Patented Oct. 23, 1934 1,978,388

UNITED STATES PATENT OFFICE

1,978,388

HEAT PRODUCING COMPOSITION AND METHOD OF CHEMICALLY GENERATING HEAT

Raymond E. Reed, Chicago, Ill., assignor to The Kendall Company, Chicago, Ill., a corporation of Massachusetts

No Drawing. Application November 7, 1932, Serial No. 641,616

10 Claims. (Cl. 44—3)

This invention relates to a composition and a method for generating heat by chemical reactions, particularly by chemical action of the composition with water.

The principal objects of the invention are to provide a composition of the type referred to which has greater heat generating capacity than has heretofore been obtainable with the compositions in use, and also to provide a composition which will remain stable over long periods of time.

The chemical heat producing compositions which have been used up to the present time usually comprise a mixture of a metal and one or more electrolytes, the metal commonly used being iron, and the electrolyte usually comprising some type of salt, the metallic ion of which is electrolytically replaceable by iron. In some cases the mixtures used also include an oxidizing agent such as manganese dioxide, or the like. These types of compositions evolve heat in the presence of moisture by reason of the replacement reaction which takes place between the iron and the metallic ion of the electrolyte. This replacement reaction is highly exothermic. For example, in the case of a composition comprising iron and cupric chloride, 290 calories of heat are liberated for every gram of ferrous chloride which is produced by replacement of the copper by iron.

I have found that the addition to a heating mixture or composition of the type above referred to, of a second metal, which is above the base metal in the electromotive series of metals, will result in the production of greater quantities of heat than has heretofore been possible. The presence of this second metal in the mixture not only results in greater heat generation, but also provides a number of additional advantages which make for a more practicable commercial composition. Among these advantages, which will be hereinafter more fully explained, may be mentioned the following: The proportion of replaceable electrolyte in the mixture may be substantially reduced without apparent decrease in the amount of heat evolved, thereby effecting a considerable saving in the cost of the mixture; electrolytes having quite limited solubility in water may be used in lieu of very soluble electrolytes, thereby giving a more stable composition; non-replaceable electrolytes, such as salts of the alkali and alkaline earth metals may be used in lieu of the replaceable electrolytes now commonly used; the class of electrolytes available need not be confined to those which are replaceable by the base metal, thus giving a wider range of selection of electrolytes; and finally, the initial peak temperature may be controlled quite accurately by regulating the proportion of the second metal used in the mixture.

Iron is the metal which is commonly preferred for use as the base metal in these mixtures, principally because of its cheapness. Among the metals above iron in the electromotive series which are available for use as the second metal, I have found that aluminum is the most satisfactory. Aluminum has the advantage of being inexpensive and is quite favorably positioned in the electromotive series, in that it will replace practically all metals other than the alkali and alkaline earth metals. Therefore, in describing the various mixtures in which the presence of a second metal has been found beneficial, I shall refer to aluminum as the example of the second metal used. However, other metals such as zinc, manganese, and magnesium have also been found to be highly useful as second metals in the mixture, and in general any metal which is above iron, or whatever metal is used in lieu of iron, in the electromotive series is to be considered as available for use as the second metal in the mixture.

I shall first give an example of the manner in which the use of aluminum permits a reduction in the amount of electrolyte necessary to produce a given amount of heat. It was found that in a composition consisting of 600 grams of iron and 20 grams of cupric chloride, the amount of cupric chloride could be reduced to 6 grams by the addition of 1.5 grams of aluminum without causing any apparent decrease in the amount of heat evolved. In this mixture the cupric chloride is the most expensive ingredient, and the use of a comparatively small amount of aluminum thus effects a very substantial saving in cost without impairing the heat generating capacity.

Among the other electrolytes on the order of cupric chloride which are useful in mixtures of this kind, and which have been found to apparently act more effectively in the presence of aluminum, may be mentioned cupric sulphate, cupric acetate, cupric nitrate, cupric formate, lead nitrate, lead acetate, mercuric chloride, and mercuric acetate.

Before giving other examples of the advantages of the use of aluminum in conjunction with iron, it may be well to explain the probable action of aluminum which enables it to increase the heat generating capacity of the mixture. In the

ordinary cupric chloride-iron mixture a considerable portion of the heat generated is due to the exothermic replacement reaction wherein copper is electrolytically replaced by iron to convert the cupric chloride to ferrous chloride. After this initial replacement reaction has taken place, additional heat is evolved by reason of the hydrolysis of ferrous chloride. However, when aluminum is added to this cupric chloride-iron mixture, the copper, instead of being replaced by iron, is replaced by aluminum, resulting in the formation of aluminum chloride. The formation of aluminum chloride results in the evolution of about twice as much heat as is evolved in the formation of a corresponding amount of ferrous chloride. This is generally true of all metals above iron in the electromotive series, namely, that the heat of formation of compounds of the metal is greater the higher the position of the metal in the electromotive series. After the aluminum chloride is formed, there is a further evolution of heat by reason of hydrolysis wherein the aluminum chloride is converted to aluminum hydroxide, this action being similar to the hydrolysis of the ferrous chloride hereinbefore referred to in connection with the cupric chloride-iron mixture. Some aluminum hydroxide also appears to be formed directly from the metallic aluminum, which in the presence of water and aluminum chloride is converted to the hydroxide. In this latter reaction the aluminum chloride evidently acts as a catalytic agent to promote the formation of aluminum hydroxide.

I shall now give an example of the second outstanding advantage of the use of aluminum in the mixture. The cupric chloride-iron mixture, hereinbefore mentioned, is highly unstable in the dry state, due to the high solubility of cupric chloride. This results in rapid aging in the presence of atmospheric moisture. This is very undesirable because chemical heat pads containing these mixtures are frequently held in storage for a number of months. When aluminum is used in the mixture I have found that it is possible to substitute for the cupric chloride, or other very soluble electrolyte, an electrolyte which has very limited solubility in water, thereby markedly increasing the resistance of the mixture to deterioration by atmospheric moisture. A very satisfactory mixture of this type is the following:

600 grams iron,
10 grams lead chloride,
2 grams aluminum (powdered).

Lead chloride, in the above mixture, has very limited solubility in water. Nevertheless, when water is added to the above mixture a very rapid evolution of heat takes place and the mixture performs exceedingly well over an extended period of time. The availability of salts of limited solubility, such as lead chloride, is due to the fact that the initial replacement reaction, instead of being between iron and lead, is between aluminum and lead. The product of this replacement, namely, aluminum chloride, then hydrolyzes, as previously explained, which action results in the evolution of further quantities of heat. Other electrolytes of limited solubility which may be used in place of lead chloride in the above mixture are lead sulphate antimonious oxychloride, cuprous chloride, and mercurous chloride.

An example of the manner in which the presence of aluminum in the mixture enables the use of electrolytes comprising salts of the non-replaceable metals, is the following:

600 grams iron,
20 grams potassium chloride,
12 grams aluminum (powdered).

The above mixture evolves very substantial amounts of heat and the generation continues over a considerable period of time. In the absence of aluminum no appreciable evolution of heat whatever takes place. The source of heat in the above mixture is probably due to two reactions. In one of these the aluminum acts upon the potassium chloride, in the presence of water, to produce aluminum hydroxide. In the other reaction the iron first acts upon the potassium chloride to form ferrouse hydroxide, and the excess aluminum then replaces the ferrous ion to form aluminum hydroxide, which action is also highly exothermic. The substitutes available for potassium chloride in the above mixture comprise the salts of magnesium, the alkaline earth and akali metals, all of which are non-replaceable by aluminum.

In actual practice I have found the preferred mixture to comprise a combination of the use of both lead chloride and potassium chloride in conjunction with aluminum and iron. This mixture has the following proportions:

	Grams
Iron filings	600
Aluminum (powdered)	2
Lead chloride	10
Potassium chloride	5

The reactions of the foregoing mixture, in all probability, consist first in the conversion of lead chloride to aluminum chloride by the metallic aluminum and thereafter a reaction between the surplus metallic aluminum and the ferrous hydroxide, the latter being formed by the action of iron on the potassium chloride and also from the products of hydrolysis of aluminum chloride. The replacement reaction accounts for the initial heating and the sustained heat is due to the action of hydrolysis which progresses more slowly.

It will be noted from the preceding examples that the aluminum is present in the mixture in comparatively small quantities. In practice I have found that the second metal, such as aluminum, need not constitute more than from about $\frac{1}{10}$ percent to 5 percent of the mixture. When present in this proportion the aluminum, or its equivalent, will increase the efficiency of the replacement reaction sufficiently to produce the desired results.

My experiments have shown that the initial peak temperature is quite dependent upon the amount of aluminum present in the mixture. For example, in the last example given above, the initial peak temperature when two grams of aluminum are used is 160° F. When three grams of aluminum are used the initial peak temperature is 175° F. With but one gram of aluminum present the initial peak temperature falls to 145° F. These temperatures are the ones obtained when 100 mesh aluminum is used. If the degree of fineness of the aluminum is reduced, the initial peak temperature will also be somewhat reduced.

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 heat pad composition for producing a moderate and sustained heat by chemical action with water, comprising a mixture of iron in finely divided condition, an electrolyte, and a small quantity of a second metal selected from the group of metals appearing above iron and below the alkaline earth metals in the electromotive series of metals.

2. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron in finely divided condition, an electrolyte, and a small quantity of finely divided aluminum.

3. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron, a small quantity of a second metal selected from the group of metals appearing above iron and below the alkaline earth metals in the electromotive series of metals, and an electrolyte comprising a salt of a metal which is replaceable by said second metal.

4. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron, a small quantity of a second metal selected from the group of metals appearing above iron and below the alkaline earth metals in the electromotive series of metals, and an electrolyte comprising a salt of a metal which is replaceable by said second metal, said salt having very limited solubility in water.

5. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron in finely divided condition, a small quantity of finely divided aluminum, and an electrolyte comprising a salt of a halogen acid.

6. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron in finely divided condition, a small quantity of finely divided aluminum, and an electrolyte comprising a halogen salt of lead.

7. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron, a small quantity of a second metal selected from the group of metals appearing above iron and below the alkaline earth metals in the electromotive series of metals, and an electrolyte comprising a salt of copper.

8. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron, a small quantity of a second metal selected from the group of metals appearing above iron and below the alkaline earth metals in the electromotive series of metals, an electrolyte comprising a salt of a metal which is replaceable by said second metal, and a second electrolyte comprising a salt of a metal appearing above said second metal in the electromotive series.

9. A heat pad composition for producing a moderate and sustained heat by chemical action with water comprising a mixture of iron in finely divided condition, together with small quantities of finely divided aluminum, lead chloride, and potassium chloride.

10. The method of chemically producing a moderate and sustained heat which consists in mixing iron in finely divided condition and a small quantity of aluminum in finely divided condition with an electrolyte, and thereafter adding water to the mixture to set up a heating reaction.

RAYMOND E. REED.