

# Jean Hellot. A pioneer of chemical technology

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**RESUMEN.** Jean Hellot (1685-1766) es considerado como uno de los fundadores de la tecnología química, metalúrgica, y textil en Francia y Europa. Aun cuando sus publicaciones fueron pocas, su impacto fue significativo en la revolución química que tuvo lugar en el siglo diecinueve. Hellot investigó el zinc y sus compuestos, los metales preciosos, la preparación del fósforo y del éter etílico, la fabricación de la porcelana y las tintas invisibles y el mecanismo de acción de los colorantes sobre las telas. Un importante descubrimiento fue la fotosensibilidad del papel impregnado con nitrato de plata.

**ABSTRACT.** Jean Hellot (1685-1766) is considered one of the founders of the chemical, metallurgical, and textile industry in France and Europe. Although he published little, his impact was significant in the chemical revolution that took place in the nineteenth century. Hellot investigated zinc and its compounds, the precious metals, the preparation of phosphorus and ethyl ether, the manufacture of porcelain and invisible inks, and the mechanism of dyeing. An important discovery was the photo sensibility of paper impregnated with silver nitrate.

## LIFE AND CAREER

There is very little information regarding the early life of Jean Hellot: most of it has been gathered in the doctoral thesis of Doru Todériciu (1927-)<sup>1</sup> and the eulogy pronounced by Jean-Paul Grandjean de Fouchy (1707-1778), permanent secretary of the *Académie Royale des Sciences* on the occasion of the death of Hellot.<sup>2</sup>

Jean Hellot was born in Paris on November 20, 1685, the son of Michel Hellot and Marie-Anne Reynaud. As the child of a well-to-do family, he received his first education at home, and according to the desires of his parents, he was supposed to have followed an ecclesiastical career. It is said that among the belongings of his grandfather, a physician, he found an old book on chemistry, the lecture of which sparked an irresistible attraction to this science. He took his first steps in chemistry through his friendship with Etienne-François Geoffroy (1672-1731), the inventor of the tables of affinities, and who in 1729 married one of Hellot's nieces. Hellot made several trips to England where he became acquainted with the physician and collector Hans Sloane (1660-1753) (whose collection became the foundation of the British Museum) and Daniel Newton. His studies were suddenly interrupted by economical

ruin after the debacle caused the application of the economical theories of John Law (1671-1729).<sup>a</sup> These circumstances led him to accept the direction of the newspaper *Gazette de France*, a position he kept between 1718 and 1738; afterwards he was able to return to his activities in chemistry. His successful journalistic activities led him to become acquainted with many of the important French figures on science, literature, and politics, among them, Philibert d'Orry (1689-1747; Minister of Finances), and Antoine Louis Rouillé (1689-1771; Foreign Secretary), which would be of great help in the development of his scientific career.

Hellot published his first paper of chemical nature in 1735<sup>3</sup> and the following year was appointed *adjoint chimiste* of the *Académie Royale des Sciences*,<sup>b</sup> replacing Charles Marie de la Condamine (1701-1774) (Paul Jacques Malouin, 1701-1708, substituted Hellot as *adjoint chimiste*). In 1739 he was promoted to *pensionnaire chimiste surnuméraire* (the number one candidate to the next position of *pensionnaire* to become open; this unexpected new rank was originated by the death of Charles-François Du Fay, 1698-1739), and finally, in 1743, he was appointed *pensionnaire chimiste*, after the death of Louis Lémery (1677-1743). In 1740 he was

<sup>a</sup>John Law was a Scottish economist who believed that money was only a means of exchange that did not constitute wealth in itself, and that national wealth depended on trade. He is said to be the father of finance, responsible for the adoption or use of paper money or bills in the world today. Law urged the establishment of a national bank to create and increase instruments of credit, and the issue of paper money backed by land, gold, or silver. It was in this context that the regent, Philippe d'Orléans, appointed Law, as Contrôleur General of Finances of France. Law's pioneering note-issuing bank was extremely successful until it collapsed and caused an economic crisis in France and across Europe. By the end of 1720 Philippe II dismissed Law, who then fled from France.

<sup>b</sup>The three ranks of the Académie of Sciences were adjoint, associé, and pensionnaire chimiste.

nominated member of the Royal Society of London. In the following years he occupied the following positions: *Inspecteur général des teintures du royaume* (1740), replacing Du Fay; contribution to the writing of the decree on the exploitation of coal mines (1744); *commissaire* of the *Académie* to develop the regulation for the refining of gold and silver objects (1745); determination of the true measure of the aune standard of the bureau of the sewing merchants of the city of Paris (1746); commissioner of the *Académie* for the inspection and analysis of the royal mines (1746); *commissioner* of the *Académie* and chemist at the Vincennes porcelain manufacture (1751); chemist with the same function at the Sèvres porcelain manufacture (1756); defender of the decree regulating the exploitation of carbon mines (1758); vice-director of the *Académie* (1750 and 1763); and director of the *Académie* (1751 and 1764).

In 1750 Hellot at the age of 65, married Mlle, Denis, a far relative of his. A year before his death he had two attacks of apoplexy, which led to his death on February 13, 1766, at the age of eighty. He is buried in the cave of the *Chapelle de la Communion*, in Grève. Paul Jacques Malouin (1701-1778), physician to the Queen replaced Hellot at the *Académie*.<sup>2</sup>

In 1669 Jean-Baptiste Colbert (1619-1683), Ministry of Finance of Louis XIV, within his general politics of economic development, created the position of Inspector of Manufactures, in order to have a mechanism to direct the bloom of France's industrial development. Orry recreated this position in 1730 and Hellot was elected to be fill it. The experience he accumulated led him to become an authority on the subjects of dyeing, mineral treatment, mines, etc.

Hellot's earliest researches were in pure chemistry, among them, on metallic zinc and its compounds,<sup>3,4</sup> an explanation for the red color of vapors of nitric acid,<sup>5</sup> on phosphorus,<sup>6</sup> on mineral acid,<sup>7</sup> on Glauber's salt,<sup>7,8</sup> and on the composition of ether.<sup>9</sup> In 1740 the Academy was asked to investigate the purity of certain samples of salt from various sources; Hellot did the major share of the careful analytical work involved.<sup>10</sup> In 1746 he examined standard measures, an investigation arising from a query about the exact length of the aune.<sup>11</sup> Another important part of Hellot's technological career was devoted to the exploitation of mines.

Hellot's contributions to metallurgy are contained in his papers on zinc and on precious metals, and in his translation Christoph Andreas Schlütter's handbook. In 1775, Henri Louis Duhamel du Monceau (1700-1781) and Jean Grosse (?-1744) quoted him with enthusiasm in the memoir where they gave account of the procedure for preparing ether, a procedure that August Siegmund Frobenius, its author, had carefully hidden, and which them and Hellot had made public.<sup>2</sup>

In 1745 he was appointed to go to Lyon to inspect the gold and silver refining operations. Upon his return he was appointed to study and assay the mines of the kingdom. It was at this time that he communicated to the *Académie* a method for performing in cold bas-relief of gold on gold and on silver, a secret that had been communicated by Du Fay, under the condition that it be made public only after the death of the author.<sup>2,12</sup>

Hellot made it known that in order to make a color solid, it was necessary that the dyes be finely reduced to that they can penetrate inside the pores of wool swollen and laundered, and that most of them were retained by a salt insoluble in air and in cold water, of

which they became part. This is the fundamental principle that became known as the key of all dyeing art, after Hellot had examined all the operations, and making it known that it was the basis of all those that gave solid colors, and is not found in any of the fast colors. At the same time he was perfecting the paste used at Sèvres, and discovered many colors to be employed.<sup>2</sup>

It was known that that colored precious stones owed their color to the mineral vapors to which they had been exposed. A piece from a mine of cobalt that came into his hands allowed him to prove this point. It served as a matrix to a large number of multifaceted crystals, all colorless and transparent. Heating this piece in a muffle up to red heat for about two hours, it released sulfurous and arsenical vapors, which made all crystals to become colored and become an assembly of the known precious stones. The sulfurous and arsenical vapors that emanated from the mine had produced this effect.<sup>2</sup>

## SCIENTIFIC CONTRIBUTION

Hellot wrote a small number of papers and books, but their impact was tremendous. Here a few of his contributions is described.

### Metal technology and mine exploitation

The first memoir presented by Hellot after his admission to the *Académie*, was about the analysis and nature of zinc.<sup>3,4</sup> Zinc has been used since ancient times, particularly as brass, its alloy with copper, although its definite chemical was established only in the 18<sup>th</sup> century. Until the 18<sup>th</sup> century brass was produced in Europe by a simultaneous smelting of copper and zinc ores. Hellot tried to determine the chemical properties of zinc and its flower (zinc oxide) by dissolving it in vinegar (diluted acetic acid), wine spirit (aqueous alcohol), salt spirit (aqueous HCl), nitre spirit (aqueous nitric acid), and sulfuric acid. His memoirs on the subject represent the first successful tentative on the analysis of zinc and an update on the preparation procedures for certain of its compounds, particularly the recovery of white vitriol (zinc sulfate) from a solution of zinc in sulfuric acid; to establish the correct nature of the compounds, and to prove definitely that zinc butter (zinc chloride) is produced by the distillation of zinc oxide in the presence of ammonium chloride.<sup>1</sup>

According to Todériciu<sup>1</sup> at the beginning of the 18<sup>th</sup> century the fabrication of metals, the natural extension of mineral exploitation, was in an apparent paradoxical situation. Although the technical aspects, and procedures and equipment for the trade were in a very advanced state, with a extense literature available, this was not the situation regarding fuels, new machinery, aeration and water draining of mines, new furnaces, and particularly, the chemical laboratory in the organization of a modern mining facility. Realizing the situation, Jean Baptiste de Machault d'Arnouville (1701-1794), Comptroller of Finances, understood the need to translate into French the best foreign book available on the subject of foundry of minerals. Hellot was chosen for this task and he selected the German treatise of Christoph Andreas Schlütter on the assays and foundry of mines.<sup>13,14</sup> Hellot's translation describes in detail the landmarks for recognizing the terrains that hide the mines, the ways for testing and extracting the minerals, the art of separating the sulfur and arsenic that mineralize the metal, foundry techniques, metal purification, ways of separating one metal from another

and eliminate foreign substances that accompany them, etc., etc.

According to Hellot, Schlütter's book contained many obscure as well as incorrect statements, and for this reason he decided to modify it in an essential way: "*I believed that it was necessary to change the order that Schlütter gave to his book and not to start with a general description of foundries but by a particular examination of minerals, in order that they be known before they are exploited at large, with the corresponding heavy expenses.*"<sup>14</sup> His two-volume *Traité sur la Fonte des Mines*, although based on Schlütter's book, constitutes by its reorganization of the sections and Hellot's additions, a true original work.<sup>15</sup> An interesting feature of Hellot's book is that it does not describe the exploitation of iron mines, in homage to an extensive work on the subject published previously by Rene-Antoine Ferchault de Réaumur (1683-1757).<sup>16</sup>

The first volume is a description of the parameters required to understand the nature of a mine, and the appropriate means for recognizing, separating, differentiating, and classifying mines. It contains a detailed inventory of all the French mineral resources, details on the construction of a laboratory for metallurgical assays of minerals, metals, and their alloys, details on the construction of a cupel oven and its instrumentation, procedures for analyzing the minerals arriving to the laboratory, (particularly for their content in gold, silver, lead, and tin), the refining of silver, the separation of tin and silver etc., etc. The second volume is centered on the problems of a foundry, roasting, foundry, smelting, refining, etc.; all this explained according to the metal being treated.

Between the publication of the first and second volume of the translation, Hellot, published an additional book related to the analytical chemistry of minerals.<sup>17</sup>

In 1763 the Duke Etienne François de Choiseul (1719-1785), the French Foreign Minister, communicated to the *Académie* a letter received from Pajot de Marcheval, Intendant of Dauphine, informing him of an unknown and alarming phenomenon that was observed in the coalmines of Briançon in his jurisdiction: An inflammable vapor concentrated at the bottom of the works and caught fire with the light of the miners, detonating violently and causing many victims. The Duke requested the help of the *Académie*, which appointed a committee formed by Duhamel, Hellot, and Étienne Mignot de Montigny (1714-1782), to investigate the facts, other phenomena of the same nature that occurred in other mining sites, and to recommend the means to avoid such accidents. The Briançon mine was particularly important because it produced the carbon used by the Royal Army; it had operated without accidents for many years, but the new phenomenon terrorized the miners and affected production.<sup>18</sup>

The committee was aware of similar occurrences in carbon mines located in other places in France and abroad. They believed that the best solution was to provide an emergency exit, to multiply the respiration shafts, so that each galley should have one such shaft at the entrance and exit to facilitate the circulation of air so as to avoid the accumulation of the injurious exhalations. They recommended increasing the circulation of the air by suspending in the respiration shafts near their connecting points, burning carbon braziers suspended from iron chains. By this means

fresh air would be sucked underground and the flammable gases burned by the fire. This was the technique used in Germany. If the local circumstances did not allow the construction of respiration shafts, then building a brick chimney, inside which the braziers were to be suspended, would provide respiration. A side opening in the chimney was to be connected by a long pipe to bring in fresh air.<sup>19</sup>

The *Académie* considered that the final report was of significant public interest and decided to publish in its journal.

Simultaneous with this work, Hellot was occupied with Mathieu Tillet (1714-1791) with the procedures for analyzing gold and silver. Since pure gold or silver do not have the necessary hardness to allow manufacturing coins or silversmith work, it was necessary to alloy them with another metal to make them hard enough for the required purposes (usually red copper for silver, and silver with a little copper for gold). The titer (content) of the precious metal depended on the use the alloy was put to and was certified by the Mint or official assayers. Hellot described he pertinent analytical procedures in one of his papers. One important result of Hellot and Tillet's work finding that the cupel always retained a small amount of the silver, and that this loss, which was ascribed to the alloying, resulting in stamping silver with a lower titer that it really had, representing a true loss to the owner. The results of this work served as the basis of an important regulation on the subject, and led to two important memoirs that Tillet read to the *Académie*.<sup>20</sup>

### Invisible inks

Existence of invisible ink was an essential factor for the activity of ministries of foreign affairs of the time. In the 18<sup>th</sup> century research on their composition was an active field that exerted the sagacity of chemists. In the eyes of the State their secret represented a value similar to that of the philosophical stone of the alchemists. Research and purchase of invisible inks was a government activity.

By occupying himself in the subject, Hellot was not only reacting to a need of his time but also to an economical one. The price of recipes for their fabrication and usage, the difficulties of chemical manipulations, or the lack of quality (accidental exposure, too early, or too easy), justified their election. However, it is necessary to add that the involvement of Hellot in the subject was greatly aided by his previous work in the domain of dyeing of wool and cotton and wool cloths. It was also an extension of his previous researches on certain mineral salts and metallic compounds (bismuth, arsenic, cobalt, etc.).<sup>1</sup>

In his first paper on the subject<sup>21</sup> Hellot described the properties of invisible inks and the ways of making them visible: Invisible inks appeared by the application of an addition material. There were two means for making them visible, or two species of invisible inks. A dissolved substance would normally disappear in the solvent, even if it were colored because the solvent would separate strongly its particles, particularly if the solution was very diluted. It was quite possible that contact with air would result in the evaporation of the solvent, causing the particles of the solute to come closer and recovering their color. Heat could also hasten the phenomenon. But heat acted both on the ink and the substrate, so that it could well be that some inks would not appear under the action of heat. If the invisible

characters were written using a glutinous substance and a fine colored powdered was added on top of it, the glutinous material would be eliminated and the writing appear. But there was more ways to make the characters appear, for example, to spray them with a new liquid or treating them with vapor. These characteristics allowed classifying invisible inks into four classes, according to the method by which they become visible: (a) air, (b) heat, (c) a colored powder, (d) a liquor or vapor. All of the available inks did not disappear once they became visible.

In order to clearly understand these differences, Hellot gave examples of the common inks. In his book on chemistry Nicolas Lémery (1645-1715) provided a detailed description of inks belonging to the first class.<sup>22</sup> The writing was done with a solution of litharge (PbO) or other lead salt dissolved in vinegar. It was then dried in the air and made visible by brushing it with a solution of an arsenic salt. The writing became first yellow and then black. It could be washed away by wetting with acid liquor such as aqua fortis (concentrated nitric acid) or a solution of potassium nitrate. It could be made to reappear again if, once the paper had dried, it was humidified again with the litharge solution. To Hellot this proved that all the effects were due to a series of precipitations and solutions.<sup>21,23</sup>

Another ink of the first class could be prepared by dissolving gold in aqua regia until saturation followed by addition of five to six parts of ordinary water. The message was now written on a white paper and let to dry away from the sun. It would remain invisible for 7 to 8 h and could be made visible (purple color) by brushing it with a solution of fine tin dissolved in aqua regia. Other metals dissolved in the same solvent did not have the same effect. The invisible ink based on gold and tin should be considered an exception to the general rule because it was based on the fact that two metallic substances, dissolved in the same solvent, changed color when mixed, without the meddling of a reaction. The purple color of the gold writing could be erased using aqua regia and made to reappear by brushing it again with the tin solution.<sup>21,23</sup>

The second class corresponded to ink that became visible in contact with air. A typical preparation consisted in adding to a gold solution in aqua regia enough water so that it would not leave yellow spots on white paper. The writing appeared only after being in contact with a large amount of air for about one hour, turning dark violet, almost black. If instead of being in contact with air it was kept in a well-closed box, or in well-pleated paper, it would remain invisible for 2 to 3 months and afterwards would turn dark violet.<sup>21,23</sup>

The third class corresponded to ink that became visible when rubbed with a brown or black powder. A typical composition contained any of the sugars expressed from fruits and plants, animal milk, and other fatty and viscous liquids. After writing and dried, the writing could be made visible by rubbing lightly with a fine powder of colored earth or carbon powder. Hellot believed that the letters became colored because they were formed by a kind of glue that retained the rubbing powder.<sup>21,23</sup>

Finally, the fourth class corresponded to the writing that appeared when heated. This very ample category comprised all the infusions and all the solutions where the dissolved matter was easily carbonized by gentle heating. A common composition was an aqueous solution of ammonium chloride. The writing appeared

only after heating or being pressed with a lukewarm iron. To Hellot it seemed that the fatty part (!) of ammonium chloride burned and was reduced to carbon, at a temperature not high enough to burn the paper. A disadvantage of this ink was that when left alone the humidity of the air would spread the writing causing the letters to blur and eventually become illegible.<sup>21,23</sup>

Hellot became particularly interested in the ink obtained from a pink material obtained from the mine of Schneeberg (Saxony) in Germany, which turned blue when heated. Hellot proved that his new invisible ink constituted a new species that should be classified as a fifth additional class. Once it had been made visible, it could be made invisible, visible again, etc., as many times as desired, without any addition, without alteration of the color, and for a long time because it was made of a well-conditioned material. Exposed to heat it appeared, exposed to cold it disappeared, and the cycle repeated as many times as desired. According to Hellot, It was only necessary for the heat to make the particles move, and by this means, to become closer. He thought that heat, perhaps, brought the particles to the surface: on cooling they descended again into the bulk of the tissue. Another important advantage of this new ink was that it could be made in different colors, such as green, blue, yellow, colombin, rose, and carmine, depending on how it was treated. Hellot reported that the final color of the writing solution depended on the additional metals present in the mineral; for example, it would be rose if the mineral did not contain fluor or quartz.<sup>21,23</sup>

Hellot was honest enough to report that he was not the first to discover the property of the solution of becoming green blue when heated. A German artisan from Stolberg (Rhineland) had shown to members of the *Académie* a rose colored salt that became blue when heated. He also showed them the mineral from which his solution was obtained. He named it *minera marchisitaë* (a name also given to a bismuth mineral). He extracted the tincture by treating the mineral with aqua fortis and fixed it with common salt. After seeing this salt, Hellot tried several classes of cobalt (cobolt), without success until he tested an arsenic bismuth mineral given to Geoffroy by the Maréchal de Villeroy. This salt had the same properties as the one shown by the German. In order to try to find the reason for the particular property of the salt, Hellot decided to investigate all the different cobolts he could find making a detailed analysis of the minerals, which could generate this special ink, particularly of bismuth and arsenic. Thus he studied the bismuth mineral of Dauphine, another cobolt, which had already been described by J.G. Linck (author of a British Pharmacopoeia, who believed that bismuth was composed of tartar, tin, and arsenic, etc., which led him to isolate and describe bismuth and to reject the thesis that it was a mixture of metallic substances). Hellot's ink, which was basically an aqueous solution of cobalt chloride, obtained from the salts present in mixed minerals rich in arsenic and bismuth, was put to a large use. The invention of ciphered messages led eventually to the decline of invisible inks.<sup>1,21,23</sup>

A interesting point of historical value is that in his first memoir about invisible ink,<sup>21</sup> Hellot wrote "*la dissolution de l'argent fin dans l'eau-forte, qu'on affoiblie ensuite par l'eau de pluie distillée...fait aussi une écriture invisible, qui tenuë bien enfermée, ne devient lisible qu'au bout de trois ou quatre mois; mais*

*elle paroît au bout d'une heure si on l'expose au soleil, parce qu'on accélère l'évaporation de l'acide...*" (the solution of silver in aqua fortis, diluted afterwards with rain water...also makes an invisible ink, which kept in the dark does not become visible before three to four months, but appear within one hour if exposed to the sun because it accelerates the evaporation of the solvent). This result permits attributing to Hellot the discovery of the photo sensibility of paper with silver nitrate, and its application in the art of photography.<sup>1</sup>

## Phosphorus

We will first summarize the work done by others before Hellot got involved in the subject.<sup>24</sup>

In the year 1669 phosphorus was accidentally discovered in human urine as "*a dark, unctuous, daubing mass*" by Hennig Brandt, a merchant and alchemist of Hamburg, while searching for a liquid capable of transmuting silver into gold. His experiments made in 1669 led to a white, waxy substance that glowed so enchantingly in the dark, and which he named cold fire (*kaltes feuer*). Brandt kept secret his method of obtaining phosphorus, but the news of the amazing discovery soon spread throughout Germany.<sup>25,26</sup>

Johann Kunckel (1630-1702), a contemporary of Brandt, was the son of an alchemist in the court of the Duke of Holstein, and one of the most competent chemists of the seventeenth century. In the third part of his book *Laboratorium Chymicum*<sup>27</sup> he gives an account of ruby glass and phosphorus, the two chemical discoveries, which he considers to be the most important of the century. In a following publication<sup>28</sup> Kunckel described the properties of phosphorus more fully but did not provide details about the method of its preparation. He had first obtained phosphorus in the form of a black soap, which glowed in spots and did not shine continuously.<sup>25,26</sup>

After visiting with Brandt, Kunckel wrote immediately to his friend, Johann Daniel Krafft (1624-1697), a commercial agent from Saxony Dresden. Krafft, without replying to Kunckel's letter, left immediately for Hamburg and bought the secret from Brandt for 200 (thalers) dollars.

Although Kunckel did not describe the method for the preparation of his phosphorus, it seems that he accomplished it, as did other chemists after him, by evaporating putrid urine to the consistency of a syrup, mixing it with sand or brick dust, and distilling at a high temperature in a fortified (coated with clay) retort, the beak of which delivered under water in the receiver. The silicic acid of the sand or brick dust liberated phosphoric acid from the phosphates of the urine and the carbonaceous material reduced this, which was present.<sup>25,26</sup> According to Homberg,<sup>29</sup> Kunckel's process was essentially as follows: Fresh urine was evaporated nearly to dryness, after which the black residue was allowed to putrefy in a cellar for several months. This material was heated, gently at first and then strongly, with twice its weight of sand, in a retort leading to a receiver containing water. After the volatile and oily constituents had distilled over, the phosphorus begun to settle out in the receiver as a white, waxy solid. To prevent fires and explosions, it was necessary to remove the flame as soon as the phosphorus began to appear, and to keep the receiver closed until it became cold. This was the part of the process, which Kunckel thought too dangerous to reveal to the public, giving as his reason the fear that dangerous accident with

phosphorus might become frequent. Kunckel not only prepared phosphorus, but also cast it in molds, which he exhibited to the Courts of Saxony and Brandenburg, although it was not a very delicate agreeable exhibition, "*because unctuous and daubing oiliness was not yet accurately separated from it, and without doubt, it was very stinking and therefore unpleasant*".<sup>30</sup> He also introduced it as a medicine, recommending pills of phosphorus for internal use, and coated them with gold and silver, evidently by allowing the pills to stand in contact with solutions of these metals. According to Kunckel these pills would save a person from apoplexy or of other sudden sickness; they counteracted all noxious and poisoned airs and were an antidote against the pestilential poison. The pills caused no vomiting and inconvenience and acted in a mysterious manner.<sup>25,26</sup> Kunckel discussed the medical properties and uses of phosphorus in his book *Treatise of the Phosphorus Mirabilis*, and its *Wonderful Shinning Pills*.<sup>28</sup> As a result of this discovery the Duke Johann Friedrich of Hanover paid him an annual pension for the rest of his life.

In 1670 Robert Boyle (1627-1691) brought over from Germany Ambrose Godfrey Hanckwitz (1660-1741) to assist him in his chemical experiments. One of Hanckwitz first assignments was to prepare phosphorus, which he did promptly and in ounce quantity and years later published the pertinent details.<sup>31</sup> Boyle's basic procedure consisted in heating sodium phosphate with sand:



Boyle called the material *icy noctiluca* (cold light), examined its properties in a systematic way, and discovered phosphoric acid as the product of oxidation.<sup>32,33</sup> In 1680 Boyle described his method of preparation in a paper deposited with the Royal Society, but not published until 1682, after his death:<sup>34</sup> "*There as taken a considerable quantity of man's urine, and of this a good part...had been well digested before it was used. Then this liquor was distilled...till the remaining substance was...a somewhat thick syrup. It was...incorporated with thrice its weight of white sand...a naked fire was administered for five or six hours...By this means there came over good store of white fumes...they were after succeeded by another sort that seemed in the receiver to give a faint bluish light, almost like that of little burning matches dipped in sulphur. And last of all...passed another substance that was judged more ponderous than the former...whence being taken out appeared by several effects and other phenomena to be such a kind of substance as we desired and expected.*"

Until 1737 the method of manufacturing phosphorus remained a secret, but in that year a stranger in Paris offered to sell the secret process to the Ministry and since it was not possible to assure that that the proposed procedure was better than the ones known, the Ministry requested the help of the Académie. The Académie appointed a committee headed by Hellot to examine the procedure being offered. On November 13, 1737 Hellot read to the Académie a 36-page long report containing the results of his findings.<sup>6</sup> The report was divided in three parts, the first one gave a short history of the discovery of phosphorus, and described the properties and reactions of phosphorus, the second part its preparation, and the third one a summary of the methods of preparation reported by different scientists.

In the introduction to his report Hellot wrote:<sup>6</sup> "*nous rendons public ce tour de main sans en rien taire, afin*

*de mettre tout artiste en état de faire l'opération et d'y réussir comme nous...que tout ce qui peut contribuer au progrès des sciences et des arts, soit mis au rang des dépenses nécessaires de l'État".*

After many experiences, Hellot concluded that the success of the procedure depended less on the composition of the mixture to be distilled and more on the proper choice of the apparatus, the construction of the oven, the intensity of the heating, and specially, in the characteristics of the recipient were the phosphorus was to be collected. He then described the properties and reactions of the element: "*Phosphorus can be kept unchanged for a very long time if it is kept under water or spirit de vin, exposed to air it dissolves, what water cannot do in 8-10 years, the humidity of the air will do it in 10-12 d, be it because phosphorus ignites in air and the flammable part evaporates only completely, uncovering the acid of phosphorus, which like any other concentrated acid, is water avid, or be it because the humidity of the air is divided in infinitely small particles that can penetrate the pores of phosphorus. It is highly probable that both causes are responsible for the deliquescence of phosphorus. The resulting material is very acid, a true spirit of salt because it does not yield a precipitate with a suspension of calcium carbonate, but with it precipitates copiously a silver solution. Phosphorus dissolves in essential oils, yielding what is known as liquid phosphorus. It also dissolves in the ethereal liquid of Frobenius, which is also a kind of essential wine oil. Both solutions become luminous and are made to crystallize.*"

Hellot then described his procedure for the preparation of phosphorus: "*A given volume of urine is evaporated. It does not matter if this urine comes from people drinking beer or wine, as long as it is fermented at least 5-6 days. The one we have employed comes from the corridors of the Royal Hospital of the Invalids, where part of the soldiers drink one beverage and the rest the other. Evaporation of the urine produces a lumpy matter, hard, black, and similar to chimney soot. The urine is put in a kettle and then heated in a brick furnace. During this operation there is frothing, the liquids thickens and begins to blacken. The resulting solid is transferred to another kettle, which can be heated to a higher temperature; the solid is continuously agitated until all the volatile salt and the fetid oil have been eliminated. It is now necessary to remove the salt from the remaining solid. This is done by mixing it with hot water and leaving the mixture for 24 hours. The water is separated, the solid dried and then ground fine. The powder is now mixed with sand and carbon powder, humidified, and then introduced in a retort. The retort is red-heated; a white blue fume is released, which corresponds to the first phosphorus. Once the fuming stops, the temperature is increased adding to the retort burning carbon. Now, the second phosphorus begins to distill in the form of a luminous violet vapor, covering all the surface of the mixture. This process lasts for a long time; this phosphorus smells like garlic, typical of Kunckel's phosphorus. Other powdered phosphorus smell like sulfur or hepar sulphuris (a mixture of various compounds of potassium and sulfur made by fusing potassium carbonate and sulfur). The choice of an appropriate retort is essential for the success of the operation; the ones made in Paris from stoneware were unable to hold the strong fire required, and broke down.*" For his purposes Hellot selected a retort made in Germany, used normally for the distillation of pure sulfuric acid.

## Ether

Ether was one of the most important substances that interested the chemists of the first half of the 18<sup>th</sup> century.<sup>1</sup> It had attracted the attention of Daniel Newton, who around 1730 had published a procedure for its preparation. According to Hellot, ether, the most volatile and most inflammable of all known liquids, was known through the efforts of Duhamel and Grosse, who in 1734 published its composition and the procedure for manufacturing it.<sup>9,18</sup> The ethereal liquor was obtained by heating gently a mixture of one part of white concentrated sulfuric acid and two parts of rectified wine spirit. After a few hours the mixture became red, even when using the best wine spirit. The retort was then heated in a sand bath and the different distillate fractions collected. Hellot examined all the fractions besides that of ether, which had been the sole objective of Duhamel and Grosse's memoir. The first fraction was a flammable acid liquid, which Johann Heinrich Pott (1692-1777) had named *acide vitriolique vineux*, and proved to be only slightly related to ether. Other German scientists had named it *spiritus naphthæ*, because it caught fire immediately when coming close to a lit candle. Hellot proposed naming it *sprit acide vineux*, to distinguish it from the ether or Frobenius' liquor other fraction, which was even more volatile and more flammable.

The fraction following the *sprit acide vineux* was an aqueous non-flammable acid liquid having a suffocating sulfurous smell. It was accompanied by white vapors that condensed into an oil sometimes white, sometimes green or yellow, which initially floated on top of the aqueous acid liquor and then settled to the bottom. After most of the aqueous acid liquor and the yellow oil it contains had distilled, the liquid remaining in the flask begun to blacken and froth. If the heating was stopped suddenly this black liquor flowed out and become mixed with all the previous distillates, yielding a mixture impossible to separate again by distillation. Hellot showed that employing an alkaline earth intermediate it was possible to prepare ether very easily, without appearance of the oil, black froth, or the sulfurous fraction.<sup>9</sup>

Hellot analyzed the methods of preparation and rectification of ether and then interpreted its behavior using Geoffroy's table of affinities. He finally explained, in his own way, the mechanism of the reaction: "*la portion la plus volatile de l'huile de vitriol se joint au principe inflammable de l'esprit de vin, que de cette union il en résulte la liquor étherée...*" (the most volatile portion of oil of vitriol, sulfuric acid, combines with the inflammable principle of spirit of wine... It is from this union that the ethereal liquor results).<sup>9</sup> It is seen that the first to speculate about the stages in the preparation of sulfuric ether, to note down the formation of an intermediate substance that in the presence of an excess of alcohol decomposes under the action of heat.<sup>1</sup>

Almost 200 years later Alexander William Williamson (1824-1904) gave the correct interpretation of the etherification reaction.<sup>35</sup>

## Dyeing

In 1548, Gioanventura Ventura Rosetti, an officer of the Venetian Army (Director of the Arsenal in Venice) known as Plictho, published in Venice the first edition of the earliest known book devoted exclusively to professional dyeing.<sup>36</sup> This book included details of dye recipes and techniques employed in Venice, Genoa,

Florence, and elsewhere in Italy, as well as the most complete record of the dyers craft at the time when the first South American dyewood was becoming available in Europe. Rosetti's book was translated into French as *Le Teinturier Parfait*<sup>37</sup> and remained as the official dyer's manual for almost 200 years, until Du Fay and Hellot entered in the picture when Philibert Orry (1689-1747), the Controller General of Finance, decided to put the French dyeing industry into a more advanced trade.

From old times the dyers in France were organized in two large guilds, grand teint and petit teint, depending of the characteristics of the dyes they used for the trade. *Grand (bon) teint* were the fast colors, characterized by high quality and price and resistance to sunlight, atmospheric air, and aging (i.e., indigo and cochineal), and were used for the luxury market. *Petit teint* were the more brilliant but fugitive colors, of lower quality and poor solidity (Brazil wood, archil, and curcuma), and were used to dye the cheaper kinds of cloth. Solidity had since then become an important factor in the classification of dyestuff into the two main categories of fast and fugitive, depending on their capacity of fixing on the textile fibers and their resistance to atmospheric air, sunlight, washing, aging, and water.

The traditional regulations by which these two guilds were governed sought to delineate sharply the kinds of goods and colors that each may handle. As for color tests, named *débouillis* tests, they consisted of boiling a swatch of the cloth under scrutiny for a specific length of time in either alum (slightly acid solution) or in soap (mildly alkaline solution), after which the color was carefully compared with the standard kept by the guild, which had been treated in a similar manner. There is no evidence that the compilers of these *débouilli* test recipes strove to explain dye fastness or were guided by any kind of theoretical considerations.<sup>38</sup>

In 1737 Orry, issued a new set of instructions for the regulation of dye works, which kept the above categories. Orry requested from Du Fay to investigate the differences between the two classes of dyes and develop the tests to identify them. Du Fay studied all the common dyestuffs and many others also, to determine, by exposing bits of colored woollens to the action of sun and air for extended periods, which substances gave true colors and which false colors. Du Fay's results supplied the technical basis for Orry's instructions of 1737.<sup>39</sup>

Du Fay used his results to present to the Académie a memoir about the dyeing process, and attempting to give a scientific explanation (based on what was known then) of the phenomenon of dyeing.<sup>40</sup> For him dyeing supposed an action in two stages. He started from the observation that the fabric to be dyed must first be prepared according to the color they are to receive. They must first receive "*un certain apprêt*" (a certain size; today, a mordant). This size, a hot liquid, caused in the fabric a characteristic alteration that prepared it to take the color. Sizing was followed by the application of the dye, administered in one or several baths of color. The nature of the tissue determined the type of mordant to be used. Proper selection of the pair helped in the total depletion of the coloring matter in the bath that in the end became colorless. Du Fay went much further than Rosetti; he was the first to recognize the chemical and non-mechanical nature of the action of acids on the tissue. For him acids did not help in

opening the pores of the tissue but in eliminating their colors. He also spoke of small particles of two colors that do not have to unite; those that evaporate slowly retain those that do it more "*easily...It is possible that these corpuscles that fill the intervals between them, do not fill them completely, some void space still remains, where other corpuscles, also colored, may locate themselves...*"<sup>41</sup>

In 1740 Hellot succeeded Du Fay as Inspecteur Général des Teintures, the title Orry had given him, and in the two following years he presented to the Académie two memoirs on the theory of dyeing.<sup>41,42</sup> In these memoirs he expressed his ideas as follows: In general, "*all the invisible mechanics of dyeing consists in swelling the pores of the body to be dyed in order to deposit particles of a foreign substance and to have them retained there by means of a coating space so that neither water, rain, or the sun rays may alter them...the coloring atom is retained more or less like a diamond is held in the bezel of a ring (comme un diamant dans le chaton d'un bague)...This constitutes the bon teint. Deposit the foreign substance only of the surface of the body, or inside pores that do not have sufficient capacity to receive it, this will be the petit teint because the smallest shock will detach the coloring atoms that are not inserted way before.*" For Hellot then, the difference between good and bad dyes laid on the fact that good dyes consisted of fine particles that could penetrate the fibers and remain there, while bad ones were simply too large.

The above description shows that Hellot believed that the process of dyeing a cloth is a mechanical process, consisting in the previous opening of its pores with the purpose of lodging in the coloring matter, which then becomes fixed by cooling the tissue or by the action of a mordant. He goes on to say that "*it is easy to conceive that the acids added to the Cuve d'Inde (indigo bath) serve to open the natural pores of the object being dyed and also to develop the color atoms of this starch...Boiling of the bath forces in the atoms by repeated collisions; the pores already swelled by the salts, swell even more, and are then retightened by the external cold when the fabric is withdrawn and thrown into cold water. Thus the coloring atom is retained by the pores or fissures of the dyed substance that has retaken its original state.*" Eventually, Jean-Antoine Chaptal (1756-1832), Pierre-Joseph Macquer (1718-1784), and Claude-Louis Berthollet (1748-1822) would describe the dyeing action according to the laws of affinity; mordants would become the intermediates of the joining and of affinity between the main color and the fabric.

Hellot was the first to become captivated by the coloring qualities and the chemical properties of indigo (a substance that changes color in contact with air). In 1760, while distilling indigo in the presence of quicklime (CaO), he obtained a product that he named anil, which is aniline. He reported that hot or cold infusions of indigo are what is called *cuves d'Inde* or *cuve of blues*. The cold vats may be used for threads or cottons, the hot vats for wool and other animal matters.<sup>42</sup>

According to Beer<sup>38</sup> Hellot's theory met with immediate success because not only it explained so many phenomena observed in the dye house; it also gave a simple explanation for the difference between fast and fugitive dyes: Fast dye particles were small and penetrated the pores deeply, while fading colors obviously had particles that were too large. It also explained why some fibers took certain colors while other did not. For example, cotton did not take scarlet

because its pores were too small. It explained why heat had to be used frequently in dyeing operations although it did not exactly said why some dyes can be applied cold.

The theory also provided an answer to the mechanism of mordant action, to which Du Fay had paid too little attention. Hellot realized that mordants were not to be classed with other auxiliary chemicals, like tartar, to which he had assigned the role of forming a thin, waterproof varnish-like layer over the color-containing pores. Mordants, he said, helped dilate the pores; when hot they also entered the pores and lined their walls; upon cooling they formed crystals, which held the trapped dye particles in a vise-like grip. Thus he explained how mordants allowed more colored particles to get into, or stay in the pores, and so accounted for the frequently darker and more intense shade resulting when a color was used in conjunction with a mordant. In contradiction to Du Fay, he believed that the line separating grand and petit dyes was an artificial one. Diderot's *Encyclopédie*, which accepted Hellot's theory without reservations, made the bold prediction that it was certain that all petit dyes would one day become faster when man discovered new mordants with which to open pores wider and subsequently bit into color particles more effectively.<sup>38</sup>

By 1748 Hellot had become convinced that the literary description of dyeing procedures was incomprehensible to dyers; two years after he expressed his opinion that the numerous editions of *Le Tinture Parfait* were "a monstrous compilation of imperfect, falsæ, and badly described formulæ." He summarized all his findings on the art and methods of dyeing in two books, *Théorie Chimique de la Teinture Etoffes*<sup>43</sup> and *L'Art de la Teinture des Laines*,<sup>44</sup> which may be considered the first scientific books on the subject, and which remained for long a standard work. In his books Hellot described the equipment and organization of dye works; took up the various vegetable substances used in dyeing, and outlined the dyeing procedures appropriate to each coloring matter used.<sup>39</sup>

The book on the art of dyeing is divided in two large sections; the first is dedicated to the dyeing equipment and grand teint, and the second to petit teint and coloring materials. One especial chapter, at the beginning of the book, is devoted to the difference between the two types of dyeing, grand and petit, on wool. The last chapter contains instructions regarding the débouillis of wool and wool fabrics. This book may be considered to be the first reference publication of textile technology in the modern meaning of the term. It is simultaneously a source of information, of vulgarization, and training, as well as a thorough working guide. It was promptly reproduced in several European countries and helped disseminate this scientific technologic across the industrial nations.

Hellot's books were a summary of the knowledge of wool dyeing; they were complemented by Pierre-Joseph Macquer's (1718-1784) book on silk dyeing<sup>45</sup> and by Henri Augustin Le Pileur d'Apligny's<sup>46-48</sup> books on dyeing cotton (1770, 1776). In this book, Macquer accepted Hellot's theories on dyeing and the mordant action without reservations, but later, after accumulating sufficient information on mordants, he concluded that the function of the mordant was to act as a chemical bridge between the dye and the fiber since it alone had a chemical affinity for both.<sup>38</sup> Le Pileur d'Apligny extended Hellot's physical explanation by trying to

distinguish between the mechanical qualities of the different textile fibers. In his view the pores in wool were large enough to receive the insoluble compound formed by, for example, the animal dye cochineal and the mordant tin chloride, whereas silk and linen were too small to absorb it.

With Claude-Louis Berthollet (1718-1822), who succeeded Macquer in 1784 as *inspecteur des teintures*, the tradition of Du Fay, Hellot, and Macquer, linking chemistry to the needs of the textile industry, reached its culmination.<sup>2</sup>

### Porcelain

When porcelain objects started arriving in Europe from China and Japan, they caught immediately the attention because of their fineness, their beautiful colors, and their multiple and elegant shapes. Nevertheless, their import did not become significant until the 16<sup>th</sup> century, and then the race begun to discover the secret of their fabrication. The chemistry of their manufacture was absolutely unknown and the only approach was one of trial and error. In 1709 Johann Friedrich Böttger (1682-1719), a German alchemist working for Augustus the Strong (1670-1733), Elector of Saxony and King of Poland, succeeded in obtaining a true porcelain, of white paste, similar in quality and properties to the one imported from the Far East. Böttger realized that the current approaches involving the mixing fine white substances like crushed egg shells into clay was not the answer, but rather his approach was to attempt to bake the clay at higher temperatures than ever before achieved in an European. The original intentions of Böttger were to melt the structure of the clay (feldspar) so as to transmute it into a new substance. His approach yielded the breakthrough, which had eluded European potters for a century and was to have profound consequences for the development for the entire European ceramic industry. Augustus the Strong proceeded immediately to put up a Royal Manufacture factory in Meissen, which in 1713 starting offering European porcelain (Böttger porcelain) for sale for the first time. In the 1720s, the Meissen factory developed a new and extensive range of enamel colors and the factory's painters excelled in chinoiserie scenes.

In France, Réaumur was the first to undertake the search for the proper composition to manufacture true porcelain (*pâte dure*). He analyzed many samples of broken pieces of Chinese, Japanese, and Meissen porcelain, and found that when exposed to a high heat, the European specimens melted while the Japanese remained unchanged. This suggested that porcelain, resembling glass somewhat in consistency and transparency, though less compact and much less transparent, was a material in a state of semi vitrification. Mixing two materials, one of which was fusible and the other infusible could achieve this state. Entrecolles, a French missionary in China, had sent Réaumur a small quantity of the materials used for making porcelain. One of these, called *Kao lin*, proved to be quite infusible, and another, *Pet un tse*, melted readily. Réaumur efforts, and of others, to find similar materials in France failed. Kaolin was later found to be very white and refractory clay, originating from the decomposition of granite feldspar. Pétuntsé was feldspar that melted at very high temperature and became transparent after solidifying. The mixture of both materials, hard paste, gave the transparency, whiteness, and solidity that characterized porcelain. Eventually, Macquer found the



appropriate type of kaolin in a sample sent to him by Villaris, a chemist of Bordeaux. In 1765 a large deposit of good quality kaolin was found in France, at St. Yrieix, near Limoges. Four years later, the production of the first true French porcelain was begun.

In the later 17<sup>th</sup> century, before the discovery of local kaolin, French potters were fabricating a product called soft paste (*paste tendre*) porcelain. It resembled true porcelain in appearance, but scratched too easily, broke easily, and could not withstand high temperature. It was fired in a kiln at a low temperature and was thus compatible with a wider variety of colors and glazes that in many cases were also richer and more vivid. The vitreous mixture was composed of Fontainebleau sand, crystallized nitre, sea salt, Alicante soda (sodium carbonate), alum, and gypsum. Vitrification required fifty hours and when completed, a mixture of about two-thirds chalk and one-third Argenteuil marlstone (an argillaceous mineral containing substantial amounts of clay-like components) was added in. Unglazed forms emerging from the kiln were called biscuit. Sculptured groups and figurines were often left in that state. A lead-based liquid glaze was poured over the objects to be covered and the piece returned to the kiln for further treatment. Colors were applied over or under the glaze according to whether they could stand the firing.

There were several factories manufacturing soft paste. The Chantilly one was founded by Louis-Henry de Bourbon (1692–1740) in 1730 and, under the patronage of Jean-Louis Orry de Fulvy (1703–1751) it was transferred to Vincennes in 1738, to be owned and run by former Chantilly workmen. Initially the raw material for porcelain kaolin was brought in from Austria, until the Limoges deposit was discovered. The new facility was granted a 20-year royal privilege *"to manufacture in France porcelains of the same quality as those made in Saxony, in order to spare consumers in this kingdom the need to disburse their funds in foreign countries in order to obtain curiosities of this kind"*.

Following Orry de Fulvy's death, the factory experienced financial difficulties, which it temporarily overcame when in 1752 Louis XV, king of France, acquired one quarter of the shares. A year later it became by royal order the designation of Manufacturer Royale de Porcelaine, and was granted official permission to mark its pieces with the royal cipher of interlaced L's. In 1756 the factory of Vincennes relocated to Sèvres, to a property owned by Madame de Pompadour (1721–64) the mistress of Louis XV and an important patron. Sèvres was also granted an exclusive privilege to make wares *"in the style of Saxony"* for 20 years. In 1759 the economical difficulties forced the investors to petition the king for relief from their engagements. Yielding to Madame Pompadour, Louis XIV bought from them the stock and took title to all the shares, stock, inventory, building and terrain.<sup>49</sup>

After becoming the mayor shareholder of the factory, the king appointed Jacques-Dominique Barberie de Courteille, Intendant des Finances, to report to him about all the affaires concerning the direction and administration of the manufacture. It was clear that a specialist was needed and the choice fell on Hellot, who at that time was serving as Director of the Académie. On 1751 Hellot received his nomination to Vincennes, signed by Jean-Baptiste de Machault. Lord d'Arnouville (1702–1794), Inspector General of Finance and Lord Chancellor: *"... it being the King's wish to learn*

*with accuracy the various secrets concerning the management of the porcelain works at Vincennes, His Majesty has appointed to this purpose M. Hellot, Director of the Academy of Sciences, and authorized him to make all necessary investigations and experiments to this end, with... anyone... who may be privy to these secrets and whom M. Hellot, in turn, will charge on His Majesty's behalf. His Majesty enjoins... anyone... who may be concerned to speak freely on this subject with M. Hellot with no secrecy and at his first request..."*<sup>50</sup> It is clear from this document that Hellot was conferred with almost absolute powers for running the facility.

Hellot inspected the factory as ordered and promptly reported to Machault that he has been delivered all the information related to the production of porcelain.

In addition to this report, Hellot wrote three booklets that are kept in the pottery archives at Sèvres. They contain hundreds of formulas, processes, and compositions for pastes, glazes, gold, and even artificial gems and invisible ink. Many of Hellot's notes regarding the composition and some of the manufacturing processes of soft paste at Vincennes and Sèvres are quoted in a paper by d'Albis.<sup>50</sup> Some interesting ones are as follows: (a) In the pottery works the paste is worked either on a wheel or with a mold for pieces like dishes, tureens, and olio pots, decanter buckets, groups of figures, etc., (b) an organic binder called the *"chymie"* was added to the modeling paste used to mold figurines, molded pieces, and dishes. Plates and dishes were obtained by pressing with a plaster mold, the two parts of which were joined by a clamp. To avoid breaking the mold, cushions were inserted between it and the wooden handles used for pressing. Production was extremely limited, (c) frit that is fired irregularly and that contains soluble elements, more or less silicate in content, produces efflorescence called *"saline vegetation"* in Vincennes porcelain. These vegetations often cause the disappearance of decorative ornaments and in places leave little holes or raised tracings of salt so that it becomes necessary to wash the pieces with a wet sponge to remove the salt and to fill in the little holes. That is not all; these salts form a crust on the bisque, that is, the pieces that have been fired and have acquired a semi-transparency in the kiln. Once the piece was molded the potter or molder always pierced a small hole in the back so that it could then be suspended from an iron support shaped like a cross or on a tripod from which it was hung while awaiting firing, (d) The best pieces, as well as those from which salt effusions had been removed, were put into the kilns. Soft-paste porcelain becomes greatly translucent when it is over fired. The pieces do not yet have a glaze and they can be fired on supports to prevent loss of shape or flaws, which develop due to the high temperatures. The pieces were stacked in saggars or boxes made of resistant clay, then fired in an oxidizing environment, which was produced by burning a white wood, (e) lead glazes are generally fired between 800 and 1100 °C. They are shinier, softer, and smoother than other glazes. Their appearance can be further improved by firing them in saggars that are themselves coated in a lead veneer. The firing was very likely at a temperature lower than that used for the bisque, because it seems that, on the one hand, one need not fear deformations, and on the other, the baking time was shorter, (f) soft-paste porcelain was decorated in three kinds of firings: *high heat*: The deep blues were obtained using a special cobalt based com-

position, low heat: These colors were applied as little squares of different thicknesses, “so that in the little squares are contained all the nuances that the color could give later on”. If they try several on the same share, this series of little squares is numbered with the same number that is placed on the color packet, (g) gilding: The idea was to mix gold leaf with a solution of gum Arabic, finely ground with a flint pestle on a porphyry plate. After grinding, the powder was carefully washed by successive decantation, then strained into different weights and dried, yielding a “fine gold” or “heavy gold.” The decorators diluted this product in a lamina with a “mordant” (binder). The “mordant,” a gluey substance, was obtained by slowly boiling and reducing a precisely weighed mixture of onions, garlic, and vinegar. It acted as a binder in painting the gold powder on the porcelain. The gilt and the iron red colors were fired at a lower temperature.

### Metronomics

Among the most important measurements of France was the aune<sup>c</sup> of Paris, for which the standard dating from 1554 represented the legal measure unit for cloths. The ville of Nantes, wanting to adopt a cloth measuring standard conforming that of the Merciers of Paris, decided on the value 3 feet, 7 pousse (inches), and 8 lines (a pousse was equivalent to 10 lines), in accordance to the ordinance of Henri II (1519-1559) and the instruction given in 1714 to the inspectors of manufacture. When comparing their standard to that of the Merciers, the city authorities were quite astonished to find that it was shorter by about three lines; consequently they requested from the Ministry of Manufacturing to pass judgment on the question. The Ministry asked the Académie to find the reason for this difference and to determine the correct length. Hellot and Charles Etienne Louis Camus (1699-1768) were appointed as commissaries.

A historical study of the origins of the standard indicated that originally the aune was supposed to be a fixed number of feet, instead of a measurement containing lines and fraction of the same. The probably reason of this inconvenience seemed to be that Charlemagne, who was simultaneously Emperor and King of France, had presumably fixed the measurement of the foot according to the Roman foot. In 1554, the time of Henri's II ordinance, the aune had been measured with a foot too long, and found to be 3 feet, 7 inches, and 8 lignes. This error had been corrected in 1688, and the aune redefined as 3 feet 7 inches and 10-5/6 lines.

Hellot and Camus made their own measurements and concluded that the correct value of the aune was 3 feet 7 inches and 10-5/6 lines.<sup>11</sup>

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<sup>c</sup>An aune was a French cloth measure, of different parts of the country (at Paris, 0.95 of an English ell), now superseded by the meter. The English ell was equal to 45 inches. A toise was exactly 6 pieds (feet) i.e. about 1.949 meters in France before 10 December 1799, and exactly 2 meters in France between 10 December 1799 and 1 January 1840.

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