

Matches-The manufacture of fire

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The phosphorus match represents the culmination of the efforts to manufacture fire by friction at will, which started with the rubbing of two wood sticks. The modern cigarette lighter corresponds to the next evolutionary step in the process.

Frazer's book *Myths of the Origin of Fire*¹ gives a fascinating description of the legends about the origin of fire in different regions of the world. From the entry *Fire* in the encyclopedias^{2,3} we learn that fire is one of the human's race essential tools, control of which helped start it on the path toward civilization. The original source of fire undoubtedly was lightning, a chance event which remained the only source of fire for many years. The use of fire is one of man's earliest habits, so when an obvious fireplace with ashes and charcoal is found near such a skull, it is pronounced human. Only after the Neolithic times there is evidence that human beings actually knew how to produce fire. Archeological evidence suggests that the controlled use of fire may date from more than 500,000 years ago. The step from the control of fire to its manufacture required hundreds of thousands of years.

According to Singer *et al.*⁴ the discovery of how to make fire was man's greatest step forward in gaining freedom from the dominance of the environment.

The first human beings to control fire gradually learned its many uses. Fire not only kept them warm and cooked their food; they also learned to use it in fire drives in hunting and warfare. The possibility of heating the dwelling enabled people to survive hard winters and to spread to more extreme climates, and to keep off predators. Man's movement into the cold northern areas was probably a direct consequence of his control of fire. Thus the making of fire and maintaining it became vital tasks, without which many early societies would have perished. The discovery of fire also made possible the production of glass, pottery, metals, etc., as well as providing light when required⁵⁻⁷.

We do not know if the chance spark from striking flint against pyrites or a spark made by friction while

drilling a hole in wood gave human beings the idea for producing fire, but interestingly enough, making of fire by friction was discovered by people in widely separated parts of the world. The most widespread method for igniting fire was through the conversion of muscular energy into heat through friction. The fire drill, a wooden rod placed in a pit in a fireboard adjacent to tinder, was the commonly used implement. The initial fire was initiated by a rapid rotatory motion imparted by spinning the drill between the palms of the hands by means of a thong, alone or in combination with a bow, or by the up and down action of a pump drill. Other frictional methods, like the fire saw, the fire thong, and the fire plow, were also used. The Eskimos, ancient Egyptians, Asian people, and a few American natives developed mechanical fire drills. A fire piston that produced heat and fire by the compression of air in a small tube of bamboo was a complex device invented and used in Asia. Percussion methods of fire production were also invented at an early time. Pyrite when struck produces a slow burning spark^{2,3}. Once steel was invented, it was used in a like manner, with flint, to produce fire. The spark was caught in tinder (dry, powdery, and easily combustible matter), which caused it to make a small glowing ember. Every traveler carried a tinderbox, containing a piece of steel, a piece of flint, and a supply of reliable tinder. Flint and steel are represented at present by the steel wheel and flint (today a metallic alloy) of the cigarette lighter.

According to Pliny⁸ (23-79 CE) "this experience was first discovered in the camps by the shepherds, when a fire was wanted and a fitting stone was at hand, for they rubbed together wood upon wood, by which attrition sparks were engendered, and then collecting any dry matter of leaves or fungi, they easily took fire."

Before the invention of matches, a common method for transferring fire was using splinters tipped with some combustible substance, such as sulphur, which catches fire readily. Small sticks of pinewood impregnated with sulphur, were already used in China in the 6th century CE, and by the Romans for catching the spark from a tinder and flint (Pliny recommended laurel and ivy woods). The burning splint (or match) could then be used to light a lamp or a fire. The property which sulphur igniting at about 150 °C explains its ancient use in making those matches, which proved such an improvement in connection with the preceding flint and steel. Sticks dipped in various elements, typically phosphorus and sulphur, were introduced sometimes in the nineteenth century. The first match was born and again friction was the key event to produce fire.

According to Heavisides⁹ “it is related that when #1 Locomotion was first placed on the rails at Aycliffe Level, for a trial trip, its boiler filled with water and wood and coal made ready for lighting, it was discovered that no one had a light. John Walker had not yet invented his friction lights. George Stephenson (1781-1848) was just on the point of dispatching a man to Aycliffe for a lighted lantern, when a navy stepped forward and presenting a burning glass, said he often lit his pipe by its aid, and perhaps it might fire the engine. The glass was tried and found successful, and Robert Metcalf it was, who with a common sun-glass and a piece of tarred oakum, actually lit the fire of Locomotion. The truth of this incident has been thoroughly corroborated, and this beyond all doubt was the first locomotive that ever moved over a public railroad and the fire was kindled in its first trial trip by the aid of the sun itself”.

Fire has also played an important role in the intellectual life of man, and most societies have had myths that attempt to explain its origin and ceremonials that employ it. The sacred fires and fire drills of religious rituals and the numerous fire gods of world mythology must be interpreted as additional evidence of both the antiquity and the importance of fire in human history^{1-3, 10-12}.

A match is a simple and convenient means of producing fire under controlled circumstances and on demand. It consists of a short wooden or cardboard stick with a small head of flammable chemicals and a striking surface. The word match comes from the French *mèche*, a wick, as in a lamp. Both words probably are derived from the Greek $\mu\upsilon\zeta\alpha$ or the

Latin *myxa*, *mixa*, or *myxus*, the wick of a lamp. In the old days it represented a short, slender piece of wood, cardboard, or (formerly) wax taper, tipped with a composition, which ignited by friction when rubbed against a roughened surface, or (originally) when brought into contact with a chemical reagent. The match, or more precisely, the slow match, was a piece of rope soaked in potassium nitrate, and dried. When lighted and blown out a red ember continued burning slowly without flame. This instrument soon found application in the development of firearms. When a cannoner wanted to discharge his piece, he touched the match to the touch-hole, which had been filled with gunpowder, and the cannon was fired. A musketeer clipped his match to the matchlock mechanism at the breech of his weapon, and pulled it back against a spring until a catch engaged. The match, then, was a way of having fire ready for when it was needed, so it is quite reasonable to transfer the name to the wooden match⁵.

Although, phosphorus was discovered in 1669 (see below) it took more than 150 years to develop the first useful phosphorus match, in spite of the many attempts made to use the element's property of instantaneous combustion in air as a source of instantaneous fire. In the interim period many devices were developed, part of them operating without the use of phosphorus, and part using this element. In what follows we will describe the main events that took place until the technology converged into the modern match.

Non-phosphorus fire

Between the years 1780 and 1830 a great variety of chemical fire making devices made their appearance. These were intermediate between mechanical methods and friction matches, and finally led to the introduction and development of the first true friction match.

The pyrophorus or pyrophosphorus (fire carrier) consisted of a sealed glass, or ampoule, containing a finely divided pyrophoric powder free of phosphorus, which ignited spontaneously when the tube was broken and the contents scattered (pyrophoric powders are chemicals in finely powdered and reactive state, which catch fire on exposure to air)¹³. One of the first pyrophorus was made by Willem Homberg (1652-1715) by mixing 3 parts of alum with 2 or 3 parts of honey, flour, and sugar, and then carefully drying the mixture, with constant agitation, in an iron pan. The mixture at first melted, and then

dried into small pieces, which were reduced to powder and then roasted again¹⁴. A portion of this powder sprinkled over dry cotton caused it to take fire. Robert Hare's (1781-1858) pyrophorus, introduced in 1831, was made by heating roasted Prussian blue to redness in a glass tube, which was then immediately thereafter sealed; while Roesling's pyrophorus was a powder to be packed on top of the tobacco in a pipe and ignited by sucking air through it. Faraday demonstrated a lead pyrophorus made from roasted lead tartrate sealed in a gas tube. On breaking the tube, the powder gave a red flash when shaken out^{6,13}.

In 1823, Johann Wolfgang Döbereiner (1780-1849) obtained a spongy platinum material by calcinating ammonium chloroplatinate. This material was shown to be able to absorb hydrogen at room conditions and on heating up to ignite a stream of air directed to it. Water was formed as a result without the spongy mass changing its aspect or its weight, and being capable of repeating the process after cooling. In those days, when there was no simple way to produce fire, Döbereiner's discovery led immediately (1824) to the manufacture of the famous hydroplatinic lamp, the *Döbereiner Feuerzeug* (Döbereiner lamp), also called *briquette à hydrogène* (hydrogen lighter). In this apparatus, hydrogen produced from zinc and sulphuric acid passes through a jet and impinges on some spongy platinum suspended on a thin platinum wire. The gas catches fire and the flame can then be transferred to a candle¹⁵. The Döbereiner lamp was used for lighting purposes for about 100 years until replaced by the phosphorus match.

Interestingly enough, a pyrophoric mixture was patented as recently as 1937¹⁶. Its basic tenet is provision of an ignition mixture that can safely be lit on the usual friction surfaces for safety matches and without evolution of obnoxious or evil smelling gases. This is achieved by replacing the phosphorus and sulphur with semi-pyrophoric metals such as magnesium, aluminium, zinc, and cobalt, having a sufficiently low ignition temperature, which on combustion do not furnish volatile combustion products but solid oxides in the form of powder. The safety mixture, ignitable by friction on rough surfaces and suitable for safety matches, comprises an oxygen-yielding substance such as potassium chlorate, a semi-pyrophoric metal, an abrasive material such as burned clay, pyrolusite (impure manganese dioxide), and a binding material such as collodion.

The pneumatic tinder box or light syringe consisted of a small metallic cylinder with an accurately fitting piston. The bottom part of the cylinder was attached by a screw, and a small amount of tinder or amadou (German tinder) was contained in the recess. By a rapid stroke of the piston driving it home, the air was suddenly compressed and the heating ignited the amadou in the recess, which was then removed for use.

Many varieties of the electropneumatic lamp or electropneumatic fire producer were invented between 1775 and 1830, the principle being the ignition of a fine jet of hydrogen gas by means of a spark from a piece of charged rosin. The inflammable lamp of Volta consisted of a small glass reservoir filled with hydrogen gas that could be pressurised by a column of water by turning a stop cock. The pedestal upon which the reservoir was placed was an electrophorus; on turning the cock a small hydrogen stream rushed out and met an electric spark from the electrophorus, which ignited the gas. The apparatus was very unsafe because of the danger of explosion resulting from the mixing of hydrogen and air.

Chemical matches, which appeared for the first time in Vienna in 1812, are an important chapter in the development of the modern match. They consisted of a mixture of potassium chlorate and sugar coloured with cinnabar, or of potassium chlorate, sulphur, and lycopodium powder (*Lycopodium Clavatum*, a club moss) agglutinated with a solution of gum Arabic. The mixture was used to coat one end of a sulphur stick, which ignited when introduced in a flask containing asbestos saturated with concentrated sulphuric acid, and resulted in the inflammation of the stick. The sulphuric matches were known as *Instant light boxes* (and later as *Empyrions*, *Chemical matches*, and *Oxymuriated matches*).

The first attempt to improve on the old sulphur match was done in 1805 by Jean Chancel, assistant to Louis-Jacques Thénard (1777-1857). Chancel's procedure for initiating combustion was using the oxidizing power of concentrated sulphuric acid to ignite a mixture of sugar and potassium chlorate, a reaction discovered previously by Claude-Louis Berthollet (1748-1822). His appliance was composed by a metal box containing a small flask full of sulphuric acid, and a number of cedar wood splints coated at one end with a mixture of potassium chlorate, sugar and a binding material, the latter commonly being a vegetable gum such as Arabic or

acacia. When the splints were dipped in the acid and withdrawn, they would burst into flames. Once Chancel's sugar was aflame it would remain so long enough to ignite the wooden splint. This provoked decomposition of the potassium chlorate into chlorine dioxide, an unstable gas which can explode when on contact with hot glass, sparks, alcohol, or indeed any organic material. Too many times the acid would leak out of the bottle and damage clothing, upholstery, and rugs. Inserting finely fibered asbestos in the bottle to absorb the acid later solved this problem. This kind of match was quite expensive and dangerous to use, so Chancel's matches never gained much popularity, although they remained in use for about forty years, in one form or another.

Later, workers continued to refine the method, culminating in the *Promethean Match*, patented in 1828 by Samuel Jones¹⁷ of London. These matches consisted of a glass bead filled with a solution of sulfuric acid coloured with indigo, hermetically closed, and coated in the outside with a composition containing potassium chlorate, sugar, and a binding material. The prepared capsule was compactly wrapped up in a roll of paper (similar to a cigarette) about 10 mm long and 1 mm wide, and coated in the igniting mixture. When the glass was broken by means of a small pair of pliers or even with the user's teeth, the chlorate ignited setting the paper on fire.

Some time afterwards, an Englishman named Heurtner opened a shop on the Strand, opposite the church of St. Clement Dane. It was named the Lighthouse, and he added this inscription to the mural literature of London: "To save your knuckles, time and trouble, use Heurtner's Empyryon, price one shilling". An ornamental, open moiré metallic box containing fifty matches and the sulphuric acid asbestos bottle was sold for one shilling. They sold well and were known colloquially as the Hugh Perry. They were not always very reliable as a contemporary account shows: "Instead of a brilliant flame, the match smouldered only and spurted acid about to the detriment of clothes and a peaceful disposition"¹⁸.

All these devices were cumbersome, tricky to use, often dangerous and unreliable, and very expensive. The search was on for an option that did not involve dangerous acids. Another alternative was based on the idea that rubbing two rough surfaces together produced heat, and in the early 1800's several commercial manufacturers produced chlorate-based

friction matches. The early matches specimens had a number of problems. Ignition was done by drawing the matches through a fold of sand paper, with pressure. Many times the tipped part was torn off without igniting; the matches were extremely difficult to light, the flame was unsteady and the initial reaction was frustratingly violent, sometimes a flaming ball flew off and landed on the carpet or a dress. In addition, the smell of emitted hydrogen sulphide gas was unpleasant. Despite these problems the new matches were responsible for a marked increase in the number of smokers.

The critical stage in the development of the chemical match took place in 1826 when John Walker (1781-1859), an English chemist and apothecary of Stockton-on-Tees, prepared and sold his *Friction Lights*, also called *Congreves* in honor of William Congreve (1772-1828), the inventor of the military rocket. Walker is often credited with inventing the friction match although his matches contained no phosphorus^{6,9}. One of the preparations he sold was percussion powder, made of a dry mixture of potassium chlorate and antimony trisulphide, kneaded with a water solution of glue. In 1827, he discovered that coating one end of wooden splints with a mixture of one part of potassium chlorate, sugar, and two parts of antimony trisulphide, bound with gum Arabic and starch, a fire could be started by passing the stick between two surfaces of sand paper held between the fingers. These *sulphuretted peroxide strikables* were gigantic, yard-long sticks that did not have the inconvenient necessity of acid, and can be considered the real precursor of today's match. They were sold in cylindrical boxes of 100 for one shilling.

Walker did not patent his invention and their manufacture was taken up by Samuel Jones who in 1830 sold them as *Jones's Lucifer Marches* (the Latin equivalent of phosphorus), a term which later became a popular name to describe phosphoric matches. This type of matches was also manufactured and sold by G. F. Watt, under the name *Watt's Chlorate Lucifer Matches*. Jones was the first person to sell matches in small, rectangular cardboard boxes. The sulphur-based matches gave off copious and noxious fumes, and the following warning was printed on the box of Jones's Lucifers: "If possible, avoid inhaling gas that escapes from the combustion of the black composition. Persons whose lungs are delicate should by no means use the Lucifers".

The Promethean matches are mentioned in many novels. For example, William Smith in his book *"Morley: Ancient and Modern"*¹⁹ says: "A friend of ours in Leeds tells us that in 1831 he was in Keswick, and was shown a very great curiosity, a box of matches. They were known as "Jones's Prometheans," and the price was 2s.6d. The matches of Jones were ignited by being dipped into a bottle containing a composition of some kind." Similarly, Charles Robert Darwin (1809-1882) in his book *The Voyage of the Beagle*²⁰, wrote: "I carried with me some Promethean matches, which I ignite by biting; it was thought to be so wonderful that a man should strike fire with his teeth, that it was usual to collect the whole family to see it; I was once offered a dollar for a single one."

The idea of using friction to generate the heat needed to ignite the match has been followed ever since, rather than using spontaneous chemical reactions to produce a flame.

According to Heavisides⁹ in 1834, John Marck opened a store in Park Row, New York, and drew public attention to two novelties. One was champagne-wine drawn like soda water from a fountain; the other a self-lighting cigar, with a match composition on the end, which was named *Loco-Foco* cigars, adopted after the rather new word "locomotive" (self-moving); hence, self-firing cigars. His patent for *self-igniting cigars* was issued on April 16, 1834. The word Loco focus was also used to name in derision the members of a faction that split off from the Democratic Party in New York in 1835, where the illuminating the gas was turned off and the hall plunged in darkness. The reformers, however, continued their work by the light of candles and of self-igniting Loco Foco matches, from which their nickname derived.

Although these friction matches worked, they were soon to be replaced by phosphorus-based matches, which ignited more reliable.

Phosphorus matches

A real match that was easily ignited by friction was not achieved until the scientists started using phosphorous in their experiments and evolved a suitable mixture for tipping the matchstick.

In the year 1669 phosphorus (from the Greek, light bearer) 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 led to a white, waxy substance that glowed so enchantingly in the dark. When his alchemical experiments revealed the light-giving element Brandt called it cold fire (kaltes feuer). Brandt kept secret his method of obtaining phosphorus, but the news of the amazing discovery soon spread throughout Germany. Brandt's discovery was an accident but his discovery of cold fire would enable inventors to produce fire on demand, an unimaginable achievement to Brandt's contemporaries²¹.

The discovery of phosphorus, followed soon after the discovery of the induced phosphorescence of certain calcium salts, had an enormous effect on contemporary chemists. The new substance shone continuously in the dark, inflamed on slight provocation, burned with a flame extraordinarily brilliant, and wasted away entirely unless kept under water²¹.

In 1670, Robert Boyle (1627-1691) prepared phosphorus by heating sodium phosphite with sand. Boyle called the material *icy noctiluca* (cold light) and examined its properties in a systematic way. Ten years later Boyle made sulphur heads on thin splits, using glue to hold them together. Then he soaked paper in dissolved phosphorus and dried it. When a piece of the paper was doubled and a sulphur head drawn through it, the sulphur caught fire. These appear to have been the first matches, but they were only a curiosity, since the phosphorus paper had to be fresh, and was as inconvenient to prepare as rare the element⁵. Boyle was convinced that the flames were caused not by friction but by something inherent in the nature of the phosphorus and sulphur themselves. However, there was no useable match created by Boyle.

One of the earliest chemical fire-making devices was the *phosphoric taper*, also called *phosphoric candle*, and *ethereal match*, introduced in France in 1781. Basically it was a 10-cm sealed glass tube containing a thin waxed taper with frayed end, and a small piece of phosphorus at its bottom. The tube carried a circle drawn around with a glazier's diamond at the end furthest from the phosphorus. The tube was immersed in hot water; the phosphorus melted and impregnated the frayed end of the paper. For obtaining a light, the tube was broken at the circle with the aid of the teeth or otherwise, and the taper withdrawn, bursting into flame upon contacting the outer air. Phosphoric candles were too expensive for

everyday use and very dangerous; they were considered more of a novelty than a practical fire-starting tool.

Other early matches, which could be both inconvenient and unsafe, were basically small bottles containing phosphorus and other substances. The *portable phosphorus box*, *phosphorus bottle*, and *pocket luminary*, which appeared in 1786 in Italy, consisted of a small metal box containing a small airtight flask coated in the inside with a thin layer of oxidised phosphorus, and a small number of wooden splints tipped with sulphur. The fire was started by introducing one of the splints in the bottle, rubbing it against the internal coating, and then withdrawn to the outside so as to cause ignition¹³. In 1810, Charles Cagniard de la Tour (1777-1859) introduced a similar device which contained partially oxidized phosphorus and was used in conjunction with a splint tipped with sulphur which was ignited by friction. An important modification, which did not require a bottle or other apparatus to ignite the splint, was the *briquette phosphorique*, invented by François Derosne in 1816, which used a sulphur tipped match to scrap inside a bottle coated internally with phosphorus. The use of the phosphorus bottle as an igniting medium is mentioned in many novels. For example, in *The Golden Magnet*²² it says: "Without a word my uncle glided away; then I heard a rustle as of paper; there was the faint glow of a match dipped in a phosphorus bottle, the illumination of a large loose piece of paper, and then a torch was lit..."

Other important developments were based on the explosive reaction that takes place when white phosphorus and sulphur are melted together and potassium chlorate is used as the oxidising trigger. A wood splint, tipped with a mixture of the three compounds, was rubbed across a rough surface. The frictional heat was enough to ignite the mixture. This type of matches was prone to spontaneous ignition but this was a small price to pay for elimination of the problems associated with the phosphorus bottle.

Between 1830 and 1834 white phosphorus-based matches, which also became known as Congreves or Lucifers, were introduced in several countries. Jacob Friedrich Kammerer, who installed his first match factory in Ludwigsburg, Germany, is often credited with the first phosphorus-based friction match, although Charles Sauria had made them two years earlier in France. Hungary claims János Irinyi (1817-1895) as the inventor. In 1837, Irinyi added

phosphorus to water, shook it in a glass foil until it became granulated and then mixed the grains with lead oxide and gum Arabic. He coated one end of pine splints with the mixture and let them dry. The result was matches that ignited quietly and smoothly. Irinyi sold his invention to István Rómer (1788-1842) who thereafter manufactured the new type of match in Austria.

In 1830, Charles Marc Sauria (1812-1895), a French chemistry student at the Collège de l'Arc in Dôle, Jura, discovered the principle of the phosphorus match. After watching a demonstration of the reaction of sulphur mixed with potassium chlorate, Sauria eventually experimented by rubbing the prepared end of his match on a wall where there was some phosphorus. Sauria added white phosphorus to remove the smell. His match immediately ignited, and so did the development of the match industry. These new matches had to be kept in an airtight box but were popular. A year later, in 1831, Sauria substituted tetraphosphorus trisulphide, P_4S_3 , for antimony sulphide, and created a very reliable and easy to ignite match. Regrettably, those involved in the manufacture of the new matches were afflicted with *phossy jaw* with necrosis of the jawbone, the principal symptom of chronic phosphorus poisoning, and there was enough white phosphorus in one pack to kill a person (see below).

Sauria, however, did not possess sufficient funds for patenting his invention, which was afterwards used of by matchmakers in Darmstadt in Germany and in Vienna. In 1884, the French government recognized the significance of Sauria's invention and granted him a tobacco shop (bureau de tabac); he was also awarded a gold medal by the Académie Nationale Agricole.

The fuzee (fusee, from French fusée, spindle, rocket, flare, fuse), also invented by Samuel Jones in 1832, was intended specifically for lighting cigars and consisted of a cardboard splint soaked in potassium nitrate solution and tipped with a phosphorus composition. The potassium nitrate kept smouldering after ignition. Jones made his fuzees in comb form so that the sensitive heads would not touch each other and one could be torn off when needed. Later they were used for setting off explosives safely, particularly in railroad warning lights. William Newton patented the original Vesta match in England in 1832²³. These matches consisted of a wax stem reinforced with several cotton threads, coated on one

end with the regular phosphorus composition giving a long-burning taper. A later variation was the Swan Vestas, which had a wooden splint soaked in wax; they were also invented by Jones in 1832.

Small phosphorus matches were first marketed in Germany in 1832, but they were extremely hazardous and were eventually prohibited in France and Germany because they were thought to be too dangerous⁵.

In 1836, in the United States, Alonzo Dwight Phillips of Springfield, Massachusetts, obtained the first patent²⁴ for manufacturing friction matches, which he called *Loco Focos*. In his patent, Phillips claimed that he had developed "certain new and useful improvements in modes of manufacturing friction matches for the instantaneous production of light. The improvements consist of a new composition of matter for producing ignition and a new mode of putting up the matches for use by which the danger of ignition from accidental friction or from other causes is obviated..." Instead of the common composition used in preparing the matches (phosphorus, chlorate of potash, sulphuret of antimony, and gum arabic or glue), Phillips suggested a paste of phosphorus, chalk, and glue. The matches were first dipped in sulphur and then in the paste. An important feature of the patent was the way in which the splints were manufactured and their accommodation in the box, so as to diminish the danger from accidental ignition. Phillips prepared the splints by cutting the wood pine into thin slabs having the thickness of veneers. The slabs were then cross cut lengthwise with the grain of the wood, comb fashion, leaving a portion at one end uncut, which held about a dozen of splints together like the back of a comb. The splints were then dipped in molten sulphur and in the ignition paste, and packaged for sale by laying the slabs into long strips of paper cut wide enough to lap over the ends of the matches. This procedure allowed withdrawing each slab without danger of accidental friction.

In 1849, Heurtner of London also brought out the Vesuvians, sometimes called *flamers* or *wind matches*, which like the fuzees were designed as out-of-doors lighting matches. They were provided with an extremely large pear-shaped head consisting generally of potassium nitrate, powdered charcoal, and wood dust all held together by glue. The head was tipped with regular phosphorus compositions and the stems were made of a number of materials, including wood, glass, and porcelain. This device was

afterwards more fully and usefully employed for firing the gunpowder in the railway fog signals^{6,13}.

An interesting fact is that when phosphorus was first introduced to the match-making industry its price was four guineas a pound; afterwards demand became so great that it had to be manufactured by the ton and the price dropped to half-a-crown a pound.

The most important event in the development of phosphorus took place in 1845 when Anton Schrötter (1802-1875), the Director of the Austrian Mint, discovered red phosphorus, an allotropic form of the element, which is insoluble and nonpoisonous²⁵. This discovery led to the fast development of the match industry. According to Schrötter it was long known that phosphorus exposed to the action of light turned red, a transformation that took place in vacuum or in the presence of any gas that did not react with phosphorus. Since none of the available theories was able to explain this phenomenon Schrötter decided to study it in more detail. Heating phosphorus in the absence of light changed its colour from white to carmine already at 500 K. Keeping the phosphorus at 513-553 K for 48-60 hours, led to the deposition of a more or less thick solid phase of amorphous phosphorus in the bottom of the vessel, while the upper layer remained ordinary phosphorus. Schrötter found that the temperature at which phosphorus changed to amorphous depends on the temperature, the time of reaction, and the action of light. The simultaneous action of light and higher temperatures made it faster. According to Schrötter, the concurrent action of light and heat resulted in the allotropic transformation of phosphorus, as proved by the fact that the new form of phosphorus reacted in the same way as white phosphorus, or that it converted back to white phosphorus by heating at temperatures about 523 K in an inert gas²¹.

Schrötter separated red phosphorus and measured many of its properties. The most important result was that it could be kept in contact with air without alteration. The amorphous phosphorus was easily attacked by nitric acid with release of gases. Mixed with potassium chlorate it detonated violently, producing light. The chemical reactivity of amorphous phosphorus was weaker than that of ordinary phosphorus, it combined with release of light, but less energetically than ordinary phosphorus. It combined with oxygen, by friction or heat, to produce a large number of oxygenated derivatives, with release of light. All these properties, including its

low hygroscopicity and lesser flammability, suggested its potential use in the manufacture of matches and percussion weapons, although a serious obstacle was how to fabricate in a large scale. In due time his predictions became true: Arthur Albright (1811-1900) in England developed a process for the mass production of red phosphorus, and the Lundström brothers in Sweden, developed and sold a safety match in which white phosphorus was replaced by red phosphorus, the phosphorus being confined to a strip on the box and the oxidizer used to tip the matches. Such safety matches could only be ignited by striking on the box and in due time would become the basis of the world production of the commodity²¹.

The safety match was invented in 1844 by the Swede Gustaf Erik Pasch (1788-1862), a professor in chemistry and a partner in J.S. Bagge & Co. Kemiska Fabrik of Stockholm, which was established in 1836 and was at that time the first match factory existing in Sweden. Pasch's idea was very simple: separation of the oxidizer and the tinder, thus removing the fire risk caused by self-ignition. The head of the match contained only potassium chlorate and no phosphorus so that ignition could only be achieved by striking the head on another surface (this is the safety match, as we know it today). The Pasch matches did not succeed because of the poor quality of the phosphorus (it contained phosphoric acid), its very high price, and because the thin cardboard used was unsuited to the friction paper, which was then placed on the lid. No one was willing to pay higher prices for safety and non-toxicity. On the other side of the box of Bagge's matchboxes was written: *Patenterade Stryksticker utan Fosfor* (patented friction matches without phosphorus). In 1855, Carl Frans Lundström and Johan Edvard Lundström (1815-1845) of Sweden, improved these matches, as explained below. The Diamond Match Company, a US company, developed and patented in 1910 a similar match using phosphorus sesquisulphide.

Samuel C. Moore patented in 1865 in the US an interesting variation of the match²⁶. In this patent the lighting substance was put on one end of the splint or match and the igniting substance on the other end, so that the match had to be broken in two and then lit by rubbing one piece against the other. As stated by Moore, this construction eliminated defacing walls, paper, or paint, and when carried in the pocket the match could be lit without seeking some other place or substance to rub it, that this, it was a self-lighting match.

The development of a specialised matchbook with both matches and a striking surface did not occur until 1890 when Joshua Pusey (1842-1906), an American investor and a prominent Pennsylvania attorney, invented book matches in 1889. The story as told, is a good example of how a need turns the wheels of invention⁷: "Pusey was fond of smoking cigars. One day the Mayor of Philadelphia invited him to a dinner party. He dressed in his best clothes, and all was fine except for one thing. The big box of wooden kitchen matches he was carrying to light his cigars, stuck out of his vest so much that he felt embarrassed. Why did matches have to be so bulky? Why could not they be made out of paper instead of wood? Paper matches would be lighter and much smaller. Fed up with carrying bulky boxes of wooden matches, he set to work to invent paper matches that would be lighter and smaller." His final design, which he patented in 1892²⁷, had matches secured to a thin paper wrapping with an attached striking surface. Unlike present-day matchbooks, Pusey positioned the striking surface on the inside of the paper fold. The paper matchbook, which Pusey called *Flexibles*, although a clear step forward, did not catch on right away. In his patent Pusey declares that the "primary object of my invention is to provide a friction-match card designed to be attached to the wall and in desirable and convenient locations, and which shall be cheap, handy, and safe, both in transportation and in use, it consists of a series of separate splints...the free ends are provided with a frictionally ignitable composition...any of the splints may be detached and lighted as an ordinary match..." A curious feature of the card was that it could be located in the dark by a line of luminous paint, painted in it. The Diamond Match Company, who had invented a similar matchbook, but with the striker located on the outside, tried in vain to challenge Pusey's patent.

During eight years Pusey tried fruitlessly to interest investors in his invention. Then in 1897, Pusey got his break. The Mendelsohn Opera Company wanted a special gimmick to advertise their New York opening. To do so they distributed matchbooks carrying their logo to advertise their New York opening. This publicity trick was so successful that demand for paper matchbooks soared. Suddenly everyone was talking about book matches and paper matches began selling as fast as they were made. In 1896, Pusey sold his rights to the Diamond Match Company for \$ 4000⁷. Nowadays, the safety-type cardboard match

(box match) developed by Pusey dominates the market all over the world.

Phosphorus necrosis

As we have seen, the main component of the new matches was white phosphorus, an extremely toxic material. The poisonous effects of white phosphorus were noted as soon as its manufacture for matches started growing. Matches containing white phosphorus, by themselves, were not only a health hazard to the matchmakers, but also to those using them because when they warmed up they could give off phosphorus fumes. Swallowing match heads was also a common method of committing suicide and swallowing match heads often poisoned small children.

Today we know that white phosphorus is physiologically a strong poison and as little as 50 mg can be fatal. Any human exposure to white phosphorus may cause severe thermal burns to the skin and eyes. Its vapour can cause acute lung irritation, followed by a build-up of fluid in the lungs. Continuous long-term inhalation of the vapour ($> 0.1 \text{ mg/m}^3$) may result in bone loss to the jawbone structure followed by loosening of teeth and swelling of the jaw. Phosphorus vapour is oxidised in air to phosphorus pentasulphide and it is the oxide that is dangerous. It is taken into the body through cavities in the teeth and often results in a complete decomposition of the jaw and extensive inflammation of the surrounding tissues. This condition is commonly referred to as phossy jaw (phosphorus necrosis). It does not attack people with sound teeth. The hazardous nature of phosphorus necrosis was appreciated early in 1839 but the production of white phosphorus continued for many years, although the match manufacturers introduced free dental treatment and regular inspections to protect their workers²¹.

Already in 1814 Mathieu Joseph Bonaventure Orfila (1787-1853), in his treatise about poisons²⁸, classified white phosphorus as a most irritant poison, although he did not remark anything regarding its local action and physiological effects. These were first described by Ambrose Tardieu and François-Zacharie Roussin²⁹ and their doctoral student Émile Fabre^{30,31}. Bone necrosis was reported only by 1840, after the industrialization of phosphorus production. In 1869, Jacques Personne (1816-1880), carried experiments on dogs to show that poisoning by phosphorus could be remedied with turpentine³². An interesting fact is that by that year police reports

showed that the toxic action of phosphorus had put it in the first place of poisonous substances used for criminal purposes. This substitution had come as a result of the wide use of chemical matches and phosphorus paste for destroying obnoxious animals. It was most dangerous because medicine had no antidote for combating its action: victims would eventually die. Personne was led to study the possibility of using turpentine as an antidote after hearing of a medical case in which an attempted suicide used phosphorus as poison and also drank turpentine oil in an effort to accelerate his death and make it certain. Surprisingly, the suicide failed²¹.

Personne made 15 experiments using dogs. All the animals were administered phosphorus; some of them received turpentine oil one or two hours after ingestion of the poison, while others received turpentine immediately after being fed phosphorus. Phosphorus was fed as either a paste or as a solution in almond oil emulsified with egg yellow. Most of the dogs which received turpentine immediately or one or two hours after phosphorus survived, although were very sick for some time. Personne postulated that phosphorus killed by hindering blood hemoglobin and depriving it of oxygen, death being fast if absorption by blood was rapid and slow if it was slow. In the first case death was actually by asphyxia, in the second it resulted from hemoglobin failure. It seemed that the absorbed turpentine hindered the action of phosphorus in blood in the same way that it hindered its combustion in air at low temperature. The turpentine ingested was eliminated without causing major health disorders^{21,32}.

There was a vociferous campaign to ban these matches once the dangers became known, but the danger problem was not resolved until the invention of amorphous (red) phosphorus in 1845.

Manufacture of safe matches started in France in 1898 and in England in 1900 by Bryant and May, the largest British match manufacturer. In 1899, in England, a Parliamentary Commission produced a report on the *Use of Phosphorus in the Manufacture of Lucifer Matches*, which gave a thorough description of the production, health hazards and safety precautions being taken by manufacturers. The replacement of white phosphorus, first by red phosphorus and from 1898 on by phosphorus sesquisulphide, was the only satisfactory solution to the problem. In 1908, legislation in England forbid the manufacture and sale of white phosphorus-based

matches (White Phosphorus Prohibition Act). It was replaced by red phosphorus, having the same properties as white phosphorus, but less energetic. Another substitute was tetraphosphorus trisulphide, P_4S_3 .

The USA was one of the last countries to adopt safer match compositions, as the original phosphoric friction matches were very cheap. However, the safety case had been made and in his 1910 Report to the Union President William Howard Taft (1857-1930) said: "I invite attention to the very serious injury caused to all those who are employed in the manufacture of phosphorus matches. The diseases incident to this are frightful, and as the matches can be made from other materials entirely innocuous, I believe that the injurious manufacture could be discontinued and ought to be discontinued by the imposition of a heavy federal tax. I recommend the adoption of this method of stamping out a very serious abuse". President Taft publicly asked Diamond Match to release their patent for the good of mankind, which they did on January 28, 1911. This opened the way for other manufacturers to abandon the use of white phosphorus and use the sesquisulphide instead. It was not possible to outlaw their production in the USA as Congress did not have such powers, so the procedure selected was not legislation but raising the tax on white phosphorus-based matches by two cents per one hundred and prohibiting interstate transportation of white phosphorus, to make them prohibitively expensive (1913).

The safety match

We have seen that the development of safety matches was a very slow process. The simple idea behind the invention to separate the oxidiser and the tinder was a creative solution and decreased the risk of fire caused by self-ignition. It also removed the risk of health problems.

An important step towards the success of the safety match was the development by Arthur Albright of a process for the large-scale industrial manufacture of high quality red phosphorus. As soon as Albright heard of Schrötter's discovery of the safer red phosphorus in 1844, he bought the patent and started to develop a safe production process. He was successful and by 1851 he was already manufacturing red (or amorphous) phosphorus in by heating white phosphorus at a controlled temperature in a closed iron pot. Interesting enough, Albright found great

difficulty in using his red phosphorus for the manufacture of strike anywhere matches.

In 1851, Albright's red phosphorus was exhibited at the Great Exhibition at the crystal Palace in London. Among the visitors to the exposition were the brothers Carl Frans Lundström and Johan Edvard Lundström, who had established in 1845 a match factory in Jönköping, Sweden (which later become the Swedish Match Company, a major world producer of safety matches). The brothers had been experimenting in vain with match and box combinations based on the safety match principle, but their boxes lost after a time the power of igniting the match heads. They were also aware of the problems of Patsch's matches, especially the deterioration of the friction surface. On seeing the new amorphous phosphorus they ordered a small sample from Albright, prepared a friction surface with it and test it using Patsch's old matches. To their satisfaction they found that the matches would ignite easily on the new friction surface, with a steady and uniform flame. As a result they ordered large amounts of phosphorus from Albright. In 1855, the Lundströms showed their safety matches at the World Exhibition in Paris and were awarded a silver medal. The matches ignited perfectly and the friction surface did not deteriorate. The principle of the safety match was that amorphous phosphorus was incorporated in the striker in the box but not in the head of the match⁴.

Phosphorus sesquisulphide was discovered by Jöns Jacob Berzelius (1779-1848) and first made in 1864 in France by George Lemoine (1841-1922) by heating white phosphorus with sulphur in the absence of air. The compound was of no interest until 1898 when Henri Sévène and Emile David Cahen, of the French government match monopoly, proved that besides being non-poisonous, it could be mixed with potassium chlorate to prepare a strike anywhere match composition, and that the match heads were not explosive. In 1898, they developed a successful formula for matches and patented it³³. Crass¹³ refers to this historic event as follows: "The successful adaptation of the sesquisulphide to the match manufacturing industry was perhaps the most outstanding contribution to the history of fire-making since Brandt's discovery of phosphorus, and its use as the active ingredient in friction match compositions was rapidly adopted by most civilized countries". Albright and Wilson were the first to make phosphorus sesquisulphide commercially and started

selling it in 1899. For matchmakers phosphorus sesquisulphide proved to be an inestimable boon because it entirely removed the risk of phosphorus necrosis and in that industry it soon replaced white phosphorus completely³⁴.

Matches today

A match consists of three basic parts: a head, which initiates combustion via various materials like phosphorus; a tinder substance to pick up and burn the flame (usually a piece of wood or cardboard); and a handle (often the same as the tinder).

The act of striking converts the red phosphorus to white by friction heat, the white phosphorus ignites and the ignition starts the combustion of the match head. The ignition of a match is a complex physical and chemical reaction. It begins with a solid state chemical reaction initiated by the frictional heat and propagated by a series of exothermic reactions. The heat of the reaction depends mainly on the composition of the head and on the way the formulation is prepared. The initial flame temperature at the match head is in the range 1350 to 1950°C, and during combustion reaches a constant value of about 1500 °C³⁵.

Common matches are usually prepared of small wood sticks treated with a solution of ammonium phosphate or borax. One end is plunged in a paraffin bath to make them more combustible, and after cooling the paraffin is coated with a paste containing a mixture of about 50% wt potassium chlorate, 4% sulphur, 1% potassium dichromate, 10% technical gelatine, 10% zinc oxide, 15-20% glass powder, and other components such as ferric oxide, manganese oxide, kieselguhr, and lamp black. Each component has a specific role in the process: Potassium chlorate provides the oxygen for ignition and burning, phosphorus sesquisulphide the sensitivity for ignition on a rough surface, sulphur is the main combustible material, potassium dichromate is added as a powerful oxidising agent and to lower the decomposition temperature of potassium chlorate, zinc oxide helps control the velocity of flame propagation in the mixture, and gelatine is the adhesive for binding the components together as well as to the splint. The glass powder acts as a binder for the molten components and kieselguhr as ash former. The ammonium phosphate or the borax has the role to stop the incandescence of the wood when the match extinguishes, that is, they play the role of inhibitor of the chemical reaction.

Red phosphorus, mixed with glass powder, colouring pigments, and glue, are normally present in the strike surface located on the side of a matchbox. Sometimes antimony trisulphide is also present in the striking strip.

Development of the match industry³⁴

By 1850, there were 60 match factories in the entire USA. In that same year, the first such factory opened in California. New York, with 18, was far ahead in both number and production. Connecticut was second with nine, and Massachusetts was third with eight. By 1860, the number of plants had increased to 75. The industry then employed 604 men and 648 women, many working part time or at home.

By 1880, however, the number of US match manufacturers dropped from a high of 79 to 37. As the larger companies had become mechanized, smaller businesses that used older, less efficient machines had been pushed to the edge of failure. Many had been forced to shut down after the stock market crash of 1873 led to a deep depression. In the same year, Swift & Courtney & Beecher and O.C. Barber, the two great giants of the industry, and ten other companies, merged to form the Diamond Match Company of Connecticut in December 1880, although production did not begin until early 1881. With the formation of Diamond Match Company, and its purchase of the rights to Pusey's matchbook in 1894, the American modern match industry was born.

The American match industry reached its height in the 1940s and 1950s but by the mid-1980s, it was unable to stand against cheap foreign imports and collapsed.

Albright & Sturges, a company founded by Arthur Albright, started making phosphorus in England in 1844 and is still one of the major world producers of phosphorus chemicals³. The partnership with Sturges was dissolved in 1855 and in 1856 Albright and John Edward Wilson formed a new partnership Albright & Wilson.

Sweden has become the leading producer of matches in the world. Although Lundström patented his match, soon the production ceased because it was too expensive to make red phosphorus. In 1864, Alexander Lagerman (1836-1904) designed the first automatic match fabricating machine, thereby opening the way to mass production of matches. It produced both matches and matchboxes, turning out filled matchboxes that were ready for sale. The success of the match-factory in Jönköping resulted in

a growing number of match producers in Sweden. By 1876 there were 38 factories operating at the same time. The phosphorus was impregnated into the striking surface on the side of the box; and the head of each match was made of ingredients, which would create enough friction and combustion to ensure a steady flame. The matches would only ignite if the matchstick was rubbed against the striking surface, and were therefore called safety matches. These matches were at first made in Stockholm, but soon the production ceased because it was too expensive to make red phosphorus. Today the safety match is the most popular match sold in the world^{36,37}.

The low price of book matches is mainly the result of high-speed mechanised production methods. Modern continuous machines are capable of producing one million matches per hour, and within another-half an-hour, deliver them as completed strikable matches, ready for cutting and stapling into books. It is estimated the average annual world consumption is about 1500 matches per person. The match faces now a very serious competition from a new form of non-phosphorus contraption: the butane lighter. Nevertheless, book matches have the important advantage in commercial advertising, with a very fast turn around in the message they carry.

References

- 1 Frazer J G, *Myths of the Origin of Fire* (MacMillan, London), 1930.
- 2 Entry *Fire*, *Encyclopaedia Britannica*, 15th edn vol. 4 (Chicago), 1987, 788.
- 3 Entry *Fire*, *Encyclopaedia Americana*, vol. 11, (Grolier, Danbury), 1991, 241.
- 4 Singer C, Holmyard E J, Hall E R & Williams T I, *A History of Technology* (Clarendon Press, Oxford), 1958.
- 5 Calvert J, *Phosphorus*, <http://www.du.edu/~jcalvert/phys/phosphor/htm>.
- 6 Childs P E, Phosphorus: From Urine to Fire, http://www.ul.ie/~childsp/CinA/Issue61/TOC25_Phosphorous.html.
- 7 *The Great Idea Finder*, <http://www.ideafinder.com/history/inventions/story079.htm>, 2000.
- 8 Pliny, *Natural History*, English translation by Eichholz D E (William Heinemann, London), 1942.
- 9 Heavisides M, *History of the Invention of the Lucifer Match* (Heavisides & Sons, Stockton-on-Tees), 1909.
- 10 Aeschylus, *Prometheus Bound*, Translated by Havelock E A (University of Washington Press, Seattle), 1968.
- 11 *Diodorus Siculus Bibliotheca Historica*, English translation by Charles Henry Oldfather (Loeb Classical Library, Heinemann, London), 1933, 4.15.2144.
- 12 Kingsley P, *Ancient Philosophy, Mystery and Magic: Empedocles and Pythagorean Tradition* (Oxford University Press), 1995.
- 13 Crass M F, *J Chem Ed*, 18 (1941), 116, 277, 316, 380, 428.
- 14 Homberg W, *Mém Acad Sci*, 10 (1692) 57.
- 15 Döbereiner J W, *Edinburgh Phil J*, 10 (1824) 153
- 16 Schmid A, *US Pat 2,103,698*, December 27, 1937.
- 17 Jones S, *Br Pat No. 3732*, 1828.
- 18 Brewer E C, *Dictionary of Phrase and Fable* (Henry Altemus Co., London), 1898.
- 19 Smith W, *Morley: Ancient and Modern* (Longmans, Green and Co, London), 1886.
- 20 Darwin C, *The Voyage of the Beagle*, chapter 3 (Dent, London), 1839; 64.
- 21 Wisniak J, *Indian J Chem Technol*, 12 (2005) 108.
- 22 Manville Fenn G, *The Golden Magnet* (Blackie and Son, London), 1883.
- 23 Newton W, *Br Pat No. 6295*, 1832.
- 24 Phillips A D, *U.S. Patent No. 68*, October 24, 1836.
- 25 Schrötter A, *Ann Chim Phys*, [3], 24 (1848) 406.
- 26 Moore S C, *US Pat No. 47848*, May 23, 1865.
- 27 Pusey J, *US Pat No. 483165*, Sept 27, 1892.
- 28 Orfila M J B, *Traité des Poisons* (Crochard, Paris), 1814.
- 29 Tardieu A & Roussin F Z, *Etude Medico-legale et Clinique de l'Empoisonnement*, Baillière et Fils, Paris, 1875.
- 30 Astier A, *Rev Hist Pharm*, 45 (1997) 385.
- 31 Fabre É, *La Dégénérescence Graisseuse Dans l'Empoisonnement Aigu Par le Phosphore*, Thèse de Médecine, Paris, 1864.
- 32 Personne J, *Compt Rendus*, 68 (1869) 543.
- 33 Sévène H & Cahen E D, *US Pat No. 614350*, November 18, 1898
- 34 Threlfall R E, *100 Years of Phosphorus Making*, Oldbury: Albright & Wilson, 1951.
- 35 Finch L C A & Ramachandran S, *Matchmaking: Science, Technology and Manufacture*, Ellis Horwood, Chichester, 1983.
- 36 Karlsson F, <http://www.enterprise.hb.se/~match/history.html>
- 37 Anonymous, *The History of Swedish Match*, Hasse, Stockholm, 1923.