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CEW: DIB V-3 DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS WASHINGTON August 21, 1934. MATCHES

From time to time the National Bureau of Standards receives letters from persons who want to know how to make matches. As a rule the writers do not say whether their intention is to make matches for sale, or for their own use. If the latter, they may as well try, but if they plan to produce matches for sale, they are héreby advised to seek a more promising way of earning a living. In spite of the reduction in the number of matches in a box, and the increased cost of a smaller package of boxes, matches are still cheap commodities. To sell them at a living profit, one must produce them on a large scale at low cost, and this requires a con-siderable investment in machinery for the various steps involved.

The Bureau has done no experimental work on matches, nor made chemical analyses to find out what commercial matches are made of. This letter circular is based upon what has been found in reference books. All the formulas come from Ullmann's Enzyklopaedie der technischen Chemie, 2nd ed., <u>10</u>, 556-576 (Urban & Schwarzen-berg, Berlin and Vienna, 1932). The article, Zundwaren, is the last in the book. It gives other formulas than those copied here, and an account of the manufacturing processes.

Thorpe's Dictionary of Applied Chemistry, 2nd ed., 4, 227-246 (Longmans, Green & Co., London, 1922), is to be found in many public and college libraries. It gives an interesting account of the history of matches and describes their manufacture, but without including formulas.

History of Matches

Apparently the first substitute for flint, steel, and tinder, or for two sticks rubbed together, by savages and Boy Scouts, was devised in 1804. A thin strip of wood was dipped into a mixture of phosphorus, oil, and wax, and was then rubbed on a piece of cork. The heat caused by the friction set fire to the phosphorus, and this ignited the other materials. Cancel, in 1805, invented a mixture of potassium chlorate and sugar, made into a paste with gum, and applied to the end of a thin stick. This match was lighted by dipping the head into sulphuric acid, which was a dangerous procedure, because the combustion started with more or less explosive violence, and the acid was apt to be spattered around.

It is not possible to give accounts of all the various devices that were invented during the ensuing few decades. The first true friction match, the forerunner of those used today, was made about 1827. The head was a mixture of potassium chlorate, antimony sulphid and gum water, made into a paste." It was lighted by rubbing on sandpaper. and a second s

White - also called yellow - phosphorus catches fire so easily that it will start to burn if held in the hand, or if allowed to lie in the air for a short time at ordinary temperatures. For this reason it was used in many of the earlier match compositions. Indeed, in this country, "parlor", or strike-anywhere matches containing white phosphorus were made until 1912. This form of the chemical cloud's is obtained, not account and the workers in workers. element is extremely poisonous and the workers in match factories suffered from it in a distressing way, so in that year Congress decided to put a stop to its use. This was accomplished by imposing an internal revenue tax of 2 cents per 100 matches. Red phosphorus, another form of the element, is not under the ban of this law, be-'cause it is not poisonous; nor is the use of phosphorus sesquisulphide objected to.

. The head of a strike-anywhere match is composed of four kinds of materials. The essential ones are combustible substances that catch fire and burn at a comparatively low temperature, and oxidizing substances that readily give up oxygen to support the combustion of the others. Mixed with these are inert materials that neither burn ' nor support combustion. They increase the friction when the match is struck, and also keep the combustion from being too rapid and violent. Finally there is some adhesive to serve as a binder to hold everything together and to make the head strong enough not to break into pieces when it is rubbed.

The heads of safety matches and the striking surfaces on the boxes contain the same kinds of materials, but in different pro-portions. When a safety match is rubbed on the box, it scrapes off a little of the striking surface. The heat produced by the friction sets fire to the new combination. The striking surface is not a bisolutely necessary, for it is possible to light one of the matches by mubbing it with a loss strate strate scrapes of a and the second by rubbing it with a long, sweeping stroke across a pane of glass or some other hard, smooth surface. The probable reason why the match can be lighted in this way is that only a small area of the match head touches the smooth surface, and all the heat produced by the friction is concentrated on this small area, so its temperature is raised to the ignition point. Rei la dre gal da Al

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The Bureau has been asked more than once how to make a pocket match box for safety matches with a prepared striking surface that will last indefinitely. The impossibility of this requirement is self-evident, because some of the composition is used up whenever a match is struck. A smooth metal surface on the box would not be large enough to provide for the necessary long sweeping stroke.

Complaint is sometimes made that there is not enough material in the striking surface to light all the matches in the box. This is cert inly not true of most of the matches sold in wooden boxes, and shows that wheever makes the complaint probably does not strike matches properly. In an experiment made to find out how many matches could be lighted if they were touched as lightly as possible against the box, the striking surfaces were not exhausted until 720 matches had been lighted. Forty is about the maximum number of matches to be expected in the average box, and 720 matches would fill 18 boxes. A repetition of the experiment might not check within 100 matches, but it is evident that there is plenty of composition on the two striking surfaces. Trouble is sometimes experienced when the matches are in paper boxes, which are so yielding that the striking surface wears off too fast.

In table 1 the commonly used combustible substances and oxidizing agents, or those that support the combustion by giving up oxygen, are listed in separate columns. This list includes only the substances in the formulas given further along. The inert materials are not shown in the table.

Combustible Substances	Oxidizing Agents
Red phosphorus, P Phosphorus sesquisulphide, P ₇ S ₄ Sulphur, S Antimony sulphide, Sb ₂ S ₇ or Sb ₂ S ₅ Pyrite, FeS ₂	Potassium chlorate, KClOz Potassium dichromate, K2Cr2O7 Lead peroxide, PbO2 Red lead (minimum), PbzO4 Barium chromate, BaCrO4 Manganese dioxide, MnO2
Rosin Gums Dextrin Glue	

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COMBUSTIBLE SUBSTANCES AND OXIDIZING AGENTS

The gums (arabic or acacia, senegal, a variety of acacia, and tragacanth), the destrin, glue, nd to some extent the rosin, ar e binders. Gums arabic and acacia dissolve in water. The same is true of the dextrin and glue. Rosin is insoluble, and tragacanth swells astonishingly, though little of it dissolves. Of the other ingredients, only the two potassium salts are soluble in water. However, because the amount of water is limited, these two salts may not dissolve completely at room temperature. So they as well as the other materials should be ground (separately) to fine powders.

• One reason for powdering the materials is to make sure that the combustible substances and the oxidizing agents shall be in close contact with one another, so that each will have its full effect on the other. Another reason is to make the final mixture uniform in composition, with each match head like every other. This would not be the case if some of the ingredients were in coarse grains, which would settle to the bottom more rapidly than the finer particles.

The materials used in making matches are chosen because a mixture of them will start to burn when heated moderately by friction. So it is very dangerous to grind a dry mixture containing both combustible substances and officizing agents. Potassium chlorate gives up its oxygen so readily that if a few grains of it and a little sulphur or one of the other combustibles are ground together, a violent explosion will result. There is no danger if two combustible substances or two oxidizing agents are mixed and ground. Danger arises only when the two classes of materials are ground together. Still, in order to be sure that no mistake will be made and discovered too late, it is a good rule not to grind any two ingredients together. Before starting to grind anything, thoroughly clean the mill, or the mortar and pestle. When the time comes to grind the final mixture, everything will be wet and there will be no danger.

The final mixture must be of such a consistency that it will make heads of the right size, or can be spread easily on the boxes. The consistency of the composition for the heads must be adjusted with the greater care. The weights of water required are given in two or three of the formulas, but it is advisable to start with a little less water than is called for. The consistency depends not only upon the amount of water, but also upon the fineness of the powder mixed with it. The finer the particles, the more water is needed to make a paste of a given consistency. If the weight of water is not given in the formula, the operator must use his judgment, helped by the formulas that tell how much water is required for a given total weight of solids.

Red/phosphorus may be contaminated with traces of phosphoric acid; and flowers of sulphur will give a strong reaction for sulphuric acid, but this is not true of roll sulphur. Both the phosphorus and the flowers of sulphur should be washed by stirring them with about twice their weight of water, letting them settle, and drawing off the water. The wet pasty mass: can be used without being dried. Sulphur is especially hard to wet with water. It tends to float, or else to sink in small masses that inclose air bubbles and

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are hard to break up. This trouble can be avoided by moistening the sulphur with a dixture of equal volumes of water and acetone before pouring the wash-water upon it. The same expedient makes the phosphorus easier to wash.

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Another way to do the washing is to plug the stem of a funnel with absorbent cotton, packed in so that water will run through easily, but the solid will be held back. The dry sulphur is placed on the cotton, the water-acetone mixture is poured into the funnel, and finally the wash-water in repeated small portions. Each portion is allowed to drain out of the funnel before another is added.

In the formulas about to be given, all parts are by weight. The unit weight can be as small or as large as desired. For experimental work, comparatively small batches will suffice. In one of the formulas there is a total of 71 parts of solid ingredients. If the unit weight is 1 gram, there will be 71 g of the dry mixture. This weight, equal to 2.5 oz. avoir., is enough to make 3000 matches. (1 oz. avoir. = 25.350 g.)

Strike-anywhere Matches.

Formula 1.- Phosphorus sesquisulphide, 9; potassium chloraté, 20; iron oxide, 11; zinc oxide, 7; glass powder, 14; glue, 10; water, 29.

Formula 2.- Phosphorus sesquisulphide, 10 to 12; potassium chlorate, 40.to 43; zinc.oxide, 5; whiting or ocher, 5; powdered quartz and glass, 20; glue, 20; water, 30 to 35.

In either case, the glue is soaked in the (cold) water until thoroughly soft, and is then melted by setting the container in a larger vessel of hot water. The solid materials are then added, a little at a time, to the glue solution. For large batches a mixing machine is used, but a fine sieve will suffice for making small amounts when experimenting.

Safety Matches and Striking Surfaces.

Only a few of the formulas given in Ullmann's Enzyklopaedie Can be copied here. In each case, the formula for a head composition and that for the accompanying striking surface are put together. All parts are by weight. Formula 1.- <u>Heads</u>. Sock gum tragacaith, 20, in-water, 300, for 24 hours. The gum will swell enormously, but not dissolve! Add to this a solution of gum senegal, 150, in-warm water, 200, and heat to boiling. Remove from the fire and add potassium chlorate, 100; potassium dichromate, 125, antimony sulphide, 33; rosin, 50; red lead or lead peroxide, 200; sulphur (powdered roll or washed flowers), 30; sienna or umber, 100; glass or pumice powder, 100; hot water, 150. Gum senegal is almost identical with gum arabic (gum acacia).

Striking surface. Dissolve dextrin, 400, in hot water, 400, and cool. Then add red phosphorus, 1000; levigated chalk, 200; umber, 300; antimony sulphide, 1000.

Formula 2.- <u>Heads</u>. Gum arabic, 10; gum tragacanth, 3; potassium chlorate, 53.8; ferric oxide, 6; glass powder, 12; potassium dichromate, 5; sulphur, 3; chalk or rosin, 1.2; manganese dioxide, 6.

S_triking surface. Antimony sulphide, 5; red phosphorus, 1.5; manganese dioxide, 1.5; glue, 4.

Formula 3.- <u>Heads</u>. Potassium chlorate, 56.8; potassium dichromate, 7; antimony sulphide, 2; lead peroxide, 11.3; umber, 5.7; glass powder, 5.7; gum arabic, 8.5; rosin, 3.

Striking surface. Red phosphorus, 34.5; antimony sulphide, 34.5; umber, 10.2; , chalk, 7; dextrin, 13.5.

The ferric oxide called for in one formula is probably colcothar, or caput mortuum, which is similar to rouge. The mineral pyrolusite is the form of man snese dioxide used. Antimony trisulphide (the mineral stibuite or antimony blende) and the artificially prepared pentasulphide are said to be used interchangeably.

At the end of each formula that has been given, the directions "Mix and grind thoroughly" are to be understood, but in accordance with the warning already stressed, this applies only to the wet mixture.

If a match made with untreated wood is lighted and let burndown half-way or more, and the flame is then blown out, the charred stick will usually continue to glow for a time. It may even burn through, and the head, carrying a spark, will fall to the ground or the floor. This sort of happening has been the cause of many fires. To prevent it, the sticks are soaked in a solution of some chemical or mixture of chemicals, among which are ammonium sulphate, ammonium phosphate, alum, borax, boric acid, etc. After

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the sticks have been "impregnated" in this way and dried, they are dipped part-way into melted paraffin, and are then kept in a steamheated oven for a time to let the paraffin soak into the wood. This treatment with paraffin makes the wood catch fire easily when the match is struck. The sticks are now ready for the dipping oper_ation that forms the heads.

It is possible to dip the sticks by hand, holding a considerable number at a time in a frame, but for manufacturing on a large scale, more or less automatic machines are used. Indeed, most of the operations in a match factory are done mechanically. It is said that much of the equipment has been designed by the match manufacturers, although some of it can be bought. For more detailed information about the different steps in the manufacture of matches, the two books already referred to can be consulted.

There are various special kinds of matches. Some strike-anywhere matches have heads made of two compositions. One, which is more easily ignited by fric_tion than the other, is applied in small quantity as a tip on the end of a head of the usual size, made of the less easily ignited composition. Familiar to everybody are the paper matches in books, whose chief purpose seems to be to serve as advertisements. Fusees have large heads that extend along the stick for about three-fourths of an inch. While this head is blazing furiously, almost anybody can light a pipe or start a camp-fire with it, even in a high wind. Sulphur matches, with the end of the stick coated with a thin layer of sulphur before dipping, were a common kind before paraffin came into general use for impregnating the sticks to make them catch fire easily. A special form was made in sheets of about 23 matches. The wood, about the thickness of an ordinary match stick, was cut part-way through, so that the matches held together, but could be pulled apart readily. In order to form separate heads when the wood was dipped into the composition, 22 narrow V-shaped notches were cut along one edge. Some years ago, similar matches, in nearly cubical blocks instead of sheets, were much used in the West. Thorpe's Dictionary of Applied Chemistry tells about still other special kinds of matches.

The names and addresses of manufacturers of the machines used in making matches can be found in trade directories.

Federal Specification EE-M-101a, Matches; Safety (full size, in boxes) gives the Government requirements in the purchase of matches. Copies can be bought from the Superintendent of Documents, Government Printing Office, Washington, D.C. They cost 5 cents apiece, and stamps will not be accepted.

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