



Charles Lauth: dyes and other compounds

Charles Lauth: tintes y otros compuestos

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Resumen

Charles Lauth (1836-1913) fue un químico francés que trabajó la mayor parte de su vida desarrollando nuevos tintes y diferentes porcelanas y cerámicas. A él le debemos la síntesis de los colorantes de anilina violeta de metilo (violeta de París), verde de metilo, negro de anilina y violeta de Lauth (tionina), así como los mejores métodos para aplicarlos a diferentes tipos de textiles. Junto con Edouard Grimaux, desarrollaron métodos para producir aldehídos aromáticos, lo que condujo a la síntesis de la esencia artificial de almendra amarga.

Palabras clave

aldehídos aromáticos; anilina; colorantes; esencia de almendra amarga; negro de anilina; metil anilina; tintes; verde de metilo; violeta de metilo

Abstract

Charles Lauth (1836-1913) was a French chemist who worked most of his life developing new dyes and different porcelains and ceramics. To him, we owe the synthesis of the aniline dyes' methyl violet (Paris violet), methyl green, aniline black, and Lauth's violet (thionine), as well as the best methods for applying them to different kinds of textiles. Together with Edouard Grimaux, they developed methods for producing aromatic aldehydes, which led to the synthesis of the artificial essence bitter almond.

Keywords

aniline; aniline black; aromatic aldehydes; bitter almond essence; dyes; methyl aniline; methyl green; methyl violet.

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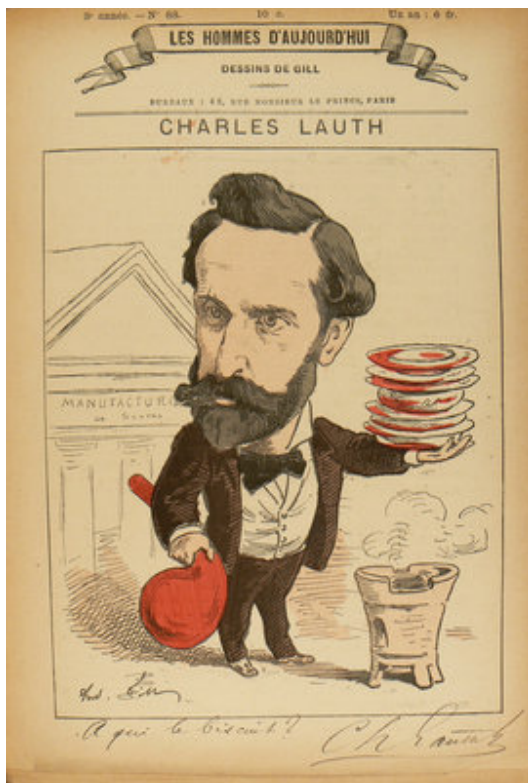


FIGURE 1. Charles Lauth (1836-1913). Caricature by Gil, 1874.

Life and career (Anonymous, 2023; Lestel, 2007; Lauth, 1892a)

Charles Lauth (Figure 1, caricature by Gil, 1874) was born in Strasbourg on September 28, 1836, the youngest son of Charles Andre Lauth, a lawyer and justice of peace, and Caroline Henriette Pauline Kern. Charles took his basic education at the local high school and after obtaining his diploma of baccalaureate in humanities in 1852 and baccalaureate in sciences in 1853, he enrolled for one year in the École Supérieure de Pharmacie and then transferred to the Faculty of Sciences of Strasbourg where he studied under Charles Gerhard (1816-1856) and became his assistant in 1855. The following year, he moved to Paris to continue his studies and work as assistant to Jean-François Persoz (1805-1868) at the Conservatoire des Arts et Métiers. After graduation, he worked for five years at the Depouilly chemical works in Clichy and then opened his own laboratory to carry on research and manufacture dyes and

chemicals. During the Franco-Prussian war (1870-1871) he served as captain-general of the 19th Battalion of the National Guard, and in 1871, during the siege of Paris, he was elected deputy to the mayor of the Vi^e arrondissement of Paris. In 1879, he was appointed director of the Sèvres porcelain factory, a position he kept until 1897 (on his retirement, he was appointed honorary director of the factory). In 1898, he was appointed director of the École Municipale de Physique et de Chimie Industrielles de la Ville de Paris, succeeding Paul Schützenberger (1829-1897). He kept this position until 1905.

Lauth married Élixa Wilhelmine Kirchleger; four children were born of this union. Lauth died in Nice, on December 2, 1913, and was buried in the Montparnasse cemetery.

Lauth participated actively in professional, academic, public, and political activities, and was rewarded accordingly. He was a member of the Conseil de Surveillance de l'Assistance Publique (1876), of the Commission Supérieure pour l'Aménagement et Utilisation des Eaux (1878), of the Conseil de Perfectionnement du Conservatoire des Arts et Métiers (1880), of the Société Industrielle de Mulhouse, of the Conseil de Perfectionnement of the École de Physique et de Chimie of Paris (1882), and of the Société Chimique de Paris and its President (1883). He was awarded a medals and diplomas by the Société Industrielle de Mulhouse (1865), the Société d'Encouragement de l'Industrie Nationale (1867), the Universal Exposition of Paris (1867), and the Universal Exposition of Vienna (1873). Furthermore, he was appointed officer de l'Académie (1881) and officier de l'Instruction Publique (1884), (national orders, founded By Napoleon, bestowed by France on distinguished academics and teachers and for valuable service to universities, education, and science). In 1878, he was appointed Chevalier of the Légion d'Honneur, promoted to Officier in 1883 and

to Commander in 1908. Lauth founded the Society of Coloring Matters in Saint-Denis and campaigned actively for the creation of the École Municipale de Physique et de Chimie Industrielles de la Ville de Paris (1882) with the collaboration of famous scientists such as Marcelin Berthelot (1827-1907) and Charles-Adolph Würtz (1817-1884).

Scientific contribution

Lauth wrote near 30 papers and books (e.g., Lauth, 1881, 1884; Danne & Lauth, 1904; Dupont & Lauth, 1902; Lauth & Depouilly, 1860; Lauth & Dutailly, 1888; Lauth & Vogt, 1885) on the topics of inorganic and organic chemistry, water, dyes, etc. As customary for candidates to the Académie des sciences, he wrote a booklet describing his research findings and their importance (Lauth, 1867, 1892). He did not make it; in 1890 he lost the election to Louis Raphael Bichoffsheim (1833-)1906. In addition to the few subjects described below, he studied the action of the hydrochlorides of the essence of turpentine on aniline and rosoline (Lauth & Oppenheim, 1867); the depuration of the sewage waters of Paris (Lauth, 1877); described in detail the manufacture of blue porcelain (blue of Sèvres) (Lauth, 1883), etc.

Dyes

Methyl violet

Lauth wrote that the comparison of the formula of aniline violet $C_{36}H_{17}N_3O_2$ with that of aniline red $C_{36}H_{20}N_4O_4$ had led him to explore the possibility that treating the red with reducing agents would transform it into violet (Lauth, 1861b).

Experiments with usual reducers failed to achieve this goal, all of them destroyed the coloring matter without given rise to the formation of aniline violet. However, treatment of a solution of red aniline (mono nitrated trianiline) with commercial alcohol, methanol, or commercial acetic, and tin dichloride $SnCl_2$, resulted in a gradual change of the initial yellow color of the mixture to brownish, then to green, and finally to blue. Lauth promptly realized that this effect was due only to the alcohol or to the substances that always accompanied it. The experiments proved that the action has been produced by aldehyde ammonia (acetaldehyde ammonia, 1-aminoethanol, $CH_3CH(OH)(NH_2)$), usually present in commercial alcohol. This substance was easily prepared by the reaction between acetaldehyde and ammonia and appeared as a trimer trihydrate. Lauth reacted the aldehyde with a solution of pure red aniline in sulfuric acid diluted in four times its volume in water and observed that after a few hours all the red color had disappeared to give way to a beautiful blue color. Addition of NaOH to the resulting liquid resulted in the formation of ammonium acetate, which remained in solution, and precipitation of aniline blue. Further experiments showed that the aldehyde could be replaced by the essences of bitter almonds, rue, and anis, and the sulfuric acid by any acid or acid salts (Lauth, 1861b).

The new dye appeared as crystals soluble in water, alcohol, ether, glycerin, etc., and dissolving in acids and alkalis. The resulting solution was precipitated by even a small amount of tannin, which formed with it a combination insoluble in water, slightly soluble in alcohol and more soluble in acetic acid. It decomposed completely at 200 °C and was also affected by sunlight. According to Lauth, the dye was able to dye wool, silk, and animalized cotton, giving them shades of very great purity. Combined with aniline red resulted in purples incomparably more beautiful than ordinary aniline purples (Lauth, 1861b).

Lauth reported that the reaction of aniline with iodic acid gave place to different products, depending on the concentration of the acid (Lauth, 1861c): (1) concentrated acid, added dropwise, produced a very energetic and exothermal reaction; the solution, initially blue, began to release iodine and aniline vapors and ended as a porous carbon residue; (2) iodic acid diluted in four times its volume of water, yielded rapidly a very dark violet solution, which on heating turned red; and (3) highly diluted acid produced a very slow reaction; after several hours the solution turned red and the walls of the vessel became covered with a green resin. The final liquor did not react with acids but turned yellow with alkalis. Addition of aqueous potassium iodate to a solution of aniline hydrochloride, produced a colorless liquor, which then turned violet and ended black. Upon heating, the violet color turned red. In short, iodic acid or potassium iodate allowed obtaining at will blue, purple, red and green colors. (Lauth, 1861c, 1867b).

Lauth added that tin dichloride, SnCl_2 , had no action on aniline but produced a very violent reaction when the aniline contained nitrobenzene. Treating the brown product with boiling water, turned it purple red, and showed all the reactions of fuchsin (Lauth, 1861c).

Methylaniline

Lauth speculated that methylaniline, $\text{C}_{14}\text{H}_9\text{N}$, a substance, which differed little from aniline, perhaps would also give dyes of practical interest. He prepared methylaniline by reacting aniline with methyl iodide, and then subjected it to the action of the various agents generally employed to transform aniline into coloring matter (Lauth, 1861d). His results indicated that methylaniline originated a variety of dyes but, unfortunately, these colors were not fast and hence inappropriate for practical use. For example, the reaction of methylaniline hydrochloride with potassium dichromate gave place to a dark blue precipitate, which purified and dissolved in diluted alcohol gave a rich violet color solution, able of dyeing silk, wool, and albuminous cotton. In contact with air or very diluted acids, the color turned gray and shortly afterwards, dirty yellow. Mixing a solution of methylaniline with another of calcium chloride produced a beautiful blue, which turned green in contact with acids, and returned to blue by washing with water (Lauth, 1861d).

Lauth also reported the preparation, properties, and reactions of dimethylaniline and the hydrate of ammonium trimethylphenyl, the byproducts of the manufacture of methylaniline (Lauth, 1867c), and the action of HCl on composite ammonium compounds (Lauth, 1873c)

Fuchsin

Lauth wrote that August Wilhelm Hoffmann (1818-1892) had published several papers devoted to the action of carbon dichloride (actually, carbon tetrachloride) on aniline (i.e., Hoffmann, 1858-1862). The ones related to the synthesis of fuchsin, indicated that the process was carried under pressure in closed vessels, a technique that many believed was inappropriate for large scale manufacture of fuchsin (Lauth, 1861e).

In 1861 Lauth reported that he had developed an improved process that allowed manufacturing fuchsin at atmospheric pressure by merely connecting the reaction vessel to a reflux condenser, which kept the chloride vapors in the vessel. This simple act eliminated the problem associated with Hoffmann's method and allowed the large-scale production of the dye (Lauth, 1861e).

In Lauth method, the mixture of aniline and carbon dichloride was heated between 170° and 180 °C for thirty hours. Initially, the reaction was very slow, the chloride volatilized very quickly, then it combined little by little, and ended being completely consumed in about two hours. After 30 hours, the contents were an almost solid black mass, red by transparency, and containing considerable quantities of fuchsin, recognizable by all its chemical and physical characteristics (Lauth, 1861e).

Aniline black

In January 1803, John Emanuel Lightfoot (1831-1872) was awarded a patent for a process for the production or development of a black color dye or stain in textile fabrics and yarns, particularly, those made of vegetable fibers (Lightfoot, 1863). Lightfoot added that prior to the date of his invention a variety of colors, other than black, derived from aniline, had been utilized in dyeing or printing textile fabrics or yarns. The patent specified that the printing or dyeing was done with a mixture of potassium chlorate, aniline, HCl, cupric chloride, acetic acid, and starch paste. The printed and dried fabric was exposed to the air (oxidation chambers) for approximately two days, and then washed in slightly alkaline water. This fixed the black, which had developed in the oxidation chamber. The acid of the aniline salt decomposed the potassium chlorate, while the cupric chloride reacted with the aniline. These two combined oxidizing actions triggered the formation of the new color, which was completely insoluble and therefore remained intimately fixed to the fabric (Lightfoot, 1863).

Lauth wrote that Lightfoot's discovery was a significant advance in the area of dyeing (Lauth, 1864). It added a new colored product derived from aniline and completed the series of brilliant colors provided by this base (i.e., red, blue, aniline violet, etc.). Aniline black differed in all respects, from other coloring matter derived from aniline, its mode of production, its fixation on fabrics, and its solidity to physical and chemical agents. Unfortunately, the Lightfoot process presented serious drawbacks, which soon caused its use to be abandoned: (1) the large quantity of copper chloride, which it contained, resulted in the attack of the steel scrapers and of serious accidents; (2) the color was very acid and stable for only a very short time at room temperature; after that, it lost its fixation power; and (3) the printed fabric was strongly attacked by the acid of the salt of aniline and of the salt of copper, with the resulting weakening of the vegetable fiber (Lauth, 1864).

The Lightfoot process was modified several times. For example, Camille Koechlin (1811-1890) instead of putting the copper in the color, he put it on the fabric by a very expensive and contaminating process. Honoré Cordillot replaced the cupric chloride by ammonium ferricyanide (Cordillot, 1863); unfortunately, its black color was preserved for a very short time, was not very intensive, required a high temperature in the oxidation chamber, and was very expensive (Lauth, 1864).

In 1864, Lauth reported on a new improvement (which he claimed was very economical and overcame the known disadvantages of Lightfoot's process and its modifications (Lauth 1864). In his process, the printing was done with a mixture of aniline hydrochloride, potassium chlorate, and an insoluble oxidizing salt, which became soluble on the fabric (for example, copper sulfide). This sulfide was transformed by the oxidizing action of chloric acid or chlorine into cupric sulfate into copper sulfate, thus turning into the Lightfoot process conditions. According to Lauth, these modifications eliminated the attack of the steel rollers, the fabric was not weakened, the black color kept for a long time and became fixed already at 20 °C, and printing could be done in every material (Lauth, 1864).

Lauth wrote that aniline black was insoluble in water, boiling soap, alkalis, and acids. Acids turned it green, and alkalis returned the original shade. Potassium dichromate increased the intensity of its shade, and concentrated, it turned reddish brown (Lauth, 1864).

In 1866 Lauth was asked by the company A. Schlumberger et Cie., to give his opinion about a new process for manufacturing for aniline black, patented by Alfred Paraf, a chemist in Manchester (Paraf, 1866). The Paraf process consisted in printing a mixture of aniline salt, potassium chlorate, and fluosilicic acid, and producing aniline black *without* the addition of metal salts, in opposition to all the processes then available (Lauth, 1866). According to the patent, the use of oxidants, such as a suitable mixture of potassium chlorate and ferric or cupric compounds, was unnecessary, the same oxidation could be obtained with the chloric acid set free by the action of fluosilicic acid on potassium chlorate.

Lauth found that incineration of calico, printed in black Paraf, left ashes containing a substantial amount of copper. In addition, when this color was prepared in porcelain vases and printed by hand with a wooden board, it produced a gray blue hue instead of black. Printed with a metal plate or roller, or preparing the color in copper vases, always produced black. All these facts indicated that the copper originated from the instantaneous action of the acid contained in Paraf black. Although the amount dissolved was extremely small, it was enough to produce the same black as in present procedures. Hence, the patent claim was erroneous, the black was the result of a foreign metal introduced during the handling of Paraf's mixture (Lauth, 1866).

In 1869 Lauth patented a process of dyeing aniline black by means of manganese dioxide, used as a mordant and oxidizing agent (Lauth, 1869), and in 1873, he published a detailed description of his new process (Lauth, 1873b). This process was based on fixing on the fiber insoluble substances rich in oxygen or chlorine (i.e., higher oxides of manganese, lead dioxide, lead chlorite, etc.) easily decomposed and unable, by dispersing in the dye bath, to decompose the salts of nitrogenated compounds with which the bath was loaded. The paper included details about the steps of mordant attachment, dyeing, and brightening (Lauth, 1873b).

Aniline green

In 1872, Lauth and Henry Baubigny (1842-1913) deposited with the Académie des sciences a sealed envelope containing information about a new process they had developed. At their request, this envelope was opened in 1873 and found to describe a new method for the manufacture of aniline green (Lauth & Baubigny, 1873).

Lauth and Baubigny wrote that aniline greens, known as green lights, were first manufactured by the reaction of aldehyde and hyposulfite or alkaline sulfides with rosalinine salts. This process was then replaced by others, one involving the reaction between alcoholic iodides on rosaniline or Paris violet (iodine green), and another, involving the dehydrogenation of dibenzyl-aniline. The first modification was the one mostly used. The high cost of iodine led Lauth and Baubigny to search and find a cheaper process; its description was the central subject of the secret document (Lauth & Baubigny, 1873). The basic feature was the replacement of methyl iodide by an alkyl group combined with a mineral acid radical (i.e., sulfate, chloride, nitrate, phosphate, etc.), or by the sulfoconjugated acids of alcoholic radicals. The preferred agent was methyl nitrate, in the presence of an alkali or an alkaline earth. The resulting energetic reaction enabled operating at low temperature, in a closed or open vessel. Lauth and Boutigny added that the purpose of their publication was to assure to themselves the priority of this discovery (Lauth & Baubigny, 1873).

Porrier, Charles Bardy, and Lauth added that aniline green was prepared by the action of oxidants such as chlorine, bromine, iodine, nitric acid, nitrates, chlorates, etc. on benzyl or dibenzylaniline, tolyl or ditolyl aniline, or their mixtures (Porrier, Bardy & Lauth, 1874).

Lauth wrote that the fact that aniline green had very little affinity for wool had led him to develop a process for overcoming this disadvantage (Lauth, 1873a). In his process, the wool was first treated with a solution of sodium hyposulfite, mixed with an acid or acid salt. The resulting aqueous emulsified sulfur fixed itself to the wool as a mordant, allowing attachment of the green dye. The sulfur of the hyposulfites softened the fibers, made them lose their elasticity, and shrink considerably. Lauth found that these effects were the result of the introduction of the sulfur into the tubes of the fiber (Lauth, 1873a).

Lauth summarized his work on the synthesis and uses of his dyes in several publications (i.e., Lauth & Depouilly, 1860; Lauth, 1874).

Dyes from diamines

In 1876, Lauth reported his first results on his research about the synthesis of new dyes derived from aromatic diamines (Lauth, 1876). A few of these substances had already been converted into dyes. For example, aniline brown was produced by the reaction of α -phenylene-diamine with nitrous acid. The diamines were obtained by reducing the nitrated derivative coming from the acetyl combination of organic bases. For example, aniline was converted into acetanilide by its reaction with acetic anhydride and glacial acetic acid in the presence of zinc dust. Acetanilide was then converted into nitracetanilide and nitraniline; and finally, the nitraniline was reduced to β -phenylene-diamine. $C_6H_4(NH_2)_2$ (Lauth, 1876).

Lauth selected a different approach, using thio- β -phenylene-diamine as the starting block. This compound was prepared by heating at 150°-180 °C a mixture of equal weights of β -phenylene-diamine and sulfur, followed by solution with diluted HCl, filtration to eliminate the excess sulfur, and oxidation of the liquor, to yield blue violet colors. This product could also be obtained by treating the HCl solution of β -phenylene-diamine with hydrogen sulfide, followed by addition of ferric chloride. The precipitated dye was separated by filtration, washed with slightly salted water, and then dissolved in boiling water. Upon cooling, the dye precipitated from the water in a crystalline state (Lauth, 1876).

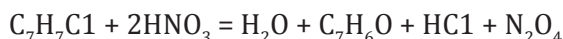
The dye was very soluble in pure water and alcohol. The solution was red in pure alcohol and fuchsin red in alcoholic NaOH. Dissolution in other reagents gave different colors. For example, violet in acetic acid and pure blue in mineral acids. Addition of metallic salts resulted in purple precipitates. Heated with aniline, it gave a blue insoluble in water and soluble in alcohol. With ammonia aldehyde, methyl iodide, etc., it transformed into increasingly green blues, which were fixed by simple immersion of the fiber into an aqueous solution (Lauth, 1876).

Lauth also studied the possibility of using the oxidation of other nitrogenated substances (i.e., azobenzoldisulfo- β -naphthol and benzosulfoazophenol), and the compounds' benzidine tetramethyl-meta-diamide, and diamidosulfo benzide and its derivatives, as a possible source of dyes (Lauth, 1882, 1891, 1892b).

Lauth was granted several patents describing his dyes, their manufacture, and use (i.e., Lauth, 1861a, 1869).

Action of chlorine and bromine on toluene and xylene

In 1866, Lauth and Edouard Grimaux (1835-1900) reported a simple process for preparing monochloro toluene, C_7H_7Cl , in large quantities. This was done by passing a stream of chlorine through toluene heated to 110° - 120° °C in a flask connected to a reflux condenser (Lauth & Grimaux, 1866a). They also found that distilling the part that passed before 170° °C and subjecting it again to the action of chlorine, resulted, after rectification, in a quantity of benzyl chloride, $C_6H_5CH_2Cl$, (passing between 170° and 180° °C) amounting to 90% of the toluene employed. Heating the benzyl chloride with diluted nitric acid, for one hour at 100° °C, oxidized it to benzaldehyde (the mayor component of the essence of bitter almonds):

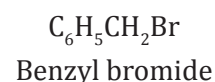
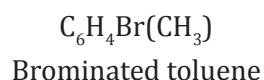


accompanied by a considerable quantity of benzoic acid, formed by the action of nitric acid and HCl (aqua regia) on the aldehyde. The yield of the aldehyde could be sensibly improved by repeating this reaction in the presence of lead nitrate, which converted with the HCl to lead nitrate, and streaming CO_2 through the reaction mixture to eliminate the nitrogen dioxide and avoid the formation of benzoic acid. Lauth and Grimaux remarked that their process provided a cheap source of synthetic essence of bitter almonds (Lauth & Grimaux, 1866a).

Lauth and Grimaux also found that the synthetic essence could also be obtained by reacting benzyl acetate, $C_7H_5OOC_2H_3$, with nitric acid. Benzyl chloride could also be used to prepare other valuable chemicals: (1) heating it for two hours at 100° °C with 10 times its weight of water and 3 times its weight of freshly precipitated lead oxide, transformed it to benzyl alcohol; (2) heating it for two hours at 100° °C a mixture of potassium phenoxide and one molecule of benzyl chloride dissolved in alcohol, resulted in the formation of benzyl phenoxide and potassium chloride. Benzyl phenoxide crystallized in small pearly scales, melting below 40° °C, and having a pleasant smell, and (3) heated for six hours at 100° °C in a closed vessel with rosaniline hydrochloride (fuchsine) or free rosaniline and alcohol, furnished a very beautiful and very pure violet (Lauth & Grimaux, 1866a).

Lauth and Grimaux also prepared benzyl valerate and reported that it decomposed on distillation (Lauth & Grimaux, 1866a).

In 1862 Rudolph Fittig (1835-1910) reported the synthesis of bromotoluene by the reaction of toluene and bromine and distillation of the product passing between 179° and 180° °C (Fittig, 1860). Lauth and Grimaux carried on the synthesis of bromotoluene by adding a mole of bromine dropwise to a mole of toluene at room temperature. This reaction, initially highly exothermic, with abundant release of HBr, slowed down and stopped after several days. The excess of bromine was then neutralized with potassium carbonate and the filtrate distilled to pass the brominated toluene, C_7H_7Br , between 179° and 180° °C, as reported by Fittig (Lauth & Grimaux, 1866b, 1867a). Mono bromotoluene was a colorless and clear liquid, with a weak odor when cold; its vapors strongly irritating the eyes. It was isomeric with benzyl bromide:



It was very stable and did not exhibit the reaction of the alkyl bromide; with potassium acetate it did not produce benzyl acetate, did not combine with alcoholic ammonia, and distilled on molten KOH without decomposition (Lauth & Grimaux, 1866b, 1867a).

In another experiment, Lauth and Grimaux tried to prepare the dibrominated derivative by reacting one mole of toluene with two moles of toluene. Neutralization of the excess bromine with potassium carbonate left a dense, colored liquid, which upon distillation began to decompose from 187 °C; up to 210 °C, with release of HBr. The black residue did not solidify over time (Lauth & Grimaux, 1866b, 1867a).

Lauth and Grimaux prepared dichlorinated toluene following the procedure of Friedrich Beilstein (1838–1906) (Beilstein, 1860), but were unable to convert its purified product into benzaldehyde by the action of mercury oxide. Inspection of the three possible isomeric formulas $C_6H_3Cl_3CH_3$, $C_6H_4ClCH_2Cl$, and $C_6H_5CHCl_2$, suggested that Beilstein's product was not enough pure, it probably contained some $C_6H_5CHCl_2$, which gave rise to benzaldehyde (Lauth & Grimaux, 1866b, 1867a).

Lauth and Grimaux applied the same chlorination procedure to pure xylene, boiling between 137° and 139 °C, and reported the results for mono and dichlorinated xylene (Lauth & Grimaux, 1867b).

Monochlorinated xylene, C_8H_9Cl , was prepared by reacting a stream of xylene with another of chlorine for several hours. This reaction resulted in the abundant release of HCl and a chlorinated product, highly irritating to the eyes. Fractional distillation and collection of the fraction passing between 190° and 195 °C indicated the presence of a monochlorinated derivative, containing by weight, 68.39% of carbon, 6.32% of hydrogen, and 25.29% of chlorine, and precipitating in the cold silver nitrate (Lauth & Grimaux, 1867b).

Kept boiling with silver acetate, it precipitated silver chloride leaving a liquid with a pleasant odor, which appeared to be tolyl acetate. Heated for one hour with a solution of one half of lead nitrate in six or seven times its weight in water, it transformed into another liquid having an odor reminiscent of the essences of bitter almonds and cinnamon. It reacted with sodium bisulfite giving tolyl aldehyde, C_8H_8O , boiling at 200 °C. All these results indicated that this material had the characteristics of a monochlorinated derivative of xylene, corresponding to the chloride of tolyl alcohol $C_6H_4(CH_2Cl)(CH_3)$ (Lauth & Grimaux, 1867b).

Lauth and Grimaux found that the portions of crude chlorinated xylene, which distilled between 230° and 260 oC, left a solid matter, which crystallized as white flakes having a strong and irritating odor. Elemental analysis indicated that it contained, by weight, 54.45% of carbon, 4.95% of hydrogen, and 40.60% of chlorine, corresponding to a dichloro derivative of toluene, $C_8H_8Cl_2$, melting at 100 °C and distilling between 240° and 245 °C with decomposition (Lauth & Grimaux, 1867b).

References

- Anonymous. France. (2023). Archives Nationales. Base Léonore, dossiers nominatifs des personnes nommées ou promues dans l'Ordre de la Légion d'Honneur.
- Beilstein, F. (1860). Über die Identität des Chlorbenzols mit dem Gechlorten Chlorbenzyl (Bichlortoluol). *Liebig's Annalen*, 126, 336-356.
- Cordillot, H. (1863). *Process or Processes for Producing Aniline Black on Cotton Fabrics or Yarns*. British Patent #3045, dated December 4, 1863.
- Danne, J. and Lauth, C. (1904). *Le Radium: Sa Préparation et ses Propriétés*. Bernager, Paris.
- Dupont, J. and Lauth, C. (1902). *L'Industrie des Matières Colorantes*. Baillièere, Paris.

- Fittig, R. (1860). Über das Monobrombenzol. *Liebig's Annalen*, 121, 361-365.
- Hoffman, A. W. (1858-1862). On Mauve and Magenta. *Royal Institution Proceedings*, 3, 468-483.
- Lauth, C. (1861a). *Preparation of Certain Colouring Matters and also a Process of Printing and Dyeing Woven Fabrics, Yarns and other Substances*. British Patent #2432 dated November 3, 1861.
- Lauth, C. (1861b). Sur un-Bleu d'Aniline. *Bull. Soc. Chim.*, 78-79; *Répertoire de Chimie Appliqué*, 3, 273-274.
- Lauth, C. (1861c). Action de l'Acide Iodique sur l'Aniline. *Répertoire de Chimie Appliqué*, 3, 274-276.
- Lauth, C. (1861d). Matières Colorante Dérivés de la Méthylaniline. *Répertoire de Chimie Appliqué*, 3, 343-347.
- Lauth, C. (1861e). Préparation de la Fuchsine para l'Action du Bichlorure de Carbone sur l'Aniline. *Répertoire de Chimie Appliqué*, 3, 416.
- Lauth, C. (1864). Sur le Noir d'Aniline. *Bulletin de la Société Chimique*, 5, 90-91.
- Lauth, C. (1866). Sur quelques Faits Nouveaux Relatifs à l'Histoire du Noir d'Aniline. *Bulletin de la Société Chimique*, 5, 90-91.
- Lauth, C. (1867a). *Notice sur les Travaux Industriels de M. Ch. Lauth*. Parent, Paris.
- Lauth, C. (1867b). On the New Aniline dye, Violet de Paris. *Laboratory*, 1, 138-139.
- Lauth, C. (1867c). Sur la Diméthylaniline et Hydrate de Triméthylphénylammonium. *Bulletin de la Société Chimique*, 7, 448-449.
- Lauth, C. (1869). *Improved Coloring Matter for Dying and Printing*. US Patent #96242 dated October 16, 1869.
- Lauth, C. (1873a). Teinture sur Laine eu Vert d'Aniline. *Bulletin de la Société Chimique*, 19, 401-403.
- Lauth, C. (1873b). Sur l'Noir d'Aniline. *Bulletin de la Société Chimique*, 19, 437-441.
- Lauth, C. (1873c). Action du Gaz Chlorhydrique sur le Ammoniaques Composées. *Comptes Rendus*, 76, 1209-1212; 77, 489-493.
- Lauth, C. (1874). Sur quelques Matières Colorantes Dérivés de l'Aniline. *Compte Rendu Association Française Avancement Science*, 349-345.
- Lauth, C. (1876). Sur une Nouvelle Classe de Matières Colorantes. *Comptes Rendus*, 82, 1441-1444.
- Lauth, C. (1877). Sur les Eaux d'Égout de Paris. *Comptes Rendus*, 84, 617-620.
- Lauth, C. (1881). *Les Produits Chimiques et Pharmaceutiques*. Imprimerie Nationale, Paris.

- Lauth, C. (1882). Sur une Benzidine Tétraméthyl-Méta-Diamidée. *Comptes Rendus*, 114, 1208-121.
- Lauth, C. (1883). Fabrication sur Porcelaine, du Bleu au Grand Feu, dit Bleu de Sèvres, *Bulletin de la Société Chimique*, 39, 435-443.
- Lauth, C. (1884). *La Manufacture Nationale de Sèvres et la Porcelaine Nouvelle*. Quantin, Paris.
- Lauth, C. (1891). Sur la Oxidation des Corps Azotiques. *Comptes Rendus*, 112, 1512-1515.
- Lauth, C. (1892a). *Notice sur ses Travaux Scientifiques*. Gauthier-Villars, Paris.
- Lauth, C. (1892b). Sur la Diamidosulfobenzide et quelques-uns de ses Dérivés. *Compt. Rendus*, 114, 1023-1024.
- Lauth, C. and Baubigny, H. (1873). Préparation de Verts d'Aniline. *Comptes Rendus*, 76, 1497.
- Lauth, C. and Depouilly, P. (1860). *Note sur les Rouges d'Aniline*. Raçon, Paris.
- Lauth, C. and Dutailly, G. (1888). *Recherches sur la Porcelaine*. Publications du Journal Le Génie Civil, Paris.
- Lauth, C. and Grimaux, E. (1866a). Recherches sur le Chlorure de Benzyle. *Comptes Rendus*, 63, 918-920. Published as booklet by Gauthier-Villars, Paris.
- Lauth, C. and Grimaux, E. (1866b). Sur les Dérivés Bromés et Chlorés du Toluène. *Bulletin de la Société Chimique*, 5, 347-349.
- Lauth, C. and Grimaux, E. (1867a). Sur le Bromure de Benzyle. *Bulletin de la Société Chimique*, 7, 108-109.
- Lauth, C. and Grimaux, E. (1867b). Sur les Dérivés Chlorés du Xylène. *Bulletin de la Société Chimique*, 7, 233-235.
- Lauth C. and Oppenheim (1867). Action des Chlorhydrates d'Essence de Térébenthine sur l'Aniline et sur la Rosaniline. *Bulletin de la Société Chimique*, 8, 6-8.
- Lauth, C, and Vogt, G. (1885). *Manufacture Nationale de Sèvres. Notes Techniques sur la Fabrication de la Porcelaine Nouvelle*. Unsinger, Paris.
- Lestel, L. (2007). *Itinéraires de Chimistes 1857-2007: 150 Ans de Chimie en France avec les Présidents de la SFC*. EDP Sciences, Paris.
- Lightfoot, J. (1863). *Improvement in Dyeing and Printing Textile Fabrics and Yarn with Aniline Black*. US Patent #38589 dated May 19, 1863.
- Paraf, A. (1866). *Improvement in Dyeing and Printing Textile Fabrics and Yarns*. US Patent # US60546A, dated December 18, 1866.
- Poirrier, A., Bardy, C., and Lauth, C. (1874). Matière Colorante Vert. *Bulletin de la Société Chimique*, 14, 138, 1874.