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EXOTHERMIC MIXTURE

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This invention in its broadest sense relates to the art of exothermic chemical compositions and more particularly to those adapted for use in therapeutic heating devices, hair-waving heater sachets, and like structures.

There are many uses for exothermic mixtures in which the exact degree of heat evolved and the duration and variations of the exothermic reactions involved must be controlled within well-defined limits as to the degree of heat and as to the extent of the heating period, all as is well understood in the art.

One object of the present invention is to produce exothermic chemical compositions in which the degree and duration of heat may be accurately controlled for the specific use intended.

Many exothermic compositions at present manufactured suffer from their undue sensitivity to deteriorating influences such as the effects of atmospheric moisture, oxygen, and carbon dioxide on the composition. Compositions which are adversely affected by these components are characterized by a declining amount of heat available from the composition, the extent of the heat loss being dependent upon such factors as temperature, humidity, the protection imparted by the package and the time elapsed since manufacture. It is another object of this invention to produce compositions which are stable to atmospheric influences without requiring reliance upon such expedients as moisture-proof wrappings, sealed metallic containers, and the like.

A further object of this invention is to produce exothermic compositions from readily available materials which require no special care in handling and which may be incorporated into a mixture of suitable physical form by the use of simple manufacturing equipment and without special control measures.

Another object of the invention is to avoid the use of substances which are toxic and might affect the comfort or health of the users, and particularly operators who handle the pads over extended periods. Some acidic substances which have been proposed for use in exothermic pads (oxalic acid, for example) may give rise to allergic disturbances in the operators.

Another object of the invention is to avoid the use of substances which are unduly volatile in reactions (hydrochloric acid, for example) and are likely to be emitted from the pads, and may be particularly objectionable because of a tendency to attack metal parts of equipment used with the pads.

The present invention contemplates the use of ordinary water as a moistening medium which when suitably applied to the exothermic composition presently to be described initiates the evolution of heat by means of oxidation-reduction reactions.

An important component of the exothermic composition is a metal or a mixture of metals. Such metals as iron, aluminum, copper, tin, bismuth, antimony, lead, magnesium, zinc, cadmium, manganese, or alloys of the same and other metals function well in exothermic compositions. However, aluminum is preferred as the principal metallic component by reason of its cheapness, convenience, and the high heat of formation of its compounds. The purpose of this component is to supply heat by means of its oxidation. Experiment has shown that the duration of the heating period may be controlled by means of the proportion of the metallic component present in the composition.

Another component of the composition is an oxidizing agent the chief purpose of which is to oxidize the metal. This component may be any one or a mixture of more than one of such highly oxygenated compounds as potassium dichromate, barium peroxide, benzoyl peroxide or other organic peroxides, potassium permanganate, the persulfate of ammonium and the alkali metals, the chlorites, chlorates and perchlorates of magnesium and the alkali metals, the perborates of the alkali metals, and the like. However, because of solubility characteristics, economy, and particularly because of the highly oxidizing decomposition products which are formed when it is acidified, potassium chlorate is one of the most convenient oxidizing agents to use. In practice it is found that the proportion of this component has a pronounced effect upon the time temperature relationship of the heating period which follows the moistening of the composition.

Certain oxides of metals which are lower in the electromotive series than the base metal selected for the composition, as, for example, cuprous and cupric oxides, are valuable addition agents. They accelerate the evolution of heat, evidently by means of replacement reactions. The preferred oxide is cuprous oxide.

Another component of the reaction is an acidic substance stable in the dry state. The group of compounds known as the organic sulfonic acids are eminently suited to perform the function of this component. Since this class of organic compounds is very large, and continually growing larger, it is impossible to name all of the sulfonic acids which will function. However, all sulfonic

acids which when placed in pure water in the proportion of one gram of sulfonic acid to ten grams of water form a mixture which is sufficiently acidic to redden a piece of blue litmus paper are considered an integral part of the invention. The solid sulfonic acids are preferred. These sulfonic acids may in general be represented by the formula, RSO_3H, where R is a substituted or unsubstituted, aliphatic or aromatic radical. The organic acid sulfates are also included in this class of components; these may be represented by the formula $R'OSO_3H$ where R' is a substituted or unsubstituted, aliphatic or aromatic radical.

As examples of this class of compounds containing the grouping $—SO_3H$, benzene sulfonic acid and paratoluene sulfonic acid may be cited.

The organic sulfinic acids are also included in this class of components; these may be represented by the formula $R''SO_2H$, where R'' is a substituted or unsubstituted, aliphatic or aromatic radical.

The acidic substance contemplated may be defined as an organic acid containing sulfur as a part of the acid group, that is, a group of atoms containing sulfur which confers acidity on the chemical structure as a whole. This includes the sulfonic acid group $—SO_3H$, acid sulfate group $—OSO_3H$, sulfinic acid group $—SO_2H$.

The above-mentioned acidic media possesses advantages over substances previously used for the same purpose in that they are solid, relatively non-hygroscopic, non-corrosive, acidic chemical entities which need not be evolved from auxiliary reactions in order to function in an exothermic mixture, and are unusually stable or passive in the presence of metals such as are likely to be used in exothermic mixes.

Another component of the composition is an inert material which functions as a diluent for the active components. This component may comprise one or more of the following: kieselguhr, kaolin, sand, pumice, gypsum, chalk, or any other cheap chemically inert material.

The following are examples of compositions which are found to be satisfactory:

Example No. 1

	Parts
Pumice	6.0
Kaolin	4.0
Potassium chlorate	1.5
Aluminum	3.0
Brass	2.0
Cuprous oxide	1.0
Linseed oil	0.1
p-Toluene sulfonic acid	0.6

Example No. 2

	Parts
Pumice	6.0
Kaolin	4.0
Potassium chlorate	1.5
Aluminum	4.0
Cuprous oxide	1.0
Mineral oil	0.1
Benzene sulfonic acid	0.6

It will be understood that the examples of satisfactory compositions suggest quantities which may be varied substantially in some instances without noticeable change in results and in other instances with changes which may be considered advantageous according to the degrees of heat produced and the time periods over which production of heat is extended. As suggestive of such variations in quantities it is noted that the inert diluent may vary from 5 to 20 parts, the aluminum from 1 to 6 parts, the brass from 0.05 to 5 parts, the potassium chlorate from 0.4 to 5 parts, the cuprous oxide from 0.05 to 4 parts. The proportion of the sulfonic acid or mixture of sulfonic acids which may be used may vary widely without departure of the composition from functioning for a specific purpose, depending upon the polarity, water-solubility and neutral equivalent of the acid or mixture of acids selected. The oil may be eliminated entirely or used in quantities as stated or substantially larger according to the mass of the other ingredients involved.

It is obvious that numerous combinations of ingredients mentioned could be selected from the above disclosure and the quantities varied to give different results as to extent and degree of heating. All such compositions are considered as embodying the present invention when they are characterized by the presence of a metal and by the production of hydrogen or hydrogen ions from a sulfur-containing acid or acids, and by means of the addition of water or a moistening medium to an otherwise inert mass, to combine with an oxidizing agent in an exothermic oxidation-reduction reaction or reactions. The exclusive use of these and other modifications of the invention as described in the accompanying claims is contemplated.

What is claimed is:

1. A composition for producing heat by chemical action, comprising a mixture of a metallic component selected from the group consisting of magnesium, aluminum, manganese, iron, cadmium, zinc, copper, tin, bismuth, antimony, lead, and active alloys of the same, a water soluble organic acid containing sulfur as a part of the acid group and stable in the dry state and capable when in solution of furnishing an acidic medium, and an oxidizing agent sufficiently active in said acidic medium to oxidize said metallic component.

2. A composition for producing heat by chemical action, comprising a mixture of a metallic component selected from the group consisting of magnesium, aluminum, manganese, iron, cadmium, zinc, copper, tin, bismuth, antimony, lead, and active alloys of the same, a water soluble organic sulfonic acid stable in the dry state and capable when in solution of furnishing an acidic medium, and an oxidizing agent sufficiently active in said acidic medium to oxidize said metallic component.

3. A composition for producing heat by chemical action, comprising a mixture of a metallic component selected from the group consisting of magnesium, aluminum, manganese, iron, cadmium, zinc, copper, tin, bismuth, antimony, lead, and active alloys of the same, an organic acid sulfate stable in the dry state and capable when in solution of furnishing an acidic medium, and an oxidizing agent sufficiently active in said acidic medium to oxidize said metallic component.

4. A composition for producing heat by chemical action, comprising a mixture of a metallic component selected from the group consisting of magnesium, aluminum, manganese, iron, cadmium, zinc, copper, tin, bismuth, antimony, lead, and active alloys of the same, an organic acid containing sulfur in the dry state and capable when in solution of furnishing an acidic medium, and an oxidizing agent sufficiently active in said acidic medium to oxidize said metallic component, the organic acid furnishing the acidic medium being selected from the group consisting of sul-

fonic acids which are represented by the formula RSO_3H, where R is a substituted or unsubstituted, aliphatic or aromatic radical.

5. A composition for producing heat by chemical action, comprising a mixture of a metallic component selected from the group consisting of magnesium, aluminum, manganese, iron, cadmium, zinc, copper, tin, bismuth, antimony, lead, and active alloys of the same, an organic acid containing sulfur in the dry state and capable when in solution of furnishing an acidic medium, and an oxidizing agent sufficiently active in said acidic medium to oxidize said metallic component, the organic acid furnishing the acidic medium being selected from the group consisting of acid sulfates which are represented by the formula $R'OSO_3H$, where R' is a substituted or unsubstituted, aliphatic or aromatic radical.

6. A composition as described in claim 1 in which the oxidizing agent is selected from the group consisting of barium peroxide, benzoyl peroxide, potassium dichromate, potassium permanganate, the persulfate of ammonium and the alkali metals, the perborates of the alkali metals, the chlorites, chlorates and perchlorates of magnesium and the alkali metals.

7. A composition as described in claim 1 which also includes an accelerating ingredient insoluble in water and stable in the mixture but being rendered active in the acidic medium.

8. A composition as described in claim 1 which also includes an accelerating ingredient selected from the group consisting of cuprous oxide and cupric oxide.

9. An exothermic mixture including aluminum, potassium chlorate, cuprous oxide, and an organic sulfonic acid.

10. An exothermic mixture including aluminum, potassium chlorate, cuprous oxide, and an organic acid sulfate.

11. An exothermic mixture including aluminum, brass, potassium chlorate, cuprous oxide, and an organic sulfonic acid.

12. An exothermic mixture including aluminum, brass, potassium chlorate, cuprous oxide, and an organic acid sulfate.

13. An exothermic mixture comprising aluminum, approximately 4 parts by weight; potassium chlorate, approximately 1.5 parts; cuprous oxide, approximately 1.0 part by weight; a water soluble organic sulfonic acid, approximately 0.6 part by weight.

14. An exothermic mixture comprising aluminum, approximately 4 parts by weight; potassium chlorate, approximately 1.5 parts; cuprous oxide, approximately 1.0 part by weight; a water soluble organic acid sulfate approximately 0.6 part by weight.

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