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CHEMICAL HEATING COMPOSITION

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This invention relates to chemical heating compositions and has as its principal object the provision of a composition for this purpose which is of light weight and quick action, in which the heat-producing power of the ingredients is, or may be, substantially expended in one heating, involving an electrolytic replacement action.

A further object of the invention is to provide a composition of the type referred to in which the ingredients are comparatively stable and inactive in the dry state, thereby minimizing the tendency to age during periods of storage in a moist atmosphere.

In my co-pending applications, Serial No. 641,616 and Serial No. 641,615, filed November 7, 1932, I have described and claimed certain improvements in the development of chemical heating compositions and methods of producing heat by chemical action upon the addition of water. In the former of these applications, I have disclosed a composition comprising a mixture of a metal such as iron, which is referred to as the base metal, an electrolyte such as lead chloride, and a second metal which is positioned above the base metal in the electromotive series of metals, aluminum being one example of the second metal which is used. In the second of my afore-mentioned application I have disclosed a heat pad composition comprising a base metal which may be iron or other metal as described therein, a replaceable electrolyte having a high degree of insolubility in water, such as cupric carbonate, and an additional ingredient or ingredients designed to effect solution of the replaceable electrolyte when water is added to the mixture, a combination of oxalic acid and barium chloride being one example of such ingredients.

In compositions of the type heretofore used in commercial heating pads, the evolution of heat is produced primarily by atmospheric oxidation of the base metal, and this action proceeds rather slowly. The average size heat pad requires about twenty ounces of the iron-base mixture in order to give a sufficient initial heat. Such a pad, it is true, could be used for from eight to twelve successive heatings, each of about eight hours' duration. However, it is an unduly heavy and bulky article for cases where only one heating period is needed.

I have found that by omitting entirely the use of iron in the mixture, and by substituting therefor, in the proper amount, a metal which is more electropositive than iron (i. e., a metal the compounds of which have higher heats of formation than those of the corresponding compounds of iron), I am able to obtain a heating combination which, for just short periods up to say, six or eight hours, will have a much greater heat generating capacity per unit weight than the iron-base type of mixture. In fact my experiments show that a composition of the type presently to be described is from fifteen to twenty times as effective as the common iron-base type of mixture, per unit weight, in the generation of heat for an initial period up to about eight hours. I am thus able to provide a convenient size pad of two or three ounces in weight which is fully as effective for a one heat period of several hours as are any of the present types which run from fifteen to twenty ounces in weight.

With few exceptions, it is a general principle that the heat of formation of a compound of a metal is greater the higher the position of the metal in the electromotive series of metals. For example, the formation of aluminum chloride under the conditions prevailing in a heat pad mixture is accompanied by the evolution of about five times as much heat as is evolved in the formation of a corresponding amount of ferrous chloride under corresponding conditions. Clearly, therefore, the use of a metal such as aluminum, in lieu of iron, as the principal metal in the mixture will result in a decidedly increased capacity for generation of heat. The metals which I have found best adapted for this use are those which are decidedly electropositive and generally may be described as those metals which are electropositive with respect to iron, that is, those metals which are positioned above iron in the electromotive series of metals. Although the alkali and alkaline earth metals are highly electropositive, they are not well adapted for use in compositions of this class because of their unstable nature. However, the stable metals appearing immediately below these metals in the electromotive series, namely magnesium, aluminum, manganese and zinc, are very satisfactory. Of this group of metals aluminum is the preferred metal because; among other things, of its comparative cheapness, and in the following examples I shall use aluminum as the example of the metal employed in the mixtures.

The simplest example of the composition which I have developed comprises approximately equal proportions of aluminum, in finely divided condition, and cupric chloride. When water is added to such a mixture, the cupric chloride dissolves and the cupric ions are then electrolytically replaced by aluminum to form aluminum chloride, this latter action being accompanied by the evolution of heat. This composition, however, is unstable in the dry state due to the high solubility and deliquescent nature of the cupric chloride. I prefer, therefore, to use in lieu of cupric chloride, other replaceable electrolytes which have a lower degree of solubility in water. For example, lead chloride, lead sulphate, antimony oxychloride, cuprous chloride, mercurous chloride, and similar replaceable salts which have rather limited solubility in water, are to be preferred to salts of the type of cupric chloride, since they have, because of their lower degree of solubility, less tendency to deteriorate or age in a moist atmosphere. In fact, the most satisfactory replaceable electrolytes are those of the type of cupric carbonate, which are highly insoluble in water, and which, therefore, provide a very stable mixture. Among the substitutes for cupric carbonate which are replaceable by aluminum, and which are highly insoluble in water may be mentioned the following: cupric phosphate, cupric oxide, cuprous oxide, metallic copper, metallic tin, metallic nickel, metallic antimony, and antimony oxide.

Due to the high degree of insolubility of cupric carbonate, and the aforementioned substitutes therefor, it is desirable to add to the mixture a substance which, upon the addition of water, will effect solution of the cupric carbonate. In general, any substance which in water solution will give a surplus of free hydrogen ions, may be used to effect solution of the cupric carbonate, or its equivalents.

I have found that the following composition, using aluminum as the metal, is highly satisfactory from the standpoint of stability as well as from the standpoint of the quantity of heat which may be generated per unit weight of the mixture:

	Grams
Aluminum	15
Cupric carbonate	15
Barium chloride	1
Aluminum sulphate	2

Upon the addition of water to the above mixture the reactions, in all probability, are substantially as follows: The barium chloride interacts with the aluminum sulphate to produce aluminum chloride in solution and a precipitate of barium sulphate. Aluminum chloride being the salt of a strong acid and a weak base, immediately hydrolyzes to produce a solution having a high concentration of free hydrogen ions. The cupric carbonate, although highly insoluble in water, readily dissolves in the acid solution thus produced and brings the copper into solution as cupric chloride. The cupric ions are then replaced by the metallic aluminum to form aluminum chloride. This reaction, as above explained, is highly exothermic. At the end of the first heating period practically all of the aluminum will normally be consumed, and the mixture spent. This is in marked contrast to the present comparatively slow acting iron-base type of mixture where the iron must necessarily be present in greatly preponderating proportion, with the consequent result that a heat pad of average capacity, employing such a mixture is unduly heavy and bulky.

The foregoing example illustrates very well the importance of using substances which will make for a stable mixture. In the dry state all of these ingredients are inactive, and the mixture will retain its full strength even after many months of storage in a fairly moist atmosphere. However, when water is added to the mixture the two electrolytes, namely barium chloride and aluminum sulphate, interact to produce aluminum chloride which compound then hydrolyzes and liberates hydrochloric acid, the latter in turn effecting solution of the cupric carbonate. In other words, the above combination of ingredients, upon the addition of water, produces the equivalent of a cupric chloride solution through the preliminary interaction of substances which, in the dry mixture, are very stable. Among the substitutes for barium chloride in the foregoing mixture may be mentioned the following: chlorides, sulphates and nitrates of ammonium and the alkali and alkaline earth metals. Among the substitutes for aluminum sulphate may be mentioned the following: the sulphates and other acid-forming compounds of magnesium, manganese and zinc. It may be added that in lieu of barium chloride and aluminum sulphate in the foregoing mixture, there may be substituted practically any substance, or combination of substances, which is stable in the dry state and which, upon the addition of water, will produce a solution which is acid in reaction. For example, oxalic acid and similar acids such as tartaric, boric, and silicic acid, may be used in lieu of the barium chloride-aluminum sulphate combination for some purposes.

Obviously, in the compositions disclosed herein, if the base metal is present in a quantity which is less than chemically equivalent to the quantity of the replaceable substance present, there will be an excess of said replaceable substance which will not contribute to the generation of heat by the composition, and the base metal may advantageously be present in relation to the replaceable substance in proportion at least slightly greater than a chemically equivalent quantity. It should also be noted, that as is well known, in computing chemically equivalent quantities the valences of the metals involved must be considered.

In the composition hereinbefore set forth by way of example, the amount of aluminum is given as 15 grams and the amount of cupric carbonate at 15 grams. To express these quantities in terms of mol. proportions, it should be noted that the commercial forms of cupric carbonate are azurite, having a molecular weight of 345, and malachite, having a molecular weight of 221. Inasmuch as the molecular weight of aluminum is 27, the proportions are, for azurite, 15/345:15/27, or approximately 13 to 1, and for malachite, 15/221: 15/27, or approximately 8 to 1.

I have found that the proportion of cupric carbonate, or equivalent replaceable electrolyte, required in the composition may be reduced by including therein a water-soluble electrolyte such as sodium chloride. For example, I have found that by adding six-tenths of a gram of sodium chloride to the aluminum, barium-chloride, aluminum-sulphate, cupric-carbonate mixture hereinbefore described, and by slightly increasing the amounts of barium chloride and aluminum sulphate, it is only necessary to use about one-tenth of the amount of cupric carbonate to maintain similar heating capacity. The mol. ratio of metal to cupric carbonate would then be, of course, approximately 130 to 1, in the case of azurite, or 80 to 1, in the case of malachite. This is an important factor from the standpoint of cost, since the replaceable electrolyte is more costly than the other electrolytes which are used.

In such a mixture the sodium chloride appears to act as a catalyst to effect conversion of aluminum to aluminum hydroxide, which reaction is highly exothermic. Practically any water-soluble electrolyte the metallic ion of which is non-replaceable by the base metal, tends to accelerate this reaction to some extent. I prefer, however, to use the halogen salts of the alkali and alkaline earth metals.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, but the appended claims should be construed as broadly as permissible in view of the prior art.

What I regard as new and desire to secure by Letters Patent is:

1. A composition for producing heat by chemical action, comprising a finely divided mixture of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, and a substance capable of supplying a metallic ion upon addition of an ionizing medium in the liquid state, the metallic ion supplied by said substance being electrolytically replaceable by said metal, said metal being present in relation to said substance in proportion greater than chemically equivalent quantities and not more than approximately 130 mols of metal to 1 mol. of said substance.

2. A combination for producing heat by chemical action, comprising a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, and a substance capable of supplying a metallic ion upon addition of water, the metallic ion supplied by said substance being electrolytically replaceable by said metal, said metal being present in relation to said substance in proportion greater than chemically equivalent quantities and not more than approximately 130 mols of the metal to 1 mol. of said substance.

3. A combination for producing heat by chemical action, comprising a base metal selected from the group consisting of magnesium, aluminum, manganese and zinc, and a substance capable of supplying a metallic ion upon addition of an aqueous medium, the metallic ion supplied by said substance being electrolytically replaceable by said base metal, said base metal being capable of generating heat by formation of metallic hydroxide in the presence of said aqueous medium, said metal being present in relation to said substance in proportion greater than chemically equivalent quantities and not more than approximately 130 mols of the metal to 1 mol. of said substance.

4. A composition for producing heat by chemical action upon addition of water, comprising a finely divided mixture of aluminum, and a replaceable substance ionizable in water and supplying a metallic ion which is electrolytically replaceable by aluminum, said aluminum being present in relation to said replaceable substance in proportion greater than chemically equivalent quantities and not more than approximately 130 mols of aluminum to 1 mol. of said substance.

5. A composition for producing heat by chemical action comprising a finely divided mixture of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, and a substance selected from the group consisting of copper and those compounds of copper which are ionizable in an aqueous ionizing medium, the metal being present in relation to said substance in proportion greater than chemically equivalent quantities and not more than approximately 130 mols of the metal to 1 mol of the said substance.

6. A composition for producing heat by chemical action comprising a finely divided mixture of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, and a substance selected from the group consisting of lead and those compounds of lead which are ionizable in an aqueous ionizing medium, the metal being present in relation to said substance in proportion greater than chemically equivalent quantities and not more than approximately 130 mols of the metal to 1 mol. of the said substance.

7. A composition for producing heat by chemical action upon the addition of water, comprising a finely divided mixture of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, a substance selected from the group consisting of those metals and derivatives thereof which are electrolytically replaceable by said metal, said substance being comparatively insoluble in water and non-reactive when mixed with said metal in the dry state, a water soluble electrolyte, and a second electrolyte which will react in a water solution of said first-mentioned electrolyte to produce an acid condition therein capable of effecting solution of said replaceable substance.

8. A composition for producing heat by chemical action upon the addition of water, comprising a finely divided mixture of aluminum, a substance selected from the group consisting of copper and those compounds of copper which are non-reactive when mixed with aluminum in the dry state and which are comparatively insoluble in water, a water soluble electrolyte and a second electrolyte which will react in a water solution of said first-mentioned electrolyte to produce an acid condition therein capable of effecting solution of said substance.

9. A composition for producing heat by chemical action upon the addition of water comprising a finely divided mixture of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, a substance selected from the group consisting of copper and those compounds of copper which are non-reactive when mixed with said metal in the dry state and which are comparatively insoluble in water, a water soluble electrolyte of the class which is stable when mixed with said metal in the dry state, and a second electrolyte of the class which is stable when mixed with said metal in the dry state but which will react in a water solution of said first-mentioned electrolyte to produce an acid condition therein capable of effecting solution of said substance.

10. A composition for producing heat by chemical action upon addition of water comprising a finely divided mixture of aluminum, cupric carbonate, a water soluble electrolyte of the class which is stable when mixed with aluminum in the dry state, and a second electrolyte of the class which is stable when mixed with aluminum in the dry state but which will react in a water solution of said first-mentioned electrolyte to produce an acid condition therein capable of effecting solution of the cupric carbonate.

11. A composition for producing heat by chemical action upon addition of water comprising a finely divided mixture of a metal selected from

the group consisting of the stable metals positioned above iron in the electromotive series of metals, barium chloride, aluminum sulphate, and an electrolyte comprising a salt of a metal which is electrolytically replaceable by said first-mentioned metal and which is non-reactive when mixed with the latter in the dry state, said salt being comparatively insoluble in water but comparatively soluble in a solution containing aluminum chloride formed as a product of the interaction of barium chloride and aluminum sulphate.

12. A composition for producing heat by chemical action upon addition of water comprising a finely divided mixture of aluminum, barium chloride, aluminum sulphate and cupric carbonate.

13. The composition for producing heat by chemical action upon addition of water comprising the combination of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, a substance selected from the group consisting of those metals and derivatives thereof which are electrolytically replaceable by said first-mentioned metal, said substance being comparatively insoluble in water and non-reactive when mixed with said metal in the dry state, a water soluble electrolyte of the class which is stable when mixed with said metal in the dry state and which in water solution will produce an acid condition capable of effecting solution of said replaceable substance and a catalyst comprising a water soluble electrolyte, the metallic ion of which is non-replaceable by said first-mentioned metal, for accelerating the conversion of said first-mentioned metal to metallic hydroxide.

14. A composition for producing heat by chemical action upon addition of water comprising a finely divided mixture of aluminum, a substance selected from the group consisting of those metals and derivatives thereof which are electrolytically replaceable by aluminum, said substance being comparatively insoluble in water and non-reactive when mixed with aluminum in the dry state, a water soluble electrolyte of the class which is stable when mixed with aluminum in the dry state, and which in water solution will produce an acid condition capable of effecting solution of said replaceable substance, and a catalyst comprising a water soluble electrolyte, the metallic ion of which is non-replaceable by aluminum, for accelerating the conversion of aluminum to aluminum hydroxide.

15. A composition for producing heat by chemical action, upon addition of water, comprising a finely divided mixture of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, a replaceable substance ionizable in water and supplying a metallic ion which is electrolytically replaceable by said metal, said metal and replaceable substance being present in the proportion of not more than 130 mols of the metal to 1 mol. of said substance, and a catalyst comprising a water soluble electrolyte, the metallic ion of which is non-replaceable by said first-mentioned metal, for accelerating the conversion of said metal to metallic hydroxide.

16. A composition for producing heat by chemical action upon addition of water comprising a finely divided mixture of aluminum, cupric carbonate, barium chloride, aluminum sulphate, and sodium chloride.

17. A combination for producing heat by chemical action upon the addition of water comprising a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, a substance selected from the group consisting of those metals and derivatives thereof which are electrolytically replaceable by said metal, said substance being comparatively insoluble in water and non-reactive when mixed with said metal in the dry state, a water soluble electrolyte of the class which is stable when mixed with said metal in the dry state, and a second electrolyte of the class which is stable when mixed with said metal in the dry state but which will react in a water solution of said first-mentioned electrolyte to produce an acid condition therein capable of effecting solution of said replaceable substance.

18. A composition for producing heat by chemical action comprising a finely divided mixture of a metal selected from the group consisting of the stable metals positioned above iron in the electromotive series of metals, a substance selected from the group consisting of those metals and derivatives thereof which are electrolytically replaceable by said first-mentioned metal, said substance being comparatively insoluble in water and non-reactive when mixed with said metal in the dry state, and an electrolyte which will, upon addition of water to the mixture, produce an acid solution capable of effecting solution of said replaceable substance, said metal being present in relation to said replaceable substance in proportion greater than chemically equivalent quantities and not more than approximately 130 mols. of the metal to 1 mol. of said substance.

RAYMOND E. REED.