

INTERMATCH SWEDEN AB Product Development Department
Box 608, 551 18 Jönköping, Sweden

A SHORT PYROTECHNIC HISTORY OF MATCHES.

Stig Johansson

This is a paper to be read at the Eleventh International Pyrotechnics Seminar, arranged by the International Pyrotechnics Society July 7-11, 1986, at Vail, Colorado, U.S.A.

Among-historical match compositions there are some, which contain what normally are considered inert substances in place of chlorate and other strong oxidizers. A thermodynamic study reveals that chalk and iron(3) oxide in fact have enough power to oxidize phosphorus. History tells that matches of these kinds have been on the market, but whether they really worked by way of pyrotechnics is not clear. Thermal analysis experiments by PDD have been planned in order to find out, since it could be interesting to know if reduction-oxidation couples shifted towards the reduction end of the oxidation scale still give good matches.

Dr. Michael Cox of Wilkinson Sword has been kind enough to check the English of the manuscript. The skilful assistance of Mr. Bertil Thorner, archivist of Swedish Match, is also gratefully acknowledged.

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A SHORT PYROTECHNIC HISTORY OF MATCHES

Stig R. Johansson Intermatch Sweden AB S-551 18 Jönköping, Sweden

.ABSTRACT

The pace at which pyrotechnic matches could develop was controlled by the development of chemistry. The ancient sulfur match played a central role as a kind of touchstone for all new chemicals of potential interest as fire making ingredients. For instance, soon after the discovery of phosphorus in the 1670's, it was found that the traditional ignition body, i.e., glowing tinder, could be replaced by the new substance.

The following milestones mark the progress of matches:

- ca 1675 Discovery of white phosphorus, P₄ by Brand in Hamburg.
- 1786 Berthollet synthesizes potassium chlorate, KClO₃.
- 1805 Chancel invents the first commercial pyrotechnic match, the dipping match (head KClO₃ + sugar, ignition body H₂SO₄).
- ca 1820 Earliest known recipes of pyrotechnic phosphorus matches (heads KNO₃ + P₄ or KClO₃ + P₄).

- 1826 Walker invents the first commercial friction match (head $\text{KClO}_3 + \text{Sb}_2\text{S}_3$, abrasive friction).
- 1830 Phosphorus match invention of Sauria (head $\text{KClO}_3 + \text{P}_4$).
- ca 1832 First commercial phosphorus match produced by Kammerer.
- 1834 Römer is granted a patent on $\text{Pb}_3\text{O}_4 + \text{P}_4$ "silent" matches.
- 1836 Irinyi invents a similar match based on PbO_2 .
- 1844 Pasch in Sweden is granted a patent on the safety match (head $\text{KClO}_3 + \text{Sb}_2\text{S}_3$, red-phosphorus friction).
- 1848 Böttger invents a similar match and incorporates Sb_2S_3 into the friction composition. Patent 1855.
- 1884 Farnham in U.S.A. invents the double-dip match (safety match head tipped with a phosphorus match composition).
- 1898 Sève and Cahen in France are granted a patent on the sesqui match.
- 1911 Fairburn applies the ' double-dip principle to sesqui matches.
- 1928 Ringer's "everlasting match", or ignition rod.

INTRODUCTION

By defining a match as a stick of arbitrary material carrying a chemical, or a mixture of chemicals, at one end or two, the first match can be identified as a splinter of wood tipped with sulfur. Such sulfur matches, or spunks, as they were called in the U.S. before 1825, were used as auxiliary matches in connection with tinder-boxes; the flint and the steel did nothing but provide the sulfur match with an ignition body of glowing tinder or amadou.

Thanks to volcanoes in the first place, sulfur has always been available to man. Sulfur matches are therefore probably as old as tinder prepared from tinder fungi, i.e., amadou. The oldest find of amadou is about nine thousand years old.

After having been a commercial product for millenia, the sulfur match began to sing its swan song some three hundred years ago by cooperating with all new chemicals of fire making potential. The prelude involved white phosphorus, which Hennig Brand, an alchemist (some say the very last one) in Hamburg, hit upon in the beginning of the 1670's in his search for the Philosophers' Stone. Pyrophoric phosphorus matches were conceived soon after. Phosphorus was used either as an ignition body or as a head material on top of the sulfur, which retained its task as auxiliary fuel. In the latter case ignition was brought about by mechanical friction. In a similar way the sulfur match was used as the base providing matches still to be developed with stem and fuel.

For further information on pyrophoric matches, which lie outside the scope of this paper, and on fire tools and matches in general, the reader is referred to Ref. 1, where another 178 references are offered.

ON PYROTECHNIC MATCHES

A pyrotechnic match is a match, which is independent of oxygen in the air for its ignition. After ignition has been accomplished, the fuel on or absorbed in the stick (or splint, as it is termed by the match industry) starts burning in air and

thus provides the flame. Even if the splint material itself is combustible, such as wood, transfer of the flame from the pyrotechnic ignition composition to the splint usually fails. An auxiliary fuel, such as sulfur or paraffin, is therefore required.

A match, whatever the type, is lighted by being brought in contact with an ignition body. This generalized term covers not only friction surfaces for friction matches, but, e.g., liquids for dipping matches and glowing tinder for sulfur matches as well.

OXYMURIATED MATCHES

Although the oxidizer of black powder, potassium nitrate, had been around for some time - two millenia, or so (Ref. 2) -, no pyrotechnic match seems to have been contemplated prior to the birth of potassium chlorate in 1786. This year Claude Berthollet in France obtained "superoxidized" hydrochloric acid by passing chlorine into a hot solution of potassium hydroxide. Muriatic acid was the name for hydrochloric acid at this time, and therefore chloric acid became oxymuriated acid. Berthollet started production of the new salt in 1790, hoping to be able to substitute it for potassium nitrate in black powder. This substitution proved impossible.

Potassium chlorate, KClO_3 , is a strong oxidizing agent. However, its first use was based on an auto-oxidation reaction triggered by concentrated sulfuric acid:



While the chlorine compound of the higher valence state, perchlorate, is rather inert, the one in the lower state, chlorine dioxide, reacts vigorously with combustible substances in the environment and causes their ignition. This is a discovery which seems to have been made in 1789 by another French chemist, viz., Bertrand Pelletier. Chlorine dioxide was not identified until 1802, and its role as a fire maker remained unknown until 1815.

In 1805, Jean Louis Chancel, demonstrator for professor Thénard at Ecole Polytechnique in Paris, invented a match consisting of a sulfur match tipped with a composition containing KClO_3 , sugar, and gum arabic. These matches, which became known as oxymuriated (or oxymuriate) matches, were ignited by dipping in concentrated sulfuric acid. For this reason they were also called dip-splints or dipping matches. Despite the acid splashing and sputtering connected with their ignition, Chancel's invention turned out very popular and marks the first commercial pyrotechnic match.

In 1822, Stephan Römer in Vienna founded Austria's first match factory for purpose of manufacturing oxymuriated matches. The first match factory in Sweden was founded by Jonas Samuel Bagge in Stockholm in 1836 for the same reason, which indicates that the product stayed on for a while. An Austrian recipe, published in 1823, runs:

18 % potassium chlorate

12 % starch
12 % flower of sulfur
4 % gum arabic.

Fire tools like the "instantaneous light box", which consisted of a bottle with sulfuric acid and a bunch of matches contained in a box of tin, soon developed. In 1808, C. Wagenmann in Germany began to make and sell such boxes, which he called "French ignition machines" or "Eupyrion,"--In England the name "Empyrion" (from Greek empyros, burning) was adopted. In 1811, Wagenmann removed the drawbacks associated with the acid by replacing it with a solid ignition body of asbestos moistened with sulfuric acid. Other technical developments solved the problems of ignition failure caused by too deep a dipping, or by dilution of the acid due to moisture absorption.

Instantaneous light boxes were used for more than forty years in U.S.A. and in Europe.

Although not a match in the true sense, but rather a fire tool, the Promethean match constitutes an interesting version of the dipping match. It was invented and patented by Samuel Jones in London in 1828. He combined the acid bottle and the match in one piece by wrapping slips of paper impregnated with ignition composition around a sealed glass tube containing the acid. When a light was required, the vesicle was nipped by a pair of pliers. Jones called the matches Instantaneous Lights and sold them under the trade name of Promethean Matches; they became also known as Jones's Prometheans. They seem to have been on the market for quite some time.

WALKER, OR "LUCIFER" MATCHES

On a brass tablet bolted on the wall of the house of 59 High Street, Stockton-on-Tees, England, one learns that John Walker "invented friction matches in April, 1827". This is very nearly true.

In 1825, or earlier, Walker, who was a pharmacist of Stockton-on-Tees, was experimenting with explosive mixtures for making percussion caps for cartridges (Ref. 3). He arrived at a percussion powder composed of equal parts of potassium chlorate and stibnite, or antimony sulfide, Sb_2S_3 . It probably occurred to him that such a composition could replace Chancel's composition of the dip-splint and result in a friction match * -So it did. He is likely to have started production and sales of the matches in his drugstore in 1826. This is a conclusion based on extrapolation: according to his sales book, which now is exhibited in the Bryant & May collection of the Science Museum in London, Walker sold his 30th tin case containing "Sulphurata Hyperoxygenata Frict.", or friction lights, as he called them, on April 7, 1827. This is the earliest record known, but judging from the sales rate after that date, the invention of the friction light, or antimony sulfide match, must have been made in 1826, which thus can be considered the year of birth of the first commercial pyrotechnic friction match. It was also the first match requiring a special friction surface. A folded piece of sandpaper was enclosed with the matches. These were not lighted by striking but by nipping the head firmly with the folded piece of abrasive paper and

suddenly withdrawing the match. This is the principle of the pull match, which thus was casually invented by Walker.

Walker's last entry in the day-book is dated September 13, 1829. He did not care about patents, and was probably not aware of his making history. As far as patents are concerned, Samuel Jones had nothing against applying for them. He copied Walker's matches in 1829 and renamed them Lucifers (literally light carriers; Walker, when hearing about this, made another interpretation and expressed his dislike of the new name). In 1832, Jones was granted a patent on the Walker match ("Matches", Brit. Pat. No. 6335). Jones says: "... said improved matches may be ignited in a bottle, as in common use, or they may be ignited by friction produced by drawing the prepared end of the match between the rough surfaces of a piece of sand, glass, or emery paper," As to the composition, he only specifies "chlorate of potash compounded or mixed with antimony in combination with sulphur (commonly called or known by the name of sulphurate of antimony), or such other chemical compound as will ignite by friction"

According to Bone (Ref. 3), who analyzed Walker's friction lights (or attrition lights, as he alternately called them), the composition contained equal parts of KCLO_3 and Sb_2S_3 * Professor Bone also confirmed the presence of gum and starch. Jones possibly changed the ratio to one part of KCIO_3 and three parts of Sb_2S_3 .

The originator himself did not enjoy any big business — he simply did not care. According to his day-book he sold 168 tin cases altogether (each case contained 100 or 84 matches, depending on whether the customer wanted to pay extra for the case or not). However, Jones's more aggressive marketing methods resulted in success; already in 1831, several manufacturers in London were competing. It would be interesting to know if Jones's patent, when it was "Inrolled the Twentieth day of May, One Thousand eight hundred and thirty-three", stopped his competitors in "England, Wales, and the Town of Berwick-upon-Tweed".

Lucifer matches soon spread to other countries. They were on the market for several years; as late as in 1840 or thereabout, J. S. Bagge in Sweden took up their production. In the long run they could not compete with phosphorus matches, which eventually became superior in all respects. In U.S.A., Ezekiel Byam was making lucifers in 1835 (Ref. 4), and already in 1827 or 1828, Römer and Hedwig Trevany in Austria had developed a dual purpose match similar to the one patented by Jones. The patent application was filed by Römer, but the patent was not granted until 1832. The same year, on September 10, Siegl was also granted a lucifer patent in Austria. In France, Savarisse and Mrs. Merckel seem to have been using the following recipe:

KCLO_3 34 %
 Sb_2S_3 61 %
Gum arabic 3 %
Gum tragacanth 2 %.

Lucifers were not easy to ignite. Mrs. Merckel therefore improved the friction surface by preparing it from KClO_4 , Pb_3O_4 , pumice, and gum.

Another way to improve on the lucifer match was to add sulfur to the composition. However, the inventor of this type of compositions did not improve on anything - he made the invention right away without knowing of Walker lights. Sulfur-strengthened lucifers became known as "sulfur matches", but should not, of course, be confused with the spunks (match history is full of confusion opportunities like this). A French recipe used in the beginning of the 1830's required a fair amount of sulfur (Ref. 5):

KClO_3	41.0 %
Sb_2S_3	18.1 %
S	12.5 %
Fe_2O_3	3.5 %
Gum arabic	24.9 %.

Iron oxide acts as a sensitizer improving the appearance of the flame.

Walker's matches usually ignited with explosive violence --- no wonder, since he used the same chlorate to antimony sulfide ratio for percussion cups! - and a shower of sparks. Oddly enough, Walker did not use sulfur tipped splints. However, sulfur dipping was soon introduced in order to facilitate the transmission of the flame from the match head to the splint (Ref. 5). Moreover, objectionable vapours were produced by the burning head. This provided one of the first instances of a manufacturer drawing attention to the danger of his products. On the box Jones printed: "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". It would be interesting to know what made him take this measure. According to Sax (Ref. 6), antimony compounds, when inhaled, "can cause injury of sufficient severity to threaten life following a single exposure lasting seconds, minutes or hours". But how did Jones know?

PHOSPHORUS MATCHES

Lots of studies and patriotic efforts have been spent on the problem of finding the true inventor of the pyrotechnic phosphorus friction match. Books have been written and memorials to individuals erected, but the simple answer to the question is, nevertheless, that no one can be appointed. Despite its commercial success, the phosphorus match seems to have lacked inventive level.

In France, Charles Sauria made phosphorus matches in December 1830. and in Germany Jakob Friedrich Kammerer started the first commercial production in 1832 or 1833. But many others seem to have developed phosphorus matches independently.

In 1917, an interesting note titled "Friction matches around 1820?"

was published by Pachinger (Ref. 7). In a collection of recipes titled "Würzburger Manuskript" and published around 1820, Pachinger found the following match compositions:

Recipe No. 119. - Vienna Friction Matches ("Wiener Streichhblzer")

KNO ₃	33 %
MnO ₂	33 %
P ₄	10 %
Gum arabic	24 %

(Pachinger gives the gum content as 21 parts out of 58, i.e., 36 %, but it has been corrected in Ref. 8 to 12 parts out of 49).

Recipe No. 82. - Phosphorus Friction Matches ("Phosphor-Reibfeuerzeug").

1 part of P₄ is melted in 4 parts of a water solution of gum arabic. Finely ground KClO₃ and some gum acidified with benzoic acid are added until a soft composition is obtained, in which sulfur matches are dipped.

These recipes are presented anonymously, like most cooking-recipes, and the idea of an inventor did not seem to enter anyone's mind. All we are told is that a Dr. Theodor Thon tried the recipes in 1820 (and presumably found them good, since they were included in the recipe book).

Thus, saltpetre was used as oxidizer around 1820, and at this time the chlorate match, to judge from "Würzburger Manuskript", was regarded as more or less established, although not commercially available.

For the time being, the track ends here. But why did Pachinger put a question mark in the title of his note? Both the Vienna and the Phosphorus Friction Matches are, according to the recipes, downright pyrotechnic friction matches. The appearance of saltpetre leads to another question: were, after all, the development of pyrotechnic friction matches independent of the existence of chlorate?

Following Kammerer, match factories were built in many places. The matches, however, caused many fires and explosion accidents and had therefore to be banned. But by substituting quadrivalent lead for KClO₃, safer matches with less violent burning characteristics resulted, and the bans could be lifted.

On January 4, 1834, Römer obtained an Austrian patent on a composition containing minium, Pb₃O₄, as substitute for part of the chlorate. -The invention was made in 1832. In 1836, János Irinyi, an Hungarian student in Vienna, developed a composition where lead dioxide, PbO₂ was entirely substituted for KClO₃. These matches, which were produced by Römer, became known as "silent matches" because of their soft ignition properties.

As it seems, Kammerer stuck to chlorate and managed to develop a fairly safe and unexplosive $\text{KClO}_3 + \text{P}_4$ match. The PbO_2 match was gradually replaced by chlorate matches, but the details of the comeback of the latter are virtually unknown.

In 1838, Rudolph Christian Böttger in Frankfurt-on-the-Main analyzed "silently burning" matches in the market and found them to be chlorate-free. Böttger recommended match manufacturers to refrain from chlorate compositions and recommended the use of the following "completely silent ignition composition":

KNO_3 26%
MnO 29
 P_4 16
Gum arabic 29

This is a slightly modified Vienna Match composition. In 1843, Böttger improves on these "completely noiselessly burning Vienna matches":

KNO_3 37%
 Pb_3O_4 or Fe_2O_3 19 %
 P_4 15 %
Smalt 7% (cobalt glass powder)
Animal glue 22 %.

For cost reason, animal glue was first substituted for gum arabic by Friedrich Moldenhauer in 1839 or 1840. In the 1840's, Moldenhauer, who was one of the first match manufacturers, used the following chlorate-free composition:

KNO_3 36 %
 P_4 18 %
 Sb_2S_3 9 %
Animal glue 36 %

and in addition some Fe_2O_3 and MgO .

Although chlorate-free compositions based on nitrates (KNO_3 or $\text{Pb}(\text{NO}_3)_2$ or quadrivalent lead (PbO_2 or Pb_3O_4 , in which compound there are two bivalent lead atoms) were "noiseless and silent". the demand for the less rapid chlorate based matches grew steadily. But as late as the 1860's, both types co-existed on the market. According to an English investigation made in 1863, all matches of British make contained KClO_3 . while none of the (inferior) foreign makes did.

Jönköping's Match Factory, the leading one in Sweden and exporter to England since 1851 (it still is), began to use the following recipe in 1863:

Pb_3O_4 52.7%
 HNO_3 26.4 %
 P_4 7.7 %
Gum 13.2 %.

Minium and nitric acid were first allowed to react:



This reaction mixture was then added to the gum solution, which contained melted and emulgated phosphorus. At this time, 1863, experiments were also made with small additions (less than 1%) of KClO_3 .

Further improvements included the addition of fillers, as shown by this recipe from 1885:

Pb_3O_4 16.7%
 $\text{Pb}(\text{NO}_3)_2$ 8.4
 P_4 19.6
Smalt 4.4 %
Venezian turpentine 0.6 %
Glue 33.4
Gum 16.9.

Some concentrated acetic acid, 50 drops, was also needed.

Chlorate-free compositions like this were used for sulfured splint. The combustion temperature was low, and since the heads were very small, the heat output was small as well; still it was enough to ignite sulfur. The demand for "Parlor Matches", where paraffin was substituted for sulfur, which gave rise to obnoxious fumes when matches were lighted, made it necessary to switch to chlorate compositions. These were hot enough to ignite paraffin, which requires higher temperature than does sulfur. Moreover, the heads were larger and gave enough heat for the vapourization process preceding the ignition. In the trade these matches were called paraffin matches, but at Jönköping's Match Factory they were termed potash matches to mark the fact that they contained KClO_3 in an amount similar to that of safety matches. One of the earliest recipes for potash matches is the following:

KClO_3 35.7
 P_4 7.2
Glass powder 10.7
Gypsum 10.7
Chalk 14.3
Glue 21.4

A "potash match" recipe from the turn of the century contained 11 ingredients:

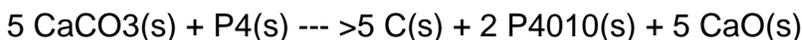
KClO_3 34.7%
 P_4 5.8
Glass powder 16.0
Gypsum 2.7
Chalk 16.0

Zinc oxide 16.3
 Asbestos 2.7
 Venezian turpentine 0.5
 Rhodamine and magenta 0.3
 Glue 16

Phosphorus match compositions used in Austria and in Germany between 1835 and 1860 contained between 32% and 61% KClO_3 with a phosphorus content decreasing from 20.5 % in 1835 to 5.5 % in 1860 (Ref. 5).

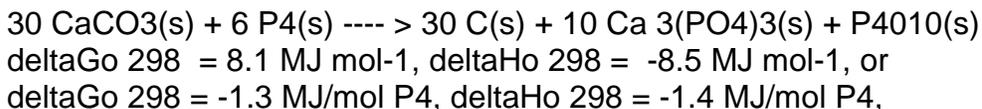
In U.S.A., the first patent on phosphorus matches was granted to Alonzo Dwight Phillips on October 24, 1836 ("Manufacture of Friction Matches", U.S. Pat. No. 68). The state of the art in U.S.A. at this time was compositions containing KClO_3 , P and Sb_2S_3 . Phillips's composition is puzzling; the inventor says bluntly that it contains simply phosphorus and chalk without the addition of KClO_3 . What kind of a match was this? Manchester says (Ref. 4): "Its advantages over the chlorate match were that it ignited from rubbing on any rough surface" - but-so-did phosphorus matches - "and without exploding or spluttering so much".

Substituting chalk, CaCO_3 , for KClO_3 is remarkable. The latter substance is a strong oxidizing agent, while the former seldom or never is looked upon as belonging to this exclusive category of chemicals. However, what CaCO_3 lacks in oxidizing power may be compensated by strong reducing power of the tinder, i.e., white phosphorus, P_4 . In fact, the following oxidation-reduction reaction is a free one ($\Delta G < 0$):

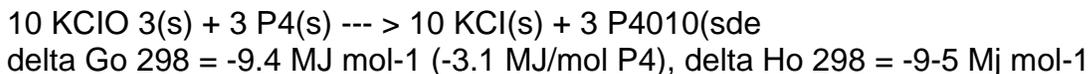


$$\Delta G_{298} = -0.10 \text{ MJ mol}^{-1}, \Delta H_{298} = -0.16 \text{ MJ mol}^{-1}$$

The oxides may react further, which makes the values far more negative:



This may be compared with the $\text{KClO}_3 + \text{P}_4$ reaction:



If chemical kinetics inhibits the pyrotechnic reactions, the pyrophoric reaction path remains:



$$\Delta G_{298} = -3.4 \text{ MJ mol}^{-1}, \Delta H_{298} = -3.4 \text{ MJ mol}^{-1}$$

If pyrophoricity initiates the reactions, then combined pyrophoric and pyrotechnic reactions become a possibility:



$$\Delta G_{298} = -19.9 \text{ MJ} \quad (-3.3 \text{ MJ/mol P}_4), \quad \Delta H_{298} = -20.3 \text{ MJ mol}^{-1}$$

Thus, the question of Phillips's match being pyrotechnic, pyrophoric, or both has to be settled by experiment.

Even if chlorate and chlorate-free compositions were used simultaneously, it was not the oxidizer that caused the final, unbearable headache, but the tinder fuel. As early as 1839, white phosphorus began to show its insidious effect of jaw decay upon match workers. Moreover, the presence of a strong poison in a ubiquitous commodity like matches led to fatal misuse for a variety of reasons. Beginning with Finland in 1872, country after country decided to ban the phosphorus match. Some countries banned domestic sales as a first step and manufacture as a second. In Sweden there were 19 years in between (1901 and 1920, respectively). This may appear more cynical than it really was. The problem of phosphorus necrosis, or phossy jaws, were largely overcome. From 1897 to 1904, the annual number of known cases was between 2 and 7 only, which meant that 0.4 % of the match workers were affected. After 1896, it was stated in a governmental document, the cases were mild and easy to cure. The document, which was dated October 19, 1906, also tells that the phosphorus problem is different in Sweden compared with other countries. The reason for banning sales of phosphorus matches in Sweden arose from their alleged use in inducing abortion, which was said to be non-existent in other countries. The reverse was true for phosphorus necrosis, which -according to the report - was no problem for Swedish match factories. So much for the explanation of those 19 years (however, at least The Jönköping Match Factory discontinued phosphorus match production already in 1913).

SAFETY MATCHES

In order of appearance in the market, lucifers and phosphorus matches, the latter also known as "congreves", were followed by the safety match. Lucifers and congreves (as to naming, the two were often confused) were strike anywhere matches, which - at least as far as congreves are concerned - caused numerous explosion accidents and fires, to say nothing of burns in the face and eyes of users. The name "safety match" derives its origin from the fact that ignition could not be brought about unless the match was struck against a special friction surface.

The safety match was invented by Professor Gustaf Erik Pasch of Stockholm, Sweden, who was granted a patent on it 30th October, 1844. Pasch was partner of Bagge's match factory, where production of the new match commenced the same year. The idea is ingenious in all its simplicity: separation of oxidizer and tinder. However, the usual tinders, P₄ and Sb₂S₃, did not work well, so Pasch prepared red phosphorus for the purpose. He retained chlorate in the match

head and put phosphorus in the friction composition, which he painted on the large, upper surface of cardboard sliding boxes. For the match head he used a lucifer composition with reduced chlorate content, so that the matches could not be lighted on rough surfaces.. As to the recipe, he only specifies that the weight of Sb_2S_3 should be half of the weight of $KClO_3$. Mrs. Merckels recipe gives the inverted ratio (vide supra).

Pasch knew that the red preparation was "completely innocuous to the health of the workers, and in addition not accompanied by any danger", to quote from his letters patent. What he didn't know was the true nature of the new tinder; in accordance with the teaching of the day - which in Swedish was given by, - e.g., Berzelius - he called it "phosphorus oxide". It was not until 1848, when Professor Anton Schrbtter of Vienna published the results of a two year investigation into the nature of red phosphorus that chemists learned that heating white phosphorus leads to a substance identical with the one generated by light and known since 30 years, i.e., elementary phosphorus in its red modification.

Due to its primitive method of preparation, Pasch's red phosphorus was contaminated with true phosphorus oxide, which made the friction surface susceptible to moisture and, as a consequence, liable to deterioration. In addition, phosphorus matches were cheaper and did not suffer from the silly idea of strike-on-the-box-only. Safety and non-toxicity were properties nobody was prepared to pay for at that time. Therefore the production of safety matches was discontinued in 1845.

In 1851, Arthur Albright in Birmingham, England found an industrial method of producing red phosphorus of high quality. When a sample of this product arrived in Jönköping in 1852, Johan Edvard Lundström prepared a friction surface and tried some old Pasch matches on it. They worked. But he was well aware of the moisture problem and did not pay too much attention to Pasch's old invention (the patent of which expired in 1852, by the way). However, in want of better ideas, the matches were brought forward and exhibited at the World Exhibition in Paris in 1855, and so were safety matches produced by two Austrian manufacturers, Furth and Preshel! Lundstrdm and Albright were both awarded silver medals, while Schrbtter got a gold one.

Inspired by Pasch, Rudolph Böttger developed a safety match in 1848, and it was this match the Austrians exhibited. Böttger did not apply for a patent until 1855, in which year

LundstrUm

also did so. A comparison between Böttger's and Lundström's recipe may be of interest:

		Böttger	Lundstrdm
Head composition:	$KClO_3$	42 %	67 %
	Sb_2S_3	---	22 %
	Pb_3O_4	42 %	---

	Gum arabic	16 %	---
	Animal glue	----	11 %
Friction composition:	Red P	56 %	38 %
	Sb ₂ S ₃	38 %	33 %
	Gum arabic	6 %	----
	Animal glue	----	29 %

Thus, Böttger brought the safety principle a step further by removing the tinder as well from the composition. No doubt, this made the "Anti-phosphorus Match", as Böttger called it, safer as far as ignition is concerned. Böttger made great fuss about his matches being safer than Lundström's (or Pasch's, rather, but the originator's name was never mentioned!), but they must have been uncomfortably insensitive. Anyhow, "Swedish Matches", which became a synonym for safety matches in many languages, turned out the winner, even if sales did not become significant until 1867.

A recipe used at Jdnkbping prior to 1860 is the following one:

Friction Composition

Gum 25 %
Red (amorphous) P 75 %.

Head Composition

KClO₃ 59.5 %
Sulfur 4.8 %
Charcoal 9.5 %
Umbra (~ FeOOH) 19.1 %
Gum 7.1 %.

This composition appears a bit insensitive and its burning characteristics not too good. One therefore tried various additions, such as Sb₂S₃ lead thiosulfate (PbS₂O₃) and MnO₂, but the break-through came when potassium dichromate, K₂Cr₂O₇, was brought into the picture. This compound turned out to be a catalyst by which burning as well as ignition properties could be easily controlled. G. Canouil in France 1857 and J. W. Hjerpe in Sweden 1862 patented such compositions (although intended for phosphorus-free friction - the spell of poison lingered for a long time on the very word of phosphorus!). A Jbnkbping formula from 1863 reflects the new developments:

Head Composition

KClO₃ 55.8 %
Pb₃O₄ 4.7 %
K₂Cr₂O₇ 2.3 %
S 9.3 %
Smalt 9.3 %
Gum 18.6 %

Friction Composition

Red P	36.3 %
Sb ₂ S ₃	36.3 %
K ₂ Cr ₂ O ₇	6.1 %
Glass powder	6.1 %
Gum	15.2 %

From here, the compositions have undergone many changes as to details, but not to the fundamental principle.

RED-PHOSPHORUS MATCHES

In parallel with the development of the safety match, substantial efforts were put into the pursuit of phosphorus-free strike anywhere matches, i.e., head compositions in which P₄ was replaced by non-toxic tinder.

Great hope was set on red phosphorus. In fact, when Albright decided to take up industrial production of this substance, he was convinced that it should end up in match heads. When the new phosphorus was presented at the 1851 World Exhibition in London, the one with the Crystal Palace and all that, red-phosphorus matches were, too. Later, in 1856, after learning of the Swedish safety match, Albright took out a patent on a dual head match ("Lucifer Matches", Brit. Pat. No. 2249). He applied by a second dipping either a red-phosphorus containing tip on a primary head of chlorate composition, or the other way round. The result was a strike anywhere safety match. If it ever entered the market, the success must have been limited.

A great number of red-phosphorus match compositions have been patented, e.g., the following developed by Camaille in France:

KClO₃ 34 %
 Red P 24 %
 Glass powder 24 %
 Gum tragacanth 48

Occasional production of red-phosphorus matches took place even during the first years of the 20th century. In Germany, after passing the white phosphorus ban 10th May, 1903, the State bought in a red-phosphorus composition containing KClO₃, red P, and PbS₂O₃, which was put at match manufacturers' disposal free of cost. These "Triumph" matches, as they were called, were produced and sold. It is remarkable that such efforts were put on the development of a match composition, whose dangerous and explosive nature never could be fully subdued, in view of the fact that reliable safety matches had been around for decennia. The reason is that the consumers still disliked to be dependent on a special friction surface; the fact that it was painted on the box in which the matches were kept and thus close at hand was not considered an extenuating circumstance.

PHOSPHORUS-FREE MATCHES

Attempts to arrive at strike anywhere compositions free from red as well as white phosphorus were also made. Some of them focused on a revival of the lucifer match. H. Hochstätter's composition, for instance, aroused a great deal of interest at Jönköping's Match Factory, which company bought the patent rights for Sweden - for controlling but not really exercising the invention. The recipe was published in 1857:

KClO ₃	19%
Kermes (amorphous Sb ₂ S ₃)	49
PbO	2
Glass powder and pumice	8
K ₂ Cr ₂ O ₇	6
Gum arabic	6

Compounds like pyrite, FeS, and, antimony oxysulfide (Sb₂S₃)Sb₂O₃ were also tried, but all phosphorus-free matches were hard to strike, and none of them succeeded commercially.

SESQUI MATCHES

Towards the end of the century, the struggle for phosphorus-free strike anywhere matches was successful, at last. In 1898, Henri Sévène and Emile David Cahen in France invented a composition, in which tetraphosphorus trisulfide, P₄S₃ or phosphorus sesqui sulfide, was substituted for white phosphorus:

KClO ₃	28%
P ₄ S ₃	13
FeOOH	15
ZnO	10
Glass powder	20
Glue	14

This composition was patented in several countries, but not in Sweden. The U.S. patent on the sesqui match was bought by The Diamond Match Company in 1900. Either because of the climatic conditions in U.S.A., which were against the match - so the company claimed - or because of lack of incentive for substituting the sesqui match for the phosphorus match, the introduction of the new match into the market was delayed. Not so in Europe; here the match worked perfectly, and in Sweden many manufacturers were ready to launch it on July 1, 1901, when the phosphorus ban came into force. In 1910, Diamond succeeded to produce good sesqui matches, and in 1911 the company deeded its patent to the public, giving anyone the right to use it free. This was a great and humane deed, indeed, meant to put an end to the detrimental phosphorus match. No ban was ever promulgated in U.S.A., but in 1913 the phosphorus match was taxed out of existence (the same method was practised [sic] by Russia in 1905).

DOUBLE-DIP MATCHES

The first ordinary double-dip match was invented by Frederick Farnham, U.S.A., in 1884. He got a patent on it in 1886 ("Match", U.S. Pat. No. 335 065). The idea was to remove the fire risks of phosphorus matches by placing a small tip of phosphorus composition on top of a safety match head. The ignition characteristics remained the same as for the traditional phosphorus match (no special friction to bother you), but handling and transport became safer because the sensitive tips could not rub against each other in the box. In addition, the small tip did not throw out burning particles, nor did a match dropped on the floor ignite when stepped upon.

In 1911, William Armstrong Fairburn of The Diamond Match Company applied the same principle to sesqui matches. These "bird's eye" or "silent" matches are similar to the Farnham match, except that the ignition tip consists of sesqui composition.

IGNITION RODS

The ignition rod, commonly known as "everlasting match", is a repeatedly strikable match comprising a core of a match composition and a jacket of an easily combustible material.

In 1928, Ferdinand Ringer in Austria patented a rod based on nitrocellulose, and around 1930 Zoltán Földi and Rezső König in Hungary developed an ignition rod with a jacket of metaldehyde. Full-scale production tests resulted in an explosion in a rod extruder, and a man was killed. After that the experiments were discontinued. The patents and the machinery were bought by The Swedish Match Company, which from 1936 through 1939 produced and sold ignition rods on a very limited scale for purpose of maintaining the patents. The product never caught on, so the company dropped the patents.

The ignition rod is rather awkward to use and is in no way competitive with normal matches. Nevertheless, several attempts to improve on it have been made, even as late as in the 1970's.

PELLET MATCHES

Pellet matches were introduced in England in 1850. They consist of a non-disposable mechanical handle and of pellets of match composition containing combustible fillers, like saw-dust. Gripped by a prehensile claw at the end- of the handle, the pellet is lighted by normal striking against a friction surface. This kind of matches comprising a bakelite box with pellets and a receptacle for the handle seems to have been in the market in the 1930's (to judge from the appearance of the bakelite). One of the brands was "Lucifax", made by the Lucifax-Fabriek in Amsterdam. Refill pellets were sold separately.

The latest, but maybe not the last, attempt to introduce a pellet match was made in 1974, when V. Solodov in the Soviet Union was granted a patent on an invention comprising a magnetic handle and pellets containing iron filings. It never appeared in the market, despite a heavy press support all over the world.

If it had, consumers would probably have learned some physics, such as what the Curie point (820°C for iron) was all about, the hard way.

REFERENCES

1. S. Johansson: "On the history of fire tools and matches".
Proc. Pyroteknikdagen 1983, Section Det. Combust., Stockholm 1985.
2. J. Hansson: "Some historical notes on black powder".
Proc. Pyroteknikdagen 1975, Section Det. Combust., Stockholm 1976.
3. W. A. Bone: "The centenary of the friction match".
Nature 119:2996(1927)495-496.
4. H. Manchester: "The Diamond Match Company".
The Diamond Match Company, New York, etc... 1935.
5. M. F. Crass Jr.: "A history of the match industry".
J. Chem. Educ. 18:3,6-9(1941).
6. N. L. Sax: "Dangerous properties of industrial materials"
Reinhold Publ. Corp., 2nd Ed., 1963, pp. 454, 2-3.
7. Pachinger: "Reibzudhblzer L-m 1820?".
GeschichtsbMttter Techn. Industrie Gewerbe 4(1917)236.
8. Gmelins Handbuch der anorganischen Chemie, 8th Ed., Phosphor, Teil A,
Verlag Chemie 1965, p.43.