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(54) Match head formulations

(57) Match head formulations suitable for the production of safety matches and matches that may be struck anywhere are described which include metal chelate complexes of iron, copper, chromium or vanadium and citric acid, lactic acid, tartaric acid and EDTA. The metal chelate complexes may be combined with conventional match head compositions in which chromium compounds, sesqui-based phosphorus compounds, sulphur compounds and oxides of zinc present or preferably combined with environmentally friendly compositions using either amorphous phosphorus or, optionally, in the case of match head formulations suitable for the production of safety matches, an iron phosphide known as ferrophosphorus. These formulations are environmentally friendly both in manufacture and use. Environmentally friendly match head formulations which may be brightly coloured are also described.

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Description

The present invention relates to match head formulations suitable for the production of safety matches as well as matches that may be struck anywhere and to matches formed when coated with the said formulations.

For many years match head formulations have contained chromium compounds, phosphorus sesquisulphide, sulphur and/or sulphur compounds and zinc oxide. These compounds are now widely recognised as having undesirable environmental properties both in relation to the manufacture of such formulations and in relation to their use and it is therefore an object of the present invention to provide a match head formulation in which these compounds are substantially absent.

One type of match in common use has a match head formulation which is ignited by an abrasive contact with any suitable roughened surface. These are referred to as 'strike anywhere' matches. A second type of match in common use has a match head formulation which is ignited by an abrasive contact with a surface containing a formulation for initiating ignition of the match head. These are referred to as 'safety matches'.

UK-A-2252312 discloses compositions which comprise phosphorus or ferrophosphorus and excluding environmentally harmful components containing sulphur, chromium or zinc. Phosphorus match compositions for safety matches as well as strike anywhere matches are disclosed, the strike anywhere formulations comprising larger proportions of phosphorus. Matches made using these formulations have excellent environmentally friendly properties. The purpose of this invention is to improve the control of the sensitivity properties whilst at the same time retaining the environmentally friendly properties of the match head.

Control of the sensitivity influences the striking force required to be applied by the user in order to ignite the match head. If it is too high, this may result in breakage of the head, or alternatively breakage of the splint before ignition has occurred. In addition if the strike force required is too high this may increase the risk of accidents by flying heads or broken splints where the heads have ignited. This is also the case with conventional match compositions that the matches may be too difficult to ignite. Alternatively if the match head is too easy to light this may lead to premature ignition creating the danger of fires. It is possible to come across matches having different properties and a problem is to achieve a guaranteed consistent desired balance of the ignition sensitivity.

It is therefore an object of the invention to provide a match head formulation which has sufficient sensitivity to guarantee consistent ignition. It is also an object of the present invention to achieve precise control over the sensitivity of the match head so that the desired consistency of sensitivity can be guaranteed. These objectives are to be achieved without detriment to the other properties of the match head formulation and which can be made by the same manufacturing techniques and without adding significantly to the cost.

According to a first aspect of the present invention there is provided a match head formulation suitable for the production of strike anywhere matches or safety matches wherein the match head formulation comprises a component which is a chelating agent such as EDTA (ethylene diamine tetra-acetic acid), citric acid, lactic acid, tartaric acid, malic acid, or gluconic or other alpha hydroxy carboxylic acids, said chelating agent being complexed with a metal which may be selected from the following: manganese, Iron, cobalt, nickel, chromium, copper or vanadium.

Preferably the metal chelate is iron citrate which is preferably in the form of ammonium iron III citrate which is soluble in water.

In a preferred embodiment of this first aspect of the present invention the density of the formulation when in the form of a wet composition is in a range from 1.1 to 1.4 g/cm^3. Preferably the composition includes potassium chlorate present is in the range from 40 to 60 percent dry weight while the red amorphous phosphorus is present in a proportion of up to 9 percent dry weight for strike anywhere matches and up to 2 per cent dry weight for safety matches. Gelatine may provide a suitable binder if present in proportions ranging from 3 to 18 percent dry weight or alternatively the binder may be in the form of animal glue. The thickener is preferably a starch present in proportions of up to 5 percent dry weight while feldspar or other siliceous minerals may be chosen as the filler. The formulation may also include an ash improver, a pigment and a bleaching agent. A foaming agent may be Arylan PWS an amine salt of an alkyl aryl sulphonic acid present in proportions of up to 0.2 percent dry weight. The formulation may also include an ash improver such as infusoria in proportions of up to 6 percent dry weight or a cellulose flour such as olivestone flour in proportions of up to 7 percent dry weight and a pigment such as iron oxide in proportions ranging from 3 to 10 percent dry weight.

The composition may also include ferrophosphorus (a mixture of iron phosphides containing typically between 18 and 25 percent phosphorus).

In a preferred embodiment of the invention the iron citrate is provided in the form of ammonium iron III citrate. Alternatively the iron citrate is provided in the form of Iron (III) citrate. Alternatively the iron citrate is provided in the form of ferrous citrate monohydrate.

In a preferred embodiment of the invention the proportion of iron citrate of the match head composition is 0.01 % to 2.14 % by dry weight. In a further preferred embodiment of the invention the proportion of iron citrate in the match head composition is 0.15 % to 1.5 % by dry weight. In a further preferred embodiment of the invention the proportion of iron citrate in the match head composition is 0.4 % to 0.9 % by dry weight.

In a further preferred embodiment of the invention the proportion of phosphorus in the match head composition in the range from 0.01 % to 9 % by dry weight.

Some examples of the present invention will now be described with reference to formulations suitable for the production of safety matches and strike anywhere matches.

In the past match head formulations suitable for the production of strike anywhere matches have contained phosphorus sesquisulphide compounds as the active ingredient. Altematively phosphorus sesquisulphide may be replaced by red amorphous phosphorus.

Example 1

A match head formulation suitable for the production of strike anywhere matches is prepared in which 48.34 percent dry weight of potassium chlorate is mixed with 12.43 percent dry weight of gelatine, 2.76 percent dry weight of starch, 20.72 percent dry weight of feldspar, 0.35 percent dry weight of Eosin, 2.76 percent dry weight of titanium dioxide, 6.90 percent dry weight of limestone, and 0.21 percent dry weight of sodium dithionite ensuring good wetting and dispersion of all the ingredients before adding 5 percent dry weight of red amorphous phosphorus as an aqueous slurry and 0.57 per cent dry weight iron citrate in the form of ammonium iron (iii) citrate.

The above formulation combines a satisfactory sensitivity and bum rate and has no propensity to produce burning fragments or dropping of hot ash. The formulation also provides cost benefits over other existing formulations. The sensitivity is improved markedly when compared to formulations not comprising the iron citrate.

The water content of the above formulation may be in the range from 40 to 50g per 100g of solids but is typically 45.6g/100g solids.

The density of the formulation when in the form of a wet composition may be in the range of 1.1 to 1.4 g/cm^3 but is typically 1.2 to 1.35 g/cm^3. This figure is lower than is usual for match head formulations of this type as a result of being more highly aerated and contributes towards an improved sensitivity and a faster drying rate. The formulation is thus able to dry even during freak spells of high atmospheric humidity.

The proportions of potassium chlorate present may range from 40 to 60 percent dry weight while the red amorphous phosphorus may be present in proportions of up to 9 and as low as 1 percent dry weight for the formulation to maintain a satisfactory performance. The iron citrate may be present in proportions between 0.01 % and 2.5 % dry weight.

The following table shows the change in sensitivity measured in grams with increasing amounts of Iron Citrate:

Table 1:

Strike anywhere composition with 5% Red Phosphorus						
% Iron Citrate	0.00	0.15	0.43	0.87	1.43	2.14
Sensitivity (g)	212	197	160	164	153	163

Equally the proportion of red phosphorus may be varied to attain the optimum level for the amount of iron citrate.

Table 2:

Strike anywhere composition with 0.6% Iron citrate					
% Red Phosphorus	0.00	1.0	2.0	3.0	4.0
Sensitivity (g)	will not strike	will not strike	272	201	163

In the above experiments the iron citrate is provided in the form of ammonium iron (III) citrate. Alternatively the iron citrate may be provided in the form of Iron (III) citrate or ferrous citrate monohydrate.

The term iron citrate will be used a the general term throughout this specification to describe chelating complexes containing iron and citrate which may not be definite compounds. The iron content can vary widely from 15 % to 28 % depending on which form of iron citrate is used. The water soluble complexes, for example, also contain ammonia. The effectiveness of any particular complex depends upon and is proportional to the iron content. The same is true if different metals are used.

The iron citrate complex may also be formed in situ by the addition of any citrate such as for example potassium citrate to the composition and an iron salt such as for example iron III sulphate. These two compounds will react together to form the soluble iron citrate complex. Many other alternative compounds could be used with the corresponding reactions producing the desired complex. This is also true for the other complexes envisaged by the invention formed from any of the metals namely, manganese, cobalt, nickel, chromium, copper or vanadium with the chelating agents; lactic acid, tartaric acid, malic acid, gluconic or other alpha hydroxy carboxylic acids or EDTA.

The gelatine is present as a binder. 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. The gelatine may be present in proportions ranging from 8 to 18 percent dry weight. In place of gelatine animal glue may provide a satisfactory binding agent.

Starch is present as a thickener to improve the head formulation during dipping and may be present in proportions ranging from I to 4 percent dry weight and still serve its function satisfactorily.

Use of amorphous phosphorus makes it difficult to achieve the clear bright colours characteristic of match head formulations based on phosphorus sesquisulphide. The muddy colour of amorphous phosphorus in the above formulation is particularly difficult to mask in the orange/yellow spectral region and consequently a colourant such as Eosin may be required to be present in proportions of up to 7 percent dry weight. An alternative colourant to produce a match head formulation in the blue/red spectral region such as Rhodamine may not need to be present to such an extent. To assist the colouring of the formulation sodium dithionite may be used to bleach the gelatine while titanium dioxide may be employed as a masking agent. The titanium dioxide may be present in proportions of up to 7 percent dry weight.

Limestone may be present in proportions ranging from 3 to 14 percent dry weight to control the pH of the formulation while feldspar is used as a filler and serves to make up the balance of the formulation.

It is to be noted that the above formulation is free of phosphorus sesquisulphide, zinc oxide and di-chromates. The absence of sulphur from the formulation reduces the smell produced on striking a match coated with the formulation. The absence of phosphorus sesquisulphide is advantageous because it is difficult to handle during manufacture. It is possible to include these components in the formulation in lower proportions than conventionally used with the inclusion of iron citrate in proportions from 0.01 % to 2.5 % to improve and control the sensitivity.

In the past match head formulations suitable for the production of safety matches have contained chromium compounds, sulphur compounds and zinc oxide and in particular have contained potassium dichromate, sulphur powder and zinc oxide. In the second example all these are absent from the formulation and have been replaced in the formulations of the present invention by red amorphous phosphorus and iron citrate.

The experiments were repeated using various combinations of metal chelate complexes, as well as the iron citrate referred to above, of citric acid, lactic acid, tartaric acid, malic acid or EDTA (ethylene diamine tetra-acetic acid) as well as gluconic acid (other alpha hydroxy carboxylic acids would also be appropriate), complexed with manganese, iron, cobalt, nickel, chromium, copper and vanadium and similar results were obtained.

Example 2

A match head formulation suitable for the production of safety matches is prepared in which 54.18 percent dry weight of potassium chlorate is mixed with 4.06 percent dry weight of gelatine, 4.06 percent dry weight of starch, 20.32 percent dry weight of feldspar, 2.71 percent dry weight of infusoria, 6.77 percent dry weight of iron oxide, 0.09 percent dry weight of Arylan PWS, and 6.77 percent dry weight of limestone ensuring good wetting and dispersion of all the ingredients before adding 0.5 percent dry weight of amorphous phosphorus as an aqueous slurry and 0.5 per cent dry weight iron (iii) citrate in the form of ammonium iron(iii) citrate.

The water content of the above formulation may be in the range 40 to 55g per 100g of solids but is typically 48.8g /100g solids.

The density of the formulation when in the form of a wet composition may be in the range from 1.0 to 1.4 g/cm^3 but is typically 1.15 g/cm^3. As in Example 1 this figure is lower than is usual for match head formulations of this type as a result of being more highly aerated and contributes towards an improved sensitivity and a faster drying rate.

It was found that the proportion of potassium chlorate present may range from 40 to 60 percent dry weight and the proportion of amorphous phosphorus may range from 0.01 to 2.0 percent dry weight for the formulation to maintain a satisfactory performance. The proportion of iron citrate may range from 0.01 % to 2.5 % dry weight.

Example 3

A match head formulation suitable for the production of safety matches is prepared in which 57.98 percent dry weight of potassium chlorate is mixed with 9.28 percent dry weight of glue, 30.97 percent dry weight of an uncoloured pre-mixture of inert materials including silica, alumino-silicates and alkaline earth carbonates, 0.09 percent dry weight of Arylan PWS, and 0.14 percent dry weight of Eosin dye before adding 1.1 percent dry weight of amorphous phosphorus and 0.43 per cent dry weight ammonium iron (iii) citrate. This example provides safety matches which red in colour.

Example 4

A match head formulation suitable for the production of safety matches is prepared in which 55.93 percent dry weight of potassium chlorate is mixed with 8.95 percent dry weight of glue, 33.56 percent dry weight of a brown pre-

mixture of inert materials including silica, alumino-silicates, alkaline earth carbonates and iron oxides (the iron oxides functioning to provide the brown head colour), 0.08 percent dry weight of Arylan PWS, before adding 1.06 percent dry weight of amorphous phosphorus and 0.42 per cent dry weight ammonium iron (iii) citrate. This example provides safety matches which are brown in colour.

The following table shows the change in sensitivity measured in grams with increasing amounts of Iron Citrate:

Table 3:

Safety composition with 0.86% Red Phosphorus						
% Iron Citrate	0.00	0.15	0.43	0.87	1.43	2.14
Sensitivity (g)	134	117	99	84	104	94

Equally the proportion of red phosphorus may be varied to attain the optimum level for the amount of iron citrate.

Table 4:

Safety composition with 0.6% Iron citrate			
% Red Phosphorus	0.00	0.29	.86
Sensitivity (g)	416	135	86

In the above experiments the iron citrate is provided in the form of ferrous citrate monohydrate. Alternatively the iron citrate may be provided in the form of Iron (III) citrate or ammonium iron (III) citrate.

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 percent dry weight. In place of gelatine animal glue may provide a satisfactory binding agent.

Again the presence of 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 percent dry weight.

It is to be noted that the above formulation is free of potassium dichromate, sulphur and zinc oxide. The absence of sulphur from the formulation reduces the smell produced on striking a match coated with the formulation. The absence of potassium dichromate is advantageous because potassium dichromate is difficult to handle during manufacture.

However it will be appreciated that according to the invention it is possible to include any of these components in place of red phosphorus in lower proportions with the addition of iron citrate. This will reduce the adverse environmental effect and also improve the sensitivity properties. The person skilled in the art will appreciate that the proportion of iron citrate used will vary according to the components used in the remainder of the composition and also according to the desired final cost of the composition.

Such safety match compositions may be formulated along the lines of the above example to combine a satisfactory sensitivity and bum rate with no propensity to produce burning fragments or dropping of hot ash. The formulation meets all the requirements of BS 3795 and provides cost benefits over other existing formulations.

Example 5

In order to achieve a more brightly coloured match head formulation suitable for the production of safety matches and having properties similar to those described with reference to Example 2 above 55.52 percent dry weight of potassium chlorate is mixed with 4.16 percent dry weight gelatine, 4.16 percent dry weight of starch, 13.88 percent dry weight of feldspar, 5.55 percent dry weight of infusoria, 0.09 percent dry weight of Arylan PWS, 6.94 percent dry weight of limestone, 6.94 percent dry weight of olivestone flour, up to 7.0 percent dry weight of a chosen pigment, and 1.39 percent dry weight of titanium dioxide ensuring good wetting and dispersion of all the ingredients before adding 0.5 percent dry weight of amorphous phosphorus as an aqueous slurry and 0.5 per cent dry weight of iron citrate in the form of ammonium iron (iii) citrate.

The following table shows the change in sensitivity measured in grams with increasing amounts of Iron Citrate:

Table 5:

Safety Match 0.86 % Red Phosphorus						
% Iron Citrate	0.00	0.15	0.43	0.87	1.43	2.14

Table 5: (continued)

Safety Match 0.86 % Red Phosphorus						
Sensitivity (g)	129	118	99	88	105	94

Equally the proportion of red phosphorus may be varied to attain the optimum level for the amount of iron citrate.

Table 6:

Safety Match composition with 0.6% Iron citrate			
% Red Phosphorus	0.00	0.29	0.86
Sensitivity (g)	416	135	86

In the above experiments the iron citrate is provided in the form of ferrous citrate monohydrate. Alternatively the iron citrate may be provided in the form of Iron (III) citrate or ammonium iron (III) citrate.

This formulation is similar to that described in Example 2 above and differs essentially only in that it may be more brightly coloured. Consequently the proportions of the chlorate, amorphous phosphorus, gelatine, starch, infusoria, Arylan PWS, limestone, and feldspar may vary within substantially the same ranges as disclosed in Example 2. Of the constituents not found in that Example olivestone flour acts as an ash improver and may be present in proportions of up to 7 percent dry weight while titanium dioxide may also be present in proportions of up to 7 percent dry weight and acts as a masking agent as described in Example 1. Olivestone flour may be substituted by other cellulose flours.

Example 6

The amorphous phosphorus of the formulations described in Examples 2 and 3 may be replaced by ferrophosphorus, a mixture of iron phosphides containing typically between 18 and 25 percent phosphorus. Ferrophosphorus is relatively inexpensive and easy to handle but is a dense black powder and therefore limits the range of colours attainable.

A match head formulation of this type suitable for the production of safety matches is provided by mixing 52.63 percent dry weight of potassium chlorate with 3.95 percent dry weight of gelatine, 3.95 percent dry weight of starch, 19.73 percent dry weight of feldspar, 6.57 percent dry weight of iron oxide and 12.66 percent dry weight of ferrophosphorus and 0.5 per cent dry weight iron citrate.

The following table shows the change in sensitivity measured in grams with increasing amounts of Iron Citrate:

Table 7:

Safety composition with 12% Ferrophosphorus						
% Iron Citrate	0.00	0.15	0.43	0.87	1.43	2.14
Sensitivity (g)	128	115	97	84	101	93

In the above experiments the iron citrate is provided in the form of ferrous citrate monohydrate. Alternatively the iron citrate may be provided in the form of Iron (III) citrate or ammonium iron (III) citrate.

The experiments were repeated using various combinations of metal chelate complexes of citric acid, lactic acid, tartaric acid, malic acid or EDTA (ethylene diamine tetra-acetic acid) as well as gluconic acid (other alpha hydroxy carboxylic acids would also be appropriate), complexed with manganese, iron, cobalt, nickel, chromium, copper and vanadium and similar results were obtained.

The ferrophosphorus is preferably ground to a particle size of up to 100 microns. The preferred size for the formulation given in example 6 is less than 5 microns. It is to be noted that with a particle size between 20 and 65 microns it is possible to produce a composition with a colour other than black by using dyes. Ferrophosphorus in this range of particle size has been found to be beneficial in a range of pyrotechnic applications.

While it was found that the proportion of potassium chlorate present may range from 40 to 60 percent dry weight the proportion of ferrophosphorus was required to exceed 5 percent dry weight in order to maintain a satisfactory performance.

The proportion of gelatine present in the formulation was found to be able to range from 3 to 12 percent dry weight while the starch could be present in proportions of up to 10 percent dry weight. As in previous examples feldspar is used as a filler and serves to make up the balance of the formulation.

If despite the nature of ferrophosphorus a more brightly coloured formulation is required the iron oxide may be

omitted and replaced by titanium dioxide and a suitable pigment each in proportions of up to 7 percent dry weight.

It will be understood that it may be possible in all the above examples to include higher amounts of iron citrate, or the metal chelate complex concemed, which may not improve the sensitivity nor adversely effect the properties of the composition in other ways but would add unnecessarily to the cost of the formulation.

Of all the metal chelate complexes, iron citrate was shown to be effective as a controller of the sensitivity of the match head composition and also is the most environmentally friendly and the most cost effective.

Claims

1. A match head formulation suitable for the production of strike anywhere matches or safety matches wherein the match head formulation comprises a component which is a chelating agent such as EDTA (ethylene diamine tetra-acetic acid), citric acid, lactic acid, tartaric acid, malic acid, or gluconic or other alpha hydroxy carboxylic acids, said chelating agent being complexed with a metal which may be selected from the following: manganese, Iron, cobalt, nickel, chromium, copper or vanadium.

2. A match head formulation according to claim 1, characterised in that the metal chelate complex is iron citrate.

3. A match head formulation according to claim 1 or 2, characterised in that it comprises potassium chlorate and red amorphous phosphorus, the balance being made up of a binder, a thickener, a filler, and a foaming agent to the exclusion of phosphorous sesquisulphide.

4. A match head formulation in accordance with any of the preceding claims 2 to 5, characterised in that the iron citrate is provided in the form of ferrous citrate monohydrate.

5. A match head formulation in accordance with any of the preceding claims 2 to 5, characterised in that the iron citrate is provided in the form of Iron (III) citrate.

6. A match head formulation in accordance with any of the preceding claims 2 to 5, characterised in that the iron citrate is provided in the form of ammonium iron (III) citrate.

7. A match head formulated in accordance with any of the preceding claims 1 to 5, characterised in that the metal chelate complex is formed in situ by adding a chelate compound, such as potassium citrate, with a metal salt, such as iron III sulphate, said chelate compound and metal salt reacting together when added to the composition to form the desired metal chelate.

8. A match head formulation in accordance with claim 1, characterised in that the proportion of the metal complex of the match head composition is 0.01 % to 2.14 % by dry weight.

9. A match head formulation in accordance with claim 1, characterised in that the proportion of the metal complex of the match head composition is 0.15 % to 1.5 % by dry weight.

10. A match head formulation in accordance with claim 1, characterised in that the proportion of the metal complex of the match head composition is 0.4 % to 0.9 % by dry weight.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 3819

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A D	EP 0 496 996 A (BRYANT & MAY LIMITED) * claims * & GB 2 252 312 A	1	C06B29/02 C06F3/00 C06B23/00
A	US 3 492 176 A (T.O. PAINE ET AL.) * claims *	1	
A	CHEMICAL ABSTRACTS, vol. 109, no. 14, 3 October 1988 Columbus, Ohio, US; abstract no. 112935j, Y. HAGIHARA ET AL.: "Effects of organoiron compounds on burning rate and slurry viscosity of AP-HTPB composite propellants." page 147; XP002041508 & KOGYO KAYAKU, vol. 49, no. 2, 1988, pages 119-123,	1	
A	US 3 923 564 A (R. LANTZ) * claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C06B C06F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 September 1997	Schut, R

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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