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PAPER A
CHEMISTRY

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LETTER FROM THE APPLICANT

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Matches have been known since the early 19th century. The first matches needed dipping in concentrated sulphuric acid in order to light them. The first friction match, similar to the ones we use today, was invented by Johnny Walker in 1829 and is still going strong. Despite the fact that the basic technology is old, many improvements have been made over the last two centuries.

As you almost certainly know, a match usually consists of a splint (which is the name for the stick) and a head. This head contains a composition that ignites when contacted with a rough surface.

Most research has been done on the composition of the head of the match, especially in view of health reasons. Only minor research effort has been put into the splint. It is important to realise that, in fact, match research has mainly focused on how to produce matches as cheaply as possible, since matches only have a very small financial margin.

To give you some background to the current state of the art of matches, as an annex we attach an advertisement for REDHEADS matches. These matches are produced by our main competitor. As far as we are aware, all matches presently on the market are similar to the ones described there.

In the past we have produced and sold matches in which fire-retardant material is incorporated at the end of the splint. This greatly improved the safety of the matches. The fire-retardant material works in such a way that the match extinguishes itself soon after ignition. These matches are safer than ordinary matches in that unintentional fires due to the continued burning of the match after the required use are avoided, thus reducing the incidence of, for example, forest fires or injuries to children. At least 25% of the splint furthest away from the head must be treated with the fire-retardant material in order to exhibit sufficient fire-retardance. Optimal results are obtained when between 30 and 40% of the splint is treated with the fire-retardant material.

Quite a few of our previous matches lost their heads during production. Even during use, a few matches per box loose their head. Overall, up to 10 percent of matches are affected, which represents a substantial financial loss. We have now found that, when using beeswax very good adhesion of the head to the splint can be obtained.

These matches work well with any type of composition of the head. However, we have also found a new composition of the head that works extremely well with the new splint.

Prior art compositions of the head usually contain phosphorus sesquisulphide and sulphur. The problem with such conventional compositions of the head is that these compounds have undesirable environmental properties, both in the production of the matches and in their use. Our research on compositions in which the above-mentioned compounds are not present has revealed a new type of composition that is not only more environmentally benign, but also provides high flexibility in the design of the matches. By varying some of the components of the composition of the head, matches can be obtained that have completely different properties. In this way, either strike anywhere matches or safety matches can be obtained. The combination of the new head and splint provides a further advantage namely that the head is fixed much better to the splint than in the prior art.

A method of manufacturing our new splint includes the steps of: (i) coating a portion of a porous match splint with a layer of beeswax, followed by (ii) coating the remaining part of the splint with a fire-retardant material.

Any porous match splint may be used, for example wood, cardboard or stiff paper. Wood is the preferred material for the luxury market. For cheaper matches, cardboard or stiff paper is preferred.

The coating with a layer of beeswax takes place at a temperature such that a substantial part of the beeswax remains on the surface of said portion of the splint. Usually, the wax is applied by dipping the splint in a wax that is kept at a temperature of between 135 and 150°C for about 5 seconds. After dipping in the wax, it is essential that the splints are kept at 55 to 60°C for 10 to 15 seconds to ensure that the wax penetrates the splint and does not solidify on the surface of the splint.

By varying the amount of beeswax along the length of the splint, the burning of the match can be adjusted to the needs of the user. For example, often more wax is applied near the head of the match so that the start of combustion is easier. To apply more wax, the coating step is performed a second time, but only to the portion that needs the additional wax.

The fire-retardant material is applied in such a way that the material adheres only to part of the splint. The fire-retardant material is preferably monoammonium phosphate ($NH_4H_2PO_4$). However, other fire-retardant materials can also be used. Examples are diammonium phosphate ($(NH_4)_2HPO_4$), ammonium sulphate ($(NH_4)_2SO_4$), and ammonium chloride (NH_4Cl). We believe that, in order to be compatible with the splint material, the fire-retardant material must be an inorganic ammonium salt. The fire-retardant material is applied by dipping part of the match in an aqueous solution of the fire-retardant material. A typical solution will contain from 1 to 5 wt.% of the fire-retardant material, preferably about 3 weight percent. After dipping in the solution, the splint needs to be dried. No special conditions for this drying are necessary.

The finished splint is then provided with a head, which is needed to ignite the mat
This can be done by dipping the splint in a liquid composition. Depending on the use o
the match, the dipping has to be performed one or more times.

As already mentioned above, the new splint can be used with any type of composition of the head. However, extremely good matches are obtained when this splint is combined with the composition developed in our laboratories. Using this composition of the head, one can obtain matches in which the head is fixed very well to the splint. This is certainly caused by the use of the beeswax, although we do not yet know the exact reason for this. In the production of prior art matches almost 10 percent of the heads fall off during packaging. Even during use, some matches still lose their head. As far as we know only paraffin waxes have been used in the prior art.

Prior art compositions of the head are based on phosphorus sesquisulphide (P_4S_3). Such compositions have several disadvantages, the most important being that they are very difficult to handle during manufacture.

The general composition found in our laboratory consists of 40-60 wt.% potassium chlorate, 0.5-9 wt.% red amorphous phosphorus, 3-18 wt.% binder, 0.1-5 wt.% thickener and balance filler. The composition may also contain optional components such as pigments, pH adjusting agents, and fragrances.

The composition in liquid form before being applied to the splint must have a density of 1.1 to 1.4 g/cm^3. It is essential that the components are used in the ranges given above, in order to achieve good adhesion to the splint.

The filler is preferably feldspar. The filler is typically present in an amount of 10 to 30 wt.%. A pH adjusting agent such as limestone, if used, is present in proportions ranging from 3 to 14 wt.%.

Of course, our new matches can also contain up to 2 wt.% of a fragrance in order to avoid smells that can be generated on burning the match. Any fragrance that is compatible with the match material can be used. Such fragrances are well known in the art of making matches.

To make specific types of matches, specific choices within this general composition need to be made. Two well-known types of matches are strike anywhere matches and safety matches. Strike anywhere matches are matches that have a match head formulation which is ignited by abrasive contact with any suitable rough surface. Safety matches are matches that have a match head formulation which is ignited by an abrasive contact with a surface containing a formulation for initiating ignition of the match head.

For strike anywhere matches it is essential that there is a relatively high amount of 2 to 9 wt.% of red amorphous phosphorus, whereas for safety matches the amount of red amorphous phosphorus should not be more than 2 wt.%. For strike anywhere matches the amount should preferably lie between 4 and 9 wt.%, more preferably between 5 and 7.5 wt.%. For safety matches the preferred concentration of red amorphous phosphorus lies between 0.5 and 2 wt.%.

The thickener is preferably a starch present in proportions of 0.1-5 wt.%.

The presence of red amorphous phosphorus makes it difficult to achieve the clear colours characteristic of match head formulations based on phosphorus sesquisulphide. The muddy colour of red amorphous phosphorus in the above formulation is particularly difficult to mask and consequently a pigment such as iron oxide is often used. If present the pigment is used in an amount of from 3 to 10 wt.%. Iron oxide pigments can give red, yellow or black colour to the head of the match, depending on which type of iron oxide is chosen (Fe_2O_3, ferric oxide, is red; $Fe_2O_3.H_2O$, hydrated ferric oxide, is yellow; Fe_3O_4, ferroferric oxide, is black). Titanium dioxide (white) may also be used as a pigment.

Gelatine is preferably used as the binder. The binder content of the formulation is lower than is usual in the prior art. The low binder content improves the drying rate. Animal glue can also be satisfactorily used as the binder.

Examples:

Example 1: Strike anywhere match

A match in accordance with one embodiment of the invention, together with a process for making the match, will now be described by way of example only, with reference to the accompanying figure, which is a schematic diagram of the match.

Referring to the figure, the match comprises a wooden match splint 1 on which is carried a match head 2. The match splint 1 is divided into three zones 3, 4, and 5. In the first zone 3, in the region of the head 2, a substantial amount of beeswax is absorbed into the splint 1. In the intermediate zone 4, next to the zone 3, a smaller amount of wax is absorbed into the splint 1 than in the first zone 3. Finally, at the end of the match remote from the head 2, the zone 5 is covered in fire-retardant material. The zone 3 is typically 5 mm long, with the zone 4 also being typically 5 mm long.

The match is formed by the following process. First, the match splint 1 is dipped in molten beeswax at a temperature of 140°C, so as to coat up to the first 10 mm of the splint 1 including the zones 3 and 4. The splint is then kept at 55°C for 10 seconds to ensure that the wax penetrates the splint. The whole splint 1 is then coated with fire-retardant material, for example monoammonium phosphate. This material will not adhere to the zones 3 and 4 of the splint 1 previously coated with wax, thus leaving only zone 5 covered with fire-retardant material. Part of the monoammonium phosphate is absorbed into the zone 5 of the splint 1. The splint 1 is then dipped again in the hot beeswax bath, so as to coat the 5 mm of the splint 1 corresponding to the first zone 3 on top of the wax already provided on the splint 1. Again the splint is kept at 55°C for 10 seconds. The head 2 of the match can then be applied by dipping as will be discussed below.

The above sequence of steps ensures the adherence of both the wax and the fire-retardant material to the splint. Furthermore, as the fire-retardant material is provided only in the zone 5 remote from the zone 3, economy of use of the rather expensive fire-retardant material is achieved. The zone 4, in which only a small portion of wax is absorbed into the splint 1, provides an intermediate region which helps to resolve the conflicting requirements of the combustion of the match, as assisted by the zone 3, and the extinction of the combustion as assisted by the zone 5.

As mentioned before, suitable ammonium salt fire-retardant materials other than monoammonium phosphate may be incorporated into the zone 5. Suitable materials include diammonium phosphate, ammonium sulphate, and ammonium chloride.

The match head formulation suitable for the production of strike anywhere matches is prepared. The match head has the following composition:

Component of match head	amount (weight percent)
feldspar	21
gelatine	12
starch	3
potassium chlorate	49
fragrance	1
titanium dioxide	3
limestone	5.5
red amorphous phosphorus	5.5

All ingredients except the red amorphous phosphorus are slurried together in water and the red amorphous phosphorus is added to the aqueous slurry.

The above formulation combines a satisfactory sensitivity (which means that it is easy to ignite) and burn rate and has no propensity to produce burning fragments or dropping of hot ash.

The water content of the above formulation may be in the range from 40 to 50g per 100g. The density of the formulation when in the form of a wet composition is in the range of 1.1 to 1.4 g/cm^3 but is typically 1.25 g/cm^3.

Starch is present as a thickener to improve the head formation during drying. In order to serve this function satisfactorily, the starch may be present in proportions ranging from 0.5 to 5.0 % dry weight.

Feldspar is used as filler and serves to make up the balance of the formulation. Limestone is used as a pH adjustment agent.

It is to be noted that the above formulation is free of phosphorus sesquisulphide a sulphur. The absence of sulphur reduces the smell produced on striking the match. As mentioned previously the absence of phosphorus sesquisulphide is advantageous because it is difficult to handle during manufacture.

Example 2: Safety match

A match head formulation suitable for the production of safety matches is prepared. The match head has the following composition:

Component of match head	**amount (weight percent)**
feldspar	21
gelatine	4
starch	4
potassium chlorate	54
fragrance	2
iron oxide	6
limestone	8
red amorphous phosphorus	1

The same procedure as shown in example 1 is followed.

The density of the formulation, when in the form of a wet composition, is in the range from 1.1 to 1.4 g/cm^3 but is typically 1.15 g/cm^3.

The gelatine is present as a binder. As in Example 1 the binder content of the formulation is lower than is usual and consequently improves the sensitivity of the formulation as well as the drying rate. Gelatine may be present in proportions ranging from 3 to 12 % dry weight without adversely affecting the sensitivity. In place of gelatine, animal glue may provide a satisfactory binding agent.

As mentioned before, the presence of red amorphous phosphorus makes it difficult to achieve clear bright colours but does not hinder the production of standard brown formulations. To this end, iron oxide is used as a pigment and may be present in proportions ranging from 3 to 10 % dry weight.

As in Example 1, limestone may be present in proportions ranging from 3 to 14 % dry weight while feldspar is used as filler and serves to make up the balance of the formulation.

It is to be noted that the above formulation is also free of phosphorus sesquisulphide.

Since this is a safety match, it can only be lighted by contact with the abrasive surface present on a matchbox.

Example 3: Fixing of the head

In the following examples, several matches according to the present invention are compared. The matches will also be compared with commercial prior art matches.

Matches A to C were made. Matches A and B are the matches of examples 1 and 2, respectively. Match C is a match in which only the splint prepared in example 1 is dipped in the commercial head composition REDHEAD. REDHEAD is a commercial product comprising potassium chlorate, phosphorus sesquisulphide and sulphur.

Match A: match of example 1
Match B: match of example 2
Match C: splint of example 1 and REDHEAD

Matches were also made using a prior art splint. Prior art splints consist merely of a material that has been impregnated with paraffin and has no flame-retardant.

Match D: prior art splint and head of example 1
Match E: prior art splint and head of example 2
Match F: prior art splint and REDHEAD (this match F is a commercial match available under the trade name REDHEADS)

For each type of match, 1000 matches were tested, according to the EMMA (European Match Maker Association) procedure. The percentages were therefore determined by counting the matches failing or passing the test (depending on the test).

The head is fixed to the match by a dipping process. As we mentioned before, the combination of splint and head composition of the present invention results in a very good fixation of the head to the splint. In this example, we will compare the loss of heads during packaging of matches.

	Loss in percent 1 dipping	Loss in percent 2 dippings	Loss in percent 3 dippings
Match A	1.5%	0.9%	0.7%
Match B	1.3%	1.1%	1.0%
Match C	3.1%	2.6%	2.3%
Match D	5.7%	4.3%	3.9%
Match E	7.1%	4.6%	4.0%
Match F	9.7%	8.4%	7.9%

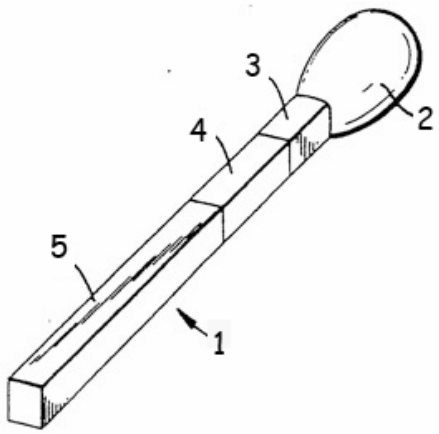
Example 4: Comparison of different matches

In this example, matches are tested for their use properties, i.e. ignition and extinguishing. Using the same matches as used in example 3, the matches are tested for success of ignition, ease of extinguishing and premature extinguishing.

It is noted that matches containing REDHEAD have a similar success of ignition. However, the materials used in the REDHEAD composition are less environmentally friendly.

	Success of ignition	Ease of extinguishing	Premature extinguishing
Match A	93%	very good	14%
Match B	87%	very good	17%
Match C	88%	good	20%
Match D	85%	poor	36%
Match E	83%	satisfactory	40%
Match F	84%	satisfactory	60%

Figure



ANNEX

Redheads

We are currently offering a complete line of matches. For home use, we provide the usual matches with wooden splints. We can offer these in several lengths, up to 20 cm. The long matches are mostly used for lighting fires in fire places. We also produce matches for promotional purposes. These matches are normally made of cardboard or stiff paper.

Our matches have very good properties, especially due to our wax-impregnated splints that provide good burning characteristics. The splints may have different levels of wax over the length of the splints in order to influence the burning characteristics. The end of the splints does not contain any wax so that the match is easy to extinguish.

The heads contain potassium chlorate, phosphorus sesquisulphide and sulphur, components that are well known in the art for their good properties. Due to a very specific test, matches with loose heads are found during production. No faulty matches will therefore arrive in the box. This results in matches that are of very high quality.