed are capable of tinting a large amount of bread. Contrary to human beings, animals like dogs and chicken do not reject the colored bread in their diet.

In spite of all his efforts, Dizé was unable to isolate the coloring factor and, for this reason, tried to

determine which component of wheat flour led to the appearance of the tint. The experimental plan he followed is a very good example of his analytical reasoning in solving a difficult problem.

First, he dissolved an amount of starch in a boiling concoction of melampyrum grains, without obtaining immediately any red tint. The starch after being dried completely remained colorless. Afterwards he digested the seeds with cold acetic acid diluted with two parts of distilled water and observed that the solution acquired a very intense tawny color while simultaneously the seeds acquired a very strong red-violet color in their external and internal parts. A portion of the liquid phase was then added to a pasty aqueous dissolution of starch and the whole dried by heating with boiling water. This time the dry starch had a light violet color. The same acetic tincture was applied to fresh gluten extracted from wheat flour and the product dried completely. The solid thus obtained had a strong violet color.

These properties of the acetic tincture of the melampyrum grain of developing a red color only after it combined with starch, even more intensely with the glutinous matter of wheat, immediately after the water and the acetic acid had been evaporated, led Dizé to believe that the acetic acid formed during the fermentation of bread might well be the factor leading to the development of the red color in bread prepared with flours containing melampyrum.

In order to test this hypothesis he baked two loaves of breads made with melampyrum flour. To one loaf he added the usual dose of brewer's yeast and had it go through the panary fermentation. The second loaf was baked unleavened. After baking, the interior of the first loaf was tinted strong red violet, while the unleavened bread was colorless. Dizé repeated this test many times, with the same results. Consideration of the facts that fermentation of the bread stops when acetic acid forms, and the phenomenon of red coloration of starch and gluten by the acetic tincture of the grains of melampyrum, led him to believe that acetic acid is the principal agent in the development of the red color during the baking of bread.

In order to test this hypothesis Dizé performed the following assays: (a) he kneaded pure flour with a wa-

ter concoction of the grains of melampyrum. The bread was baked in a platinum capsule and remained colorless; (b) another loaf of bread was prepared with the same amount of pure flour and enough of the acetic tincture. The bread was baked in the capsule as before, and at the end of the process it was strongly colored red violet; (c) the same amount of melampyrum meal was kneaded with enough acetic acid diluted with two thirds of water and the bread placed immediately in the platinum capsule and baked. It acquired the same color as that in the previous essay; (d) in order to test if the water and the acetic acid were the only means for extracting the coloring matter from melampyrum grains, Dizé digested the seeds in cold alcohol of 38 °Bé strength. The alcohol took only a very slight greenish color. He now mixed this alcoholic tincture with three times its weight of water and used it to knead a bread of pure wheat flour. Baking produced no color. Finally, he made a second test with the same alcoholic tincture to which he added acetic acid. Once again, the bread did not become colored.

From these results Dizé concluded that field melampyrum contains a coloring substance, which is very soluble in water and stains it mauve yellow. This substance is totally dissolved by acetic acid, and changes its color to violet red when in contact with starch, and particularly with gluten during the baking of bread. Unleavened bread prepared with melampyrum flour does not come under the action of acetic acid, and hence it does not become colored. When the acid is present, either by addition to unleavened bread or as a result of bread fermentation, then in both cases the bread takes the violet coloration of starch, and, particularly that of gluten.

According to Dizé this peculiar action of acetic acid upon the coloring matter of the grain of melampyrum during bread baking offers a good testing procedure for detecting its presence in wheat flour. He recommended that the essay be done as follows: Take 15 g of the flour to be tested and prepare a paste with enough acetic acid diluted with two parts of water. Place the dough in a silver spoon and heat it long enough to bake the bread. If the flour in question contains melampyrum the interior of the bread will be colored red violet.¹³

Preservation of meat^{14,15}

Jean Andres Cazalet (1776-1821), a chemist, experimented on ways to preserve meat by desiccation. The basic procedure, which had been discovered in 1769 by the pharmacist Vilaris in Bordeaux, consisted in drying the meat, cut into small pieces, in a large stove capable of holding up to 1 500 pounds of meat. The load was kept at about 68 °C for 72 h. The resulting product had the same dryness and solidity as dried wood. Part of the fat oozed out but the largest portion remained in the cellular tissue. Nevertheless, all the fat remained solid at the end of the process and had an excellent sweet taste. The dried meat, having the same color as cooked meat, was taken out of the oven, submerged in gelatin syrup made from bones, and then returned to the oven. The additional drying left the meat covered by a layer of solid gelatin looking like varnish. In this final state it could be kept for years without any alteration whatsoever. The water eliminated during the process could be restored with that used to prepare a broth.

When it was desired to cook the meat, it was first washed with water to eliminate the varnish and the water thrown away. The washed meat was left to temper for 12 h in the water that was to be used to prepare the broth and then cooked for 3 to 4 min to finish the cooking initiated in the stove. Salt and cloves were added and the resulting broth had a nice color and consistency, and excellent taste. Comparison of the Vilaris process with that proposed by Dizé shows that the latter differs in doing a preliminary cooking of the meat to separate the albumin from the meat and facilitate its drying. In addition, Dizé's method involves cooking the meat while drying at a higher temperature and lacks the Vilaris's varnishing step, which assures the conservation. An important characteristic of Dizé's process is the coating of the dried meat with concentrated gelatin in order to realize simultaneously the cooking. This step gives the dry meat the property of softening well in water, and permits obtaining the broth immediately.¹⁴

Basically Dizé's process consists in cooking a boneless and fat free piece of beef meat, for 25 to 30 min in hot water, while heating the water slowly to separate the albumin as froth. The meat is then let to dry in air by exposing it for 12 h over a

wicker screen or a net. Afterwards it is completely dried in a stove operating at 68 °C. The dry meat is now coated with a concentrated solution of gelatin to varnish its surface, the gelatin layer is dried and the whole operation finished by storing the product in hermetically closed containers.¹⁴

Users of the product were aware that cooking desiccated meat does not produce meat having the same softness as the fresh product, a disadvantage common with dried fruit and vegetables. A good part of the aroma has evaporated together with the humidity. In addition, dried meat recovers the lost water with difficulty and never returns to its original volume. Also, the fibrin after losing its humidity does not recover its original flexibility, it becomes somewhat hard and its presence is easily felt during chewing. Nevertheless, although dried meat does not represent a succulent dinner, it can easily replace fresh meat during certain stages of a long trip and food prepared from it is unquestionably tastier than with salted meat. Dried meat is not hygroscopic, it can be kept for a long time without changing its nutritional value and the reduction in weight and volume makes it very convenient for transport. The only precaution to be taken during sea voyages or war is to keep it in barrels lined internally with white iron, to prevent attack by rats.

Dizé believed that should the government decide to examine thoroughly the question of meat preservation by desiccation, it could use his process as departing point.^{14,15}

The reaction between alkalis and sodium sulfate¹⁶

In 1803, some years after, the confiscation of the Saint-Denis works, Dizé published the details of the critical step that he developed to make the Le Blanc process viable, that is, the one related to the elimination of the sulfur compounds present in the raw soda.

When heating a mixture of charcoal with an alkaline sulfate to a high temperature the oxygen of the sulfate burns the charcoal and the sulfur combines with the alkali to form a sulfide. This combination of sulfur and alkali is not easy to break up particularly when operating with large loads. Repeated heating of the sulfide at a controlled temperature is not enough for vaporizing the sulfur; whatever sulfur are eliminated burns forming sulfur dioxide that

combines with the alkali. The operation instead of becoming simpler turns quite complicated because it results in a mixture of alkaline sulfide and sulfite.

Addition of calcium carbonate to the mixture, in the mode it was practiced at the beginning of the operations of soda manufacture in Saint-Denis, was a cheap way to facilitate enormously the decomposition of the sodium sulfide. Nevertheless, the soda produced still contained sulfide and sulfite, easily identified by their odor and in the crystallization of the soda salt. Mixing with iron instead of calcium carbonate (or using both substances simultaneously) did not improve the results significantly. Purification of the soda was achieved only after repeated washings, calcinations, and crystallizations.

This was the initial state of the knowledge on the ways for purifying in a large scale and cheaply the alkalis prepared by the decomposition of alkaline sulfates.

Dizé then gave a more detailed description of the process he developed at Saint-Denis for decomposing alkaline sulfides and sulfites to produce pure sodium carbonate. After reacting the sodium sulfate with a mixture of charcoal and calcium carbonate, the raw sodium carbonate was washed with lye in order to eliminate the alkali. The resulting solution was usually yellow colored and its odor reminded that of a sulfide. Addition of a few drops of diluted sulfuric acid precipitated the sulfur while hydrogen sulfide and sulfur dioxide were released violently. The solution was then evaporated to dryness and the resulting sodium carbonate crystals released hydrogen sulfide and sulfur dioxide when treated with sulfuric acid. This carbonate was less pure than that from the first crystallization. To eliminate the dissolved sulfur and the sulfite the solution was first brought to boiling and then semi-glassy lead oxide in powdery state was added. The lead oxide reacted from the sulfur in the alkali precipitating insoluble lead sulfide and oxidizing the sulfite to sulfate. The lye became transparent while the lead oxide changed its color from red to strong chestnut or blackish, depending on the amount of sulfur contained in the alkali. Addition of diluted sulfuric acid resulted only in the release of carbon dioxide, without precipitation. The purified lye precipitated white lead nitrate and green cupric

sulfate while before treatment with lead oxide it precipitated lead and copper as their sulfides, both having dark chestnut brown color. It was clear then that semi-glassy lead oxide can be used to purify in a large scale the soda originating from the decomposition of the sulfate.

In the following stage of development, Dizé found that substitution of the lead oxide with manganese oxide, well pulverized, led to the same results. This was a significant improvement of the process because manganese oxide not only was cheaper but also could be recycled many times after calcination. These findings led Dizé to explore the possibility of using manganese oxide for decomposing barium sulfide and produce barite.¹⁶

At that time, the common procedure for making barium hydroxide involved reacting barium sulfate with charcoal to yield a barium sulfide soluble in water. The sulfide was then decomposed with nitric acid and the acid eliminated by distillation, leaving a solid residue of pure alkali in the alembic. The procedure was very expensive because of the large quantity of nitric acid required. Dizé believed that barite could become a valuable material in the arts, if it were available at a reasonable price.

After much experimentation Dizé developed the following alternative process: Barium sulfide was first prepared by decomposing barium sulfate with charcoal, it was afterwards dissolved in water and the solution clarified by decantation. The clear solution was then boiled with powdered manganese oxide until its yellow color disappeared and became clear and limpid. During boiling the intensity of the sulfurous odor diminished and was replaced by an alkaline odor; at the end of the process the taste of the liquor became very caustic. Cooling the solution separated the barite by crystallization. Again, this barite precipitated lead nitrate and cupric sulfate as a white and a blue precipitate, respectively. Sodium hydroxide and barium hydroxide prepared by this procedure were very pure and commercially attractive.¹⁶

Sodium carbonate

The development of sodium carbonate as a commodity and the life and works of Nicolas Le Blanc (1742-1806) have been described in previous publications,^{17,18} hence only the main details will be repeated here.

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 imported from Eastern Europe and the Colonies, from seaweeds growing in Scotland, Ireland, Norway, and Northern France, and from barilla, a salty plant growing mainly in Alicante, in the Mediterranean coast of Spain. The two carbonates were an essential raw material for the textile, glassmaking and soap industries. Before the Revolution the *Académie des Sciences* had expressed the wish that French industries should search for a process for manufacturing sodium carbonate starting from sea salt, thus liberating the country from its foreign dependence for the raw material.¹⁸

About 1777 Jean Claude de la Méthière (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. Louis-Jacques Thénard (1777-1857) *et al.* had analyzed de la Méthière process and commented 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, which could be converted economically into sodium carbonate only with the help of carbon dioxide.¹⁹

Le Blanc began to work on the soda problem about 1784 and by 1787 he understood that its solution lay in modifying La Méthière's impractical process. After much experimental work he developed a process in which the first step was the production of sodium sulfate by reacting sodium chloride with sulfuric acid. The sulfate was then reduced with coal to the sulfide, which in turn was reacted with chalk or lime to form soda and calcium sulfide.¹⁸

The Duc d'Orléans was interested in industrial investments and on hearing about Le Blanc's achievements, requested from Darcet to certify the merits of the soda process before he would finance it. Darcet, who at that time was fully occupied with his work at the Mint suggested to Le Blanc to use the services of his assistant Dizé: "*Je ne puis m'occuper de suite de votre affaire; si vous êtes pressé, je chargerai Dizé, mon élève, de constater votre procédé*" (Pres-

ently, I cannot occupy myself with your request, if it urges you I can ask Dizé, my student, to verify your procedure). Le Blanc agreed and thus, on March 1789, under the supervision of Dizé, the first trials of the process were initiated in Darcet's private laboratory. The incineration method consisted in burning a mixture of three parts of powdered charcoal with one of dry sodium sulfate. The operation was finished when the charcoal had burned completely and was reduced to ashes. The first experiments yielded a mixture of sodium sulfide and sulfur dioxide, strongly combined. This series of experiments lasted 15 d during which Le Blanc tried unsuccessfully to solve the problem by performing the calcinations with different varieties of charcoal. Le Blanc was dismayed, claiming that before he had succeeded in obtaining pure soda by this procedure. Nevertheless, Darcet declared that the negative results did not allow him to give a favorable opinion to the Duc or Orleans. At Le Blanc's request, he agreed to postpone his report and offered to Le Blanc his laboratory at the Collège de France for continuing the research in collaboration with Dizé. Dizé and Le Blanc embarked in a new set of experiments, which lasted three months. Its was at the end of this period, when the funds were almost exhausted, that Dizé observed during an experiment the fusion of part of the mixture prepared with a concentrated solution of sodium hydrosulfide, limestone, and a little of powdered charcoal. This portion, after being dissolved in water, filtered, and analyzed with acids and lead nitrate, was substantially less sulfurized than the soda from the numerous experiments done previously. Dizé promptly communicated this discovery to Darcet, who advised him to repeat the experiment in a crucible heated under mixing to the temperature at which there was complete fusion. The experiment was performed the next day and after 24 h Dizé and Le Blanc noticed for the first time the presence of crystals of sodium carbonate with all its distinguishing characteristics. Le Blanc was so flabbergasted that these experiences had given better results his original process that next morning he did not report to continue the work. Two days afterwards, when Dizé arrived at the laboratory he found Le Blanc already working, well ahead in the experiment, and busy pulverizing a sample of soda.

When Dizé remarked that this sample was similar to the last run, Le Blanc replied that the new procedure was actually the same he had proposed originally. Dizé, extremely irritated by Le Blanc's attitude, answered him: "*Il est bien étonnant que vous n'en ayez jamais parlé, surtout lorsque vous vous êtes présenté à M. Darcet, et que vous ayez souffert qu'on demandât des fond à M. d'Orléans pour chercher avec tant de peine ce que vous prétendiez connaître si bien!*" *Voici trois mois que nous tourmentons pour vos intérêts! Comment donc peut-il se faire que, pendant le cours de nos travaux, je vous aie vu si désolé, lorsque'un mot de votre part pouvait mettre fin à toute difficulté?* (It is astonishing that you have never talked, especially when you were introduced to M. Darcet, and so insistent when demanding funds from M d'Orléans to investigate with so much work what you now claim to know so well. It is already three months that we torment ourselves for your benefit. How can it be that during the three months of our work I have seen you so desolate, when one word from you would have put an end to all difficulties?).^{1,18}

What was left now was establishing the optimum amounts of coal and calcium carbonate required and to try the process on a larger scale. Dizé, by himself, constructed at the Collège de France a small reverberation furnace; about three foot long, where larger mixtures could be treated and at the same time observe the phenomena that took place at different stages during the decomposition of sodium carbonate. Ultimately, Dizé and Le Blanc prepared one batch of 30 pounds of raw soda and another of 16 pounds of crystals.¹

These two products were the basis of Darcet's positive report to the Duc, and as a result the Duc promised to invest 200 000 francs to build a factory. In this activity Le Blanc did not intervene much since he lacked experience on industrial operations (he was a physician) or theoretical calculations. After Darcet proposed that Dizé be part of the projected society an official agreement was signed in 1791 between the Duc of Orléans, represented by Henri Shée, the operations secretary of the Duc, Dizé and Le Blanc. The factory to be built would manufacture sodium carbonate, ammonium chloride, and also white lead by a procedure developed by Dizé.¹⁸

It was at this time (September 25, 1791) that without considering Dizé, Le Blanc took out a patent on the soda process in his name only. The patent, which was secret so that no public disclosure was necessary, granted Le Blanc the exclusive right to work or license his process for a period of fifteen years. This act led to much argument between Le Blanc and Dizé, who demanded his rights.¹

A plant was built near Saint-Denis, at a place known as Maison-de Seine, four miles from Paris, with easy access for the 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.¹⁸

The crisis

Meanwhile, this industrial discovery had made a strong impression in the industrial world and its importance did not slip by from the government. Jean-Antoine Carny (1751-1830), commissioner of gunpowder, wishing to put an end to the state of debility of French commerce, exhausted by the war, and to provide for the lack of natural soda that was no longer imported to satisfy the pressing needs of industry, appealed to the *Comité de Salut Publique* to demand the publishing of all the available private procedures for manufacturing soda and make France a new source of the material. Shortly thereafter the Committee issued a decree ordering all citizens who had initiated manufacturing facilities, or had obtained patents for producing soda from marine salt, to make known to the Commission the location of their manufacturing plants, the state of their facilities, their manufacturing procedures, the amounts of soda they were selling, the amounts they could supply, and the time it would take to initiate manufacturing operations.¹

After all the required information was collected, a special committee was appointed to examine the processes and to survey the factories. Its members were Jean Darcet (1725-1801), Bertrand Pelletier (1761-1797), Claude Hugo Lelièvre (1752-1835), and Alexander Giroud. Their lengthy report was published in June 1794 and a considerable part of it dealt with the Le Blanc process²⁰: "We have inspected their establish-

ment, we have verified their process and we believe it is certain to be successful. This new works 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 process of citizen Le Blanc, 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."

Although France was at war, the report in all its details was made public. In spite of being protected by a patent, it provided a full description of Le Blanc'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.). This publicity gave birth in France to a very large number of manufacturers of soda and the imperial government later recognized the production of these factories by canceling the tax on marine salt destined to the production of soda. The French process produced soda at about 60 % the price of the one imported from Spain and the large amounts of HCl produced as by-product contributed in a very large measure to the development of the bleaching industry, manufacture of paper, manufacture of chlorine, etc. After the peace of 1812 English industrialists learned the details of the Le Blanc process and began making soda in increasing amounts in England.

With regards to the future dispute about the paternity of the process, the committee reports stated, among other things: "*Ce procédé, don't le citoyen Le Blanc est l'auteur, consiste... (This procedure, of which citizen Le Blanc is the author, consists...).* L'établissement est déjà tout formé à Franciade; le citoyen Dizé, l'un des co-associés, en a dirigé particulièrement la construction; elle est faite de manière qu'il peut servir également à toute espèce d'usages et

de procédés de ce genre; c'est une justice que lui rendent ses co-associés" (The establishment has already been built up in Franciade, citizen Dizé, one of the co-associates, has personally directed the construction; it is of such a nature that it can serve equally well for the use and procedures of its nature, it is a recognition given to him by its associates). That is, Le Blanc is the owner of the idea and Dizé has brought it into practice.

The injustice

The exploitation of Saint-Dennis was in full production when the tragic death (by the guillotine) of the Duc of Orléans (1793) precipitated its demise. According to the laws of the Revolution government, all the possessions of a person found guilty of treason were confiscated and became property of the state. Since the Saint-Denis factory was operated by a society financed by the Duc, the Finance Ministry hit the infant industry with a stringent forced administration of 12 years, expelling from their property the surviving associates, seizing the social capital, selling all the soda stock, dismantling the society, and making the patent public property. On February 1794, the authorities closed the factory and Le Blanc found himself without his patent and without the factory, all now property of the State. Le Blanc was ordered to vacate the premises and was also notified that his salary would cease after April 1, 1794. Thus, from day to the other, Le Blanc's dreams were shattered; instead of looking forward to a very profitable business he was ruined and dependent on a small government salary to support his family. From there on his life was a long downward road of futile fighting for his rights.^{1,18}

As mentioned above, Dizé, as soon as the Duc was imprisoned, read the picture clearly and joined the Army ambulatory hospital, to escape the consequences of being under suspicion because of his relations with the Duc.

Although a special law about patents of invention accorded an indemnification for the case where its use was interrupted by a government act, it was not until the Empire that the partners could obtain liquidation, already requested under the *Directoire*. A strange fact is that each partner carried out the fight for indemnification separately. In addition, Dizé's initial attitude was

passive and joined the battle quite late.

The author will now describe the struggle of Le Blanc and Dizé until the settling of the fight.

Le Blanc's efforts

Le Blanc spent nearly eight years suing for ownership of his plant and petitioning incessantly for reimbursement for the losses he had incurred. Finally, in April 1801, the Minister of Finance ordered that the works at St. Denis be provisionally handed back to Le Blanc 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. Dizé and Shée took the easy way out and agreed to dissolve the partnership and sell to Le Blanc their part of the society, the property, and the factory at Franciade. Le Blanc took over the operation under severe limitations because the factory was to remain confiscated until the State got its share and the Tribunal de Commerce issue its decision regarding the conflict between Le Blanc's and the State.¹⁸

After four years of discussions, the Tribunal 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. Le Blanc presented to the board a long report, in which he fixed the total losses incurred by the society as 2 243 000 francs. The report of the arbitrators, handed in on November 8, 1805, assigned a total indemnification of only 280 777 francs, of which the Nation was credited with 164 160 francs, Le Blanc and Dizé 52 473 francs each, and Shée 11 660 francs. Even this inadequate sum was never paid to Le Blanc, Dizé, Shée, or their children.

The tribunal's decision was the final blow to Le Blanc; he could not take it anymore and on January 16, 1806 he committed suicide.

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, and second, Joseph de Fermon (1752-1831), the Liquidator General, who was en-

titled to issue non-redeemable five per cent bonds in this amount, delayed payment until he had learned the details. On November 5, 1807, De Fermon rejected the resolution and the opinion of the arbitrators and ruled out that the indemnity in no case could not exceed the value of the factory. Consequently the account had been squared when the soda works had been turned back to Le Blanc and his partners.¹⁸

Dizé's efforts

After Le Blanc's death Dizé bought the Saint-Denis works and indemnified Shée and Le Blanc's inheritors. Shortly thereafter, Gautier, Barrera, Aufrye, and Jean Darcet's children, who had failed at their attempts to manufacture soda by means of barium sulfate in the facilities they owned at la Gare, near Paris, approached Dizé and requested renting his facilities. This offer was accepted immediately and the new partners started without delay to manufacture soda following the Le Blanc and Dizé procedure, as published by the *Comité de Salut Publique* in 1794.¹

At this stage, Dizé decided to appeal to the State Council, which could become his only support. Unfortunately, at that time, the Imperial government had issued the two decrees declaring the erasure of all debts of the State (February 25, 1808 and December 13, 1809) and Dizé was unable to find a lawyer who would dare to plead in favor of a liquidation dating back to 1796. All defenders feared their disbaring, which was tacitly implied in the decrees, if they dared to claim against the State. Everything had been planned in advance to crush any efforts and proceedings and to rebuff the justice invoked; the denial was flagrant.¹

On May 9, 1809, all the French manufactures of soda and the soap manufacturers in Marseille, petitioned the Legislative to exempt from the tax on marine salt all manufacturers of soda. This exemption was granted upon recommendation of the State Council. Ironically, on one hand the government granted this exemption, which carried a substantial economic benefit for the manufacturers, and on the other hand disregarded the rights of the inventors that led to the establishment of the industry.¹

Dizé continued with his claims during the different governments, until on March 9, 1818, he received

from Louis Emmanuel Corvetto (1756-1821), the Minister of Finances, a harsh answer in which he threatened that if Dizé did not desist of his reclamations against the Revenue, the authorities would reopen the case from the very beginning. Dizé understood the hint and decided to keep silent.¹

After the change of government to the constitutional one, Dizé renewed his claims, and again he got a sharp reply: "*Vous ne serez jamais payé*" (you will never be paid).¹

Towards the end of 1855, at the conclusion of the First International Exposition in Paris, the descendants of Nicolas Le Blanc addressed to the Emperor Napoleon III a petition requesting reparation for the damages caused to their grandfather. The *Académie des Sciences* was requested to emit its opinion on the legitimacy of the reclamation for aid. On hearing about this petition, Léon Dureteste, Dizé's son-in-law, approached the Académie in the name of Dizé's widow and children, demanding their share: "*Je viens d'être informé que la famille de Le Blanc s'occupe de faire valoir auprès de l'Empereur les services que son chef a rendus à l'État en créant l'industrie de la soude artificielle et que l'Académie est saisie de l'examen de ses titres. Je viens au nom de la veuve de M. Dizé et de ses enfants réclamer pour M. Dizé la part qui lui revient dans la découverte de la soude artificielle et dans la création de cette importante industrie. Les titres de M. Dizé résultent d'un grand nombre de pièces authentiques imprimées et manuscrites que je tiens à la disposition de l'Académie*" (I have been informed that the Le Blanc family is busy in the Emperor's court, trying to embellish the services that their head has contributed to the State by the creation of the industry of artificial soda and that the Academy is handling the evaluation of the titles. In the name of M. Dizé widow and children, I claim his part in the discovery of artificial soda and the creation of this important industry. Dizé's titles are the result of a large number of authentic documents, printed or manuscript that I put at the disposition of the Académie).

The Chemistry Section of the *Académie des Sciences* was requested to emit its opinion on the legitimacy of the reclamation for aid by both families. The Académie appointed an evaluation committee consisting of the most important

chemists of the time: François Ernest Ballard (1833-1894), Michel Eugène Chevreul (1786-1889), Jean-Baptiste André Dumas (1800-1884), Théophile-Jules Pelouze (1807-1867), Victor Regnault (1810-1878), and Thénard.¹⁸

The report, delivered on March 31, 1856, and published in the journal of the Académie¹⁹ pointed out that taking into account that the events had taken place more than sixty years ago, and that all the participants and witnesses had passed away, the commission could only base its opinion on written evidence, without considering oral tradition or old personal claims.²¹ The commission understood that Le Blanc and Dizé had put up together the first soda factory and that Dizé, in 1810, four years after Le Blanc's death, had published an historical account of the discovery which differed from others.²²

The commission by a majority of five to one established unequivocally that the manufacturing process belonged wholly and irrevocably to Nicolas Le Blanc. Its main arguments were the following: (1) the discovery of the process was solely due to Le Blanc, (2) Dizé's collaboration was limited to help in determining the best proportions of the raw materials and to aid in laying out and starting the factory, (3) any testimonial to the inventor of the process should be made to Le Blanc's memory and addressed to his descendants, and (4) 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. Chevreul gave the dissenting opinion, based on the following facts: (a) Dizé was an associate of the Duc, Le Blanc, and Shée, as attested by the notarized documents signed on February 12, 1790, and January 27, 1791. These documents fixed the relative parts of the partners to the net benefits to be obtained from soda, sal ammoniac, white lead, and any other product they would manufacture in the future, (b) the manufacturing process certified by Darcet on March 14, 1790, called for heating in a crucible 100 parts of sodium sulfate, 50 parts of limestone, and 25 parts of charcoal, (c) in Le Blanc's patent, taken a year after, a mixture composed of 100 parts of sodium sulfate, 100 parts of limestone and 50 parts of charcoal, was reacted in a reverberating fur-

nace. Chevreul added that, without examining the question if Le Blanc had or not the right to take a patent in his name, after he had associated with Dizé, Shée, and the Duc, he wanted to ask: does not Dizé have a large part in the modification of the procedure certified by Darcet in 1790? Chevreul believed that the answer to the question was very simple: Dizé, aged 20 and odd years, was the chemist of the society, and it is by this title that he become associated with a Prince, a 40-year old physician (Le Blanc) associated with the court of the Prince, and a businessman (Shée). That this is the correct reason is clearly justified in the sentence of the 1797 report about manufacturing procedures,²⁰ in which it is said about Dizé "*C'est une justice que lui rendent ses co-associés*" (see above). Chevreul ended his opinion stating that to accept that the discovery of the soda manufacturing procedure belonged totally to Le Blanc was contrary to his convictions.

In a separate letter to Dureteste, dated March 31, 1856, Chevreul promised to provide more details for the reasons for his dissenting opinion in a book (*Histoire de la Chimie*) which he intended to publish (and never did): "*Dans mon Histoire de la Chimie j'exposerai nettement mon opinion sur la découverte de la préparation de la soude.*"¹⁹

The report was sent to the Emperor, where it was filed, without further action.

CONCLUSION

Although most historians agree in assigning the discovery of the process to Le Blanc alone, it seems reasonable to assign part of it to Dizé. Le Blanc proposed the basic reactions, but it was Dizé who found the way to make them an industrial reality.

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