

## MATCHES

The word match is of uncertain origin. In common parlance, a match is a short, slender, elongated piece of wood or cardboard, suitably impregnated and tipped to permit, through pyrochemical action between dry solids with a binder, the creation of a small transient flame. The word match also is used for fuse lines which after ignition on one end serve as fire-transfer agents in fireworks and for explosives (qv). Such items belong in the field of pyrotechnics (qv).

The development of the ordinary match followed thousands of years of firemaking by laborious means. It has been perfected in the twentieth century and its formulations have remained basically unchanged. Progress has been achieved in selection of modifying components, mainly in the control of the drying process of the freshly dipped matches, also in the mixing procedures. The mechanical equipment for cutting out the match stems and assembling the match books has become more and more efficient as to precision and speed of production.

The history of the modern match has been well presented (1). White (also called yellow) phosphorus, discovered by Hennig Brand (1669) and described as easily ignited on slight warming or rubbing, was first applied by Robert Boyle (1680) to the ignition of sulfur-tipped wood splints. Between 1780 and 1830, numerous match-like contrivances used this ignition principle. After the discovery of potassium chlorate by Berthollet (ca 1786), its combination with white phosphorus and modifying ingredients led to the manufacture of the friction (strike-anywhere) match which became the most popular means of ignition in the United States until July 1, 1913 when an Internal Revenue tax of two cents per one hundred matches terminated its production. The act followed numerous prohibitions and similar punitive taxation in other countries because of the hazard that the phosphorus constituted to the health of the workers during the days of primitive hand-dipping methods. Vapors of the white phosphorus entering the body, mainly through defective teeth, caused a permanent necrotic destruction of the bones (phossy jaw). Also, these matches were sometimes used in suicide attempts or caused the death of children.

A direct descendant of these matches is the nontoxic modern double-tipped strike-anywhere (SAW), the large "kitchen" match version, or the smaller "penny box" variety. It is based on the invention of two Frenchmen, Henri Sévène and Emile David Cahen, who used the nonpoisonous compound tetraphosphorus trisulfide,  $P_4S_3$ , as a phosphorus substitute and acquired a U.S. patent in 1898.

Other early match-like devices were based on the property of various combustible substances mixed with potassium chlorate to ignite when moistened with strong acid. More important was the property of chlorates to form mixtures with combustibles of low ignition point which were ignited by friction (John Walker, 1827). However, such matches containing essentially potassium chlorate, antimony sulfide, and later sulfur (lucifers), rubbed within a fold of glass powder-coated paper, were hard to initiate and unreliable.

The modern safety match owes its qualities to the discovery by Schrötter (1844) of the red, nonpoisonous but easily ignitable variety of phosphorus called red phosphorus. Pasch in Sweden and Böttger in Germany (1845) prepared striking surfaces containing the new material, thus separating the two principal fire-producing components, the chlorate in the match head as the oxidizer and the most sensitive fuel-type material in the striker. This type of match was much improved and made an article of commerce by J. E. Lundstrom in Jonköping, Sweden (1855). However, the United States was quite slow to accept this safety match. The

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“one-hand” phosphorus match and its successor, the double-tipped SAW match, were easier to handle and more reliable, whereas the early safety matches were often sputtering, hard-striking, and explosive.

The final step in the development of the modern match was the invention of the safety-type cardboard match ascribed to Joshua Pusey (1892), now called the book match. It dominates the American match industry and is gaining in popularity in other countries although it was rather slow in gaining acceptance because it was somewhat more difficult to ignite than the wood-splint match.

### 1. Mechanism of Fire Production

The essential chemical reaction takes place on contact of potassium chlorate [3811-04-9] and red phosphorus [7723-14-0] which by itself is one of the most unpredictably hazardous dry reactions in pyrochemistry (see Chlorine oxygen acid and salts,  $\text{HClO}_3$ ; Phosphorus). This reaction has been the cause of serious injury to chemistry students who mix the two materials without permission, only vaguely aware of their explosive potential. In the match head, and separately in the striker, each of two materials is embedded in a matrix of glue so that, on striking under mild friction, a few particles of both materials come harmlessly in contact and react with formation of well-contained sparks. The modifying materials in the match head function as sensitizers (sulfur or rosin), burning-rate modifiers (potassium dichromate [7778-50-9] or lead thiosulfate [13478-50-7]), and ash-formers (diatomaceous earth, powdered glass, etc); the latter serve to hold the glowing residue safely together by a sintering process. The glue, starch, and paraffin in the stem below the head act as flame-forming fuels and the neutralizers account for the practically indefinite storage stability of well-made matches. In the striker, the glass powder controls proper bite and sensitivity. The binder is insolubilized to prevent staining of clothing caused by rain or perspiration.

The SAW match is similar to the safety match except that it is richer in fuel, and gives a billowing somewhat wind-resistant flame. The phosphorus sulfide [1314-85-8] in the tip provides the ignitability on any solid surface, and a little of the same material in the base bulb adds to wind resistance, but otherwise the base is underbalanced in active materials to prevent self-ignition from rubbing during transportation.

### 2. Manufacture

The low price of book matches is mainly the result of high speed, mechanized production methods. Book matches are punched from 1-mm thick, lined chipboard in strips of one hundred splints of ca 3.2 mm width each. In an eight-hour shift, a single machine can produce about  $20 \times 10^6$  match splints and deliver them half an hour later as completed, strikable matches, ready for cutting and stapling into books. In this half hour, the tips of the punched-out splints are first immersed in molten paraffin wax, without which no persistent flame and fire transfer is possible (see Waxes). Immediately following wax application, the tip composition is affixed by dipping the ends of the strips into a thick but smoothly fluid suspension carried on a cylinder rotating in a relatively small tank at the same speed as the match strips move over it in the clamps of an endless chain. As soon as an evenly rounded match tip has been formed, the matches enter a dryer where the main object is not so much the speedy removal of the water in the match composition as the prior congealing of the match head, which takes place at a temperature of about  $24^\circ\text{C}$  and a relative humidity of 45 to 55%. This drying technique is one of the most important parts of the manufacture, and it is responsible for the amazingly uniform quality and ease of ignition of the modern match.

The match-cover board is an approximately 0.4-mm thick, coated or lined chipboard, or sometimes a fancy grade of a variety of decorative and more expensive cardboards, on which a striking strip is printed by a roller coating process from a thin slurry of a composition described below. The cover is more or less elaborately printed with an advertising message. Although the technique of printing varies, it is possible on some presses

to apply all the colors, as well as a one-color underprint (inside of cover), on one printing press in one successive operation.

The most common size is a book of 20 or 28 (30) matches, and the 40-match size offers additional advertising area. "Ten-strike" matches are included in military food packages and are sometimes used for advertising purposes.

Wooden matches can be made by a veneering method whereby aspen wood is peeled from a section of a log and cut into splints which have a square cross section of 0.25–0.4 cm thickness, depending on the length of the match. The alternative method consists in cutting round splints from selected blocks of white pine by means of rows of cutting dies each resembling a large darning needle of which the eye is the cutter. The splints in both types of operation are forced into holes in cast-iron plates and are thus transported through the various dipping operations.

A third type of commercial matches popular in South America is the wax vestas with a center of cotton threads or of a rolled and compressed thin and tough paper surrounded by and impregnated with wax; each match is a miniature candle of long (ca 1 min) burning time.

Two processes precede the affixing of the heads for wooden matches. The first one is glow-proofing of the splint by impregnation with ammonium phosphate or a mixture of it with boric acid. In paper matches, the impregnation is conveniently done during the fabrication of the paper. This suppresses continuation of glowing of the carbonized splint after discard and also prevents the burned part with the still-hot tip from falling off and singeing clothing (see also Flame retardants). The second impregnation is the soaking up of paraffin wax into the stem for a certain length to assure flame forming and fire transfer to the wood. Head formation is similar to the process described for book matches except that for SAW matches a smaller second tip is affixed to the larger bulb. The rollers in the dipping tank over which the splints travel are grooved, the first roller deeply for the base tip, the second roller shallow-grooved for the SAW tip. The same equipment, simply leaving out the second dipping, can be used for wooden safety matches. A formaldehyde bath, sometimes also employed with paper matches, aids in congealing and subsequent proper drying of the match head. The wooden match industry, still prevalent in Europe, has been described (2).

### 2.1. Nonstandard and Military Matches

Because match manufacture is a series of high speed and highly mechanized operations, any variation that involves dimensional or incisive procedural changes is a significant undertaking which is only warranted if continual high production is to result. Hence, specialties that occasionally appear on the market are actually fireworks items, made laboriously and at relatively high cost by hand-dipping with limited mechanization. Such matches produce a colored flame, give off perfume or fumigating vapors, or furnish a persistent glow or flame for the purpose of burning in a strong draft. In order to do these things effectively, an enlarged elongated bulb is necessary.

An interesting variation of the regular match is the pull match. It is a paper match, considerably thinner and narrower than a regular book match because it needs very little stiffness when being used. The tip part of the match is enclosed in a strip of corrugated paper glued to a flat cardboard (such as a box of cigarettes) and the inside of the corrugated board is covered with striking material. On pulling the match fast enough out of the corrugation, the tip passes and engages the striker and becomes lit.

A curious item is the repeatedly ignitable match. It resembles a tiny pencil, the center part being a safety match composition which is surrounded by a cool-burning chemical mixture whose essential ingredient is nearly always metaldehyde. Notwithstanding the exaggerated claims for its performance, this match, although ignitable a few times in succession, is economically not competitive with the book match and definitely technically inferior.

The principle of the safety match is also used in the pull-wire fuse lighter used to start a fuse train for the ignition of fireworks items or more frequently for blasting work. This is a reversed pull match whereby

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the striker material is coated on a pull wire, and the match head material is within a small metal cup in a cardboard tube. Pulling the coated wire vigorously out of the device ignites the match mixture in the tube for fire transfer to the tubular fuse train.

Match buttons and strikers are built-in components of certain flares such as the well-known red-burning railroad fusee (3) and of some fire-starting devices invented during World War II to help marooned military personnel to light a fire with a minimum of effort.

During World War II, the Quartermaster Corps of the United States requested development of a SAW match that would withstand at least six hours submersion in water. Although no match is strikable after prolonged exposure to extremely high humidity, it is possible to prevent infiltration of moisture temporarily, and especially attack by liquid water, by coating the match head and part of the stem with nitrocellulose lacquer. This is impractical for the safety match because it makes striking progressively more difficult the thicker the coating becomes. It is, however, possible to protect SAW matches so as to withstand 6 to 10 h of submersion in water and still be readily ignitable. Large numbers of matches protected in this manner were made during World War II by at least two large wood match manufacturers in the United States. Federal specifications for matches include a Type III, Class 2, water-resistance strike-anywhere wooden match for performance after two hours submersion in water (4). For prolonged exposure to high humidity, the only safe protection is heat-sealing in plastic pockets and then canning (see also Waterproofing and water repellancy).

### 2.2. Formulations

Because match manufacturer has become a combination of high speed machinery design and operation, commercial art work and engraving, as well as of pyrotechnical processing, the latter is only a small though highly important part of the match business. Formulations are by no means a closely guarded secret, mainly since they are only a starting point on the way to producing a satisfactory match and striker adapted to the specific conditions of manufacture. The formulations given (Tables 1 and 2) with some adjustments permit the preparation of workable but not necessarily salable matches (5).

European matches, mostly of brown or black tips, are basically identical with U.S. matches in their formulations, except that they contain in addition red iron oxide or manganese dioxide of pigment grade in the match heads (2). Match materials, testing methods, and related matters have been reviewed (7, 8).

## 3. Economic Aspects

For 1976 the Consumer Product Safety Commission estimated that the total of all flame producers, ie, book matches (made from cardboard), individual (wooden) stick matches, and lighters, amounted to  $645 \times 10^9$  of such fire resources or "lights." Paper matches accounted for about 65% or  $420 \times 10^9$ , lighters for 25% or  $160 \times 10^9$ , and wooden matches, the remaining 10% or  $65 \times 10^9$ .

The rising popularity of disposable butane lighters and especially the increasing volumes of very inexpensive imported lighters has resulted in a tremendous decline in the use of matches. By 1992 the total lights market had grown to  $695 \times 10^9$ ; however, the relative market share of lighters had grown to approximately 86% or  $600 \times 10^9$ , whereas the share of paper matches had declined to 12% or  $83 \times 10^9$ , and wooden matches to just 2% or  $12 \times 10^9$ .

Some 98% of all these light sources are used for tobacco products and although disposable lighters continue to gain market share from matches, the overall lights market has begun to decline. Annual sales for the U.S. match industry in 1992 were approximately  $60 \times 10^6$ .

The cost and selling price for matches increase considerably with higher quality cover paper, elaborateness of printed messages on and inside the cover (and sometimes even on the splint), and size of the order. In any case, the customer receives exactly the same high quality matches and striking strip.

**Table 1. Composition of Commercial Safety Matches and Strikers**

Component	%
Match	
animal (hide) glue	9–11
starch	2–3
sulfur	3–5
potassium chlorate	45–55
neutralizer (ZnO, CaCO <sub>3</sub> )	3
diatomaceous earth	5–6
other siliceous fillers (powdered glass, “fine” silica)	15–32
burning-rate catalyst (K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> or PbS <sub>2</sub> O <sub>3</sub> )	to suit
water-soluble dye	to suit
Strikers	
animal glue or caseina	16
red phosphorus	50
calcium carbonate	5
powdered glass	25
carbon black	4

<sup>a</sup> Suitably insolubilized according to Ref. 6, or lightly brushed with diluted formaldehyde after application.

**Table 2. SAW (Strike-Anywhere) Match Composition**

Component	Tip composition, %	Base composition, %
animal glue	11	12
extender (starch)	4	5
paraffin		2
potassium chlorate	32	37
phosphorus sesquisulfide, P <sub>4</sub> S <sub>3</sub>	10	3
sulfur		6
rosin	4	6
dammar gum		3
infusorial earth (diatomite)		3
powdered glass and other fillers	33	21.5
potassium dichromate		0.5
zinc oxide	6	1

Book matches are an important medium of advertising since they represent a truly utilitarian item which is more often given away than sold. Advertisers seeking national distribution pay for the message on many millions of books without entering otherwise in the sale of the matches (resale advertising match). Large merchandisers such as supermarkets, convenience stores, drug stores, and discount chains frequently purchase matches bearing their own advertising for resale (resale private label).

Individual establishments, including restaurants, hotels, banks, trucking companies, etc, buy the books with their personal message for their own distribution (special reproduction). On the smallest scale, a generalized so-called stock design permits establishments, who may need only a few thousand books a year, to buy and give away matches carrying their message by grouping several small orders in one production run, thereby avoiding a larger outlay for customized artwork and printing plates.

#### 4. Toxicity and Other Safety Aspects

Because small children may suck on matches, the question of toxicity is often raised and the lingering, vague, though unwarranted idea of phosphorus poisoning may cause concern to laymen and even to physicians. Potassium chlorate is the only active material that can be extracted in more than traces from a match head and only 9 mg are contained in one head. This, even multiplied by the content of a whole book, is far below any toxic amount (19) for even a small child. No poisonous properties whatsoever can be imputed to the striking strip. SAW matches are similarly harmless but, because of their easy flammability, they should be entirely kept out of a household with smaller children. The same warning may apply to all wooden matches.

Safety-match strips arranged for decorative purposes in the form of flower pots are especially undesirable items, since an accidental ignition causes a dangerous flaring of many matches at one time.

Safety matches can be ignited by friction alone only when, with some deftness, they are rubbed on cardboard or glass. Accidental ignition is nearly always due to careless or absent-minded handling. In packaged condition, large numbers of safety matchbooks, if ignited in one spot, flare momentarily and harmlessly, often not igniting the adjoining matchbooks.

Exploding matches (other than for practical jokes) have virtually disappeared with modern manufacturing methods, ie, drying of the heads under controlled conditions. The occasional match that ignites and ejects sparking portions is generally a result of excessive pressure during lighting or of an accidentally cracked match head.

Sometimes a match ignites promptly but only a weak and unsatisfactory flame follows. This is the result of prolonged exposure of the matches to a temperature above 54°C in storage. The defect is caused by gradual dissipation of the paraffin wax throughout the splint and is evidenced by the disappearance of the line of demarcation, which is clearly visible in book matches. Otherwise, all safety matches tolerate exposure to elevated temperatures until about 177°C is reached. A U.S. Government specification requires that safety matches withstand exposure for two hours at 90°C (4). Earlier specifications stipulated a minimum acceptable nonignition temperature of 170°C. SAW matches are much more heat sensitive but still tolerate heating below a self-ignition temperature of 120 to 150°C.

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