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POWDERED MIXTURES FOR FLAMELESS HEATERS

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Annotation
The article gives a review of the literature on the main groups of powder mixtures for the exothermic reaction for flameless heaters. The use of powder mixtures of different compositions for creating safe and highly efficient heaters in the field of chemical heat sources is considered. Specific features of the properties of powder mixtures are indicated depending on the structural features of the composites
Keywords: flameless heaters, exothermic reaction, powder mixtures, heat transfer sources, self-heating.

Introduction

The history of many inventions in the field of chemical heat sources used to equip self-contained heating devices and vessels for flameless cooking or heating food goes far into the past. The need to provide soldiers with a device for heating individual military rations was recognized long before the development of the nameless Ration Heater (FTW). Prior analyses of heating systems showed that an optimal device for heating rations in isolated areas would be lightweight, safe and convenient to use, inexpensive, require little or no set up, heat food rapidly, allow heat-on-the-move capability and not produce a flame. A flameless heating device could be used at night without producing a visual signature and would not be affected by wind or inclement weather. Thus, the technology of manufacturing self-heating packaging has been known for over a hundred years. With a wide variety of their compositions, powder mixtures for flameless heaters have reached wide application. In one known type of flameless ration heater, an exothermic reaction is provided by calcium carbonate, sodium carbonate, calcium oxide and aluminum powder mixture can be employed. In another type of flameless ration heater, readily oxidized metals such as magnesium which is activated by adding water and is contained within a pouch [1,2].

Powder mixtures based on metals

Exothermic mixtures for flameless heaters began to be used in 1973. To carry out exothermic oxidation-reduction reactions were widely used the compositions between the metal from the group Fe, Mg, Al, Zn and oxides of metals of variable valences MnO_2, PbO_2, Ni_2O_3 [3], and also between magnesium and copper chloride [4].

The U.S. Army Natick Research, Development and Engineering Center (Natick) contracted Power Applications Inc., Dong Island to determine the feasibility of using their patented self-contained electrochemical heat source, Hot Sheet™, as a means of heating the Meal, Ready-to-Eatentree. Hot Sheet was a nontoxic, electrochemical heating element which consisted of a magnesium anode, a carbon electrode and an electrolyte salt. Patent claims suggested that it could be used to heat a pan of food by simply adding water to the Hot Sheet assembly. At the completion of this contract, it was determined that the Hot Sheet heating element geometry and configuration would have to be modified, optimized and integrated into a package to effectively heat the packaged entree [1].

Between 1983 and 1986 the inventors of the chemical heating pads obtained a patent on the construction of the flexible heating pad material for food heating and medical applications. Soon after the patent was filed, the principal inventor formed a corporation called «ZestoTherm» in Cincinnati, Ohio. ZestoTherm continued to modify the heating pad by adding sodium chloride directly to the pad matrix so that plain water could be used to activate it instead of salt water. This heating pad later became a commercially available food heater. The electrochemical heater pads are activated by the addition of water. After reacting with water, a nontoxic residue is produced which consists of a weak solution of magnesium hydroxide [$Mg(OH)_2$] in a saline solution. The reactions and reaction products between the magnesium anode and iron cathode are divided into three types [1]:

1. Electrochemical Reaction:
Air Cathode: $O_2 + 2H_2O + 4e \rightarrow 4\ OH^-$
Anode: $2Mg \rightarrow 2Mg^{+2} + 4e^-$
Net Electrochemical Reaction:
$2Mg + O_2 + 2H_2O \rightarrow 2Mg(OH)_2$

2. Corrosion Reaction:
$Mg + H_2O \rightarrow Mg(OH)_2$
$Mg^{2+} + 2Cl^- \rightarrow MgCl_2$

3. Hydrolysis Reaction:
$MgCl_2 + H_2O + OH^- \rightarrow Mg(OH)Cl\text{-}(H_2O) + Cl^-$

A magnesium-iron alloy of the "mechanical mixture" type and methods for their preparation are known [5]. The alloy is prepared in a ball mill from a mixture of sawdust magnesium and iron powder in an inert solvent. After evaporation of the solvent and separation of excess iron, the resulting residue is a magnesium alloy containing up to 10% by weight of iron. The alloy actively reacts with water in the presence of a small amount of sodium chloride with specific heat of reaction up to 5.6 kJ/g (Mg).

A disadvantage of such a mixture is the high rate of reaction with water, which causes its use in the device for producing hydrogen [6] and does not allow its efficient use in heat exchangers. Of interest are methods for the production of magnesium alloys [7] with iron, iron oxide, zinc, chromium, aluminum and manganese with a phase interface between magnesium and said metal. In one case, the alloys are produced by mechanical pressing of small metal particles into larger magnesium particles, in another case by the introduction of solid metal particles into molten magnesium and subsequent cooling, which ensures an even distribution of the catalyst in the magnesium volume. Both methods are aimed at the formation of micro electrochemical cells.

A device is known for obtaining a high temperature for heating a diver according to the patent [8], for which magnesium alloys formed mechanically in a ball mill from magnesium powders and metals, including copper, titanium, chromium, nickel, as well as powder carbon (graphite). The disadvantage is that, in order to prevent body burns, alloys with extremely low specific heat dissipation characteristics are proposed.

An exothermic composition for a flameless heater is known which contains magnesium alloy powder with iron, prepared in a ball mill, NaCl salt, surfactant and food acid anhydride or free food acid as a pH regulator. The acid can also be impregnated with a porous package in which the exothermic composition is located. The acid controls the pH environment between 4 and 7, so that the magnesium reaction with water does not flow too vigorously at low pH and too slowly at high pH. The disadvantage of this composition is the presence of surfactants, acid anhydrides or free acids, which reduces the content of the main component - the magnesium alloy, therefore, reduces the total heat release of the proposed composition. The closest technical solution is a powder mixture that reacts exothermically with water in a flameless heater (prototype) consisting of two nonwoven polyester sheets forming a plurality of pockets. A disadvantage is the presence of a large number of components of the exothermic mixture, in particular a deformer, an inert filler and an optional NaCl powder mixture. The inert filler is included in the mixture as a regulator of the rate of reaction of magnesium with water. As a consequence, the composition of the mixture is characterized by an insufficiently high content of the main component – a magnesium alloy, and this reduces the total heat release of the composition [9].

The electrochemical heater pads are activated by the addition of water. After reacting with water, a nontoxic residue is produced which consists of a weak solution of magnesium hydroxide [$Mg(OH)_2$] in a saline solution. According to the patent, the flameless heater using 4g of Mg·5 at % Fe is capable of increasing the temperature of 151g of food approximately 55 °C; with an initial temperature of 21 °C, and final temperature of 76 °C. Higher temperatures can be achieved by using heater pads with more supercorroding alloy. Some heat escapes the package in the form of steam and hydrogen gas. The hydrogen gas dissipates rapidly and does not present a hazard for individual package use. Attempts to ignite the hydrogen with an open flame and spark have failed to produce ignition. Heat from the heater pads is transferred to the food by conduction. The heat is produced by the reaction of magnesium metal and water to form hydrogen and magnesium hydroxide, as below [10]:

$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$ + heat [$\Delta H = -351$ kJ/(mol Mg)]

The article [11] presents a new flameless electromagnetic heater for the army for heating the diet in the field. It uses hysteresis and vortex thermal power in solid iron and thermal short-circuit power in short copper rods to heat the ration. The mathematical model of a flameless heater is shown on the basis of the inverse problem of increasing temperature and losses in electric machines. As a result of analysis of finite elements of the three-dimensional time step, the distribution of the magnetic field and the eddy current and the short-circuit current signal in the heater are given, and the thermal power of the heater with different rotational speeds is calculated. Finally, the experiment is presented and the temperature rise curves of the heater are drawn at different speeds. The research conducted in this article has built a basic platform for further studies of such heaters.

As mentioned above studies, magnesium-based compositions have several disadvantages. The property of magnesium is known to interact with water with the release of heat. The reaction takes place at a pH of the medium below 8.5. Increasing the pH leads to passivation of the surface, which interferes with the interaction, and magnesium ceases to displace hydrogen from the water. The practical use of this interaction is complicated by the fact that to regulate the reaction rate of magnesium with water, it is necessary to introduce additional compounds that affect the pH of the medium. Acid anhydrides and free acids can be used as process accelerators, and salts of strong bases and weak acids, for example bicarbonates, carbonates, phosphates and polyphosphates of alkali metals, calcium hydroxide, etc., may act as a slowing reaction. The disadvantage is the low specific heat of reaction, less than 5 kJ /g (magnesium), and the presence of additional compounds that, in a mixture with magnesium, are a ballast that reduces the content of the main fuel-releasing component. To increase the effect of heat release, alloys of magnesium with a metal catalyst are used, forming a micro-galvanic element with it. In the presence of an electrolyte, the reaction of magnesium with water is electrochemical. Also besides, the compositions are characterized by uneven heat release, intense only in the initial stage of oxidation-reduction reactions, which is an essential disadvantage for the process of heat exchange with a heated object. Another disadvantage is that the nature of oxidation-reduction reactions does not allow contact of the components of the mixture under storage conditions and predetermines a complex multi-compartment design of heaters, compresses and other products. To start the reaction, the components must be thoroughly mixed, which predetermines the inconvenience of their use [12].

Powder mixtures based on carbonates

Along with magnesium-containing composites, also studied compounds with alkali metal carbonates. The history of the use of alkali metal carbonates has also been investigated since the earliest times. Canned cans, in which the alkaline metal carbonates were the heating component, were made from the beginning of the 1900s and were intended primarily for use in mountain expeditions and exploration. For example,the American balloonist Alan Ramsey Howley, who in 1910 won with his partner in the balloon race for the Gordon Bennett Cup, said that he took with him three self-heating soup cans. Another American, archaeologist Hiram Bingham, in his book "Land of the Incas" mentioned how he ate self-heating canned food during his travels through South America from 1909 to 1915. However, despite this, "smart" packaging is not widely used. The fact is that all the self-heating canned food for the period of the war was reserved for the needs of the army and returned to the shelves only six years later. But even then they did not become a commodity of mass demand, mainly because of high prices. So self-heating technology for a long time remained on the "armament" of the military. A modern pioneer in the field of self-heating technology in the packaging is Matthew Searle, who currently heads the company Steam To Go, and in 2002 he was the director of development at Thermotic Developments, which developed the Hot when you want for Nescafe coffee. In the base of the standard 330ml cans for drinks, a thermoblock consisting of two compartments was placed: one contained water, and in the other - calcium oxide, better known as quicklime [13].

The authors of the work [14] have investigated and determined compositions based on alkaline-earths to carry out exothermic reactions. The present invention seeks to provide an improved flameless heater and an improved heater operable to provide a controlled exothermic reaction upon the addition of water with a reduction in the emission of emission of hydrogen. The present invention further seeks to provide, specifically, an improved heater operable to provide a controlled exothermic reaction upon the addition of water with substantially no emission of hydrogen gas.

In accordance with aspect of the invention, there is provided a heat source, suitable for a meal-ready-to-eat package, wherein the heat source comprises a substantially dry powdered composition of an alkaline earth peroxide, an alkali carbonate and a reducing agent; wherein, in the presence of water, the alkaline earth peroxide and the alkali carbonate produce peroxide in solution which reacts with the reducing agent to provide thermal energy as a reaction product. The alkaline earth peroxide is calcium peroxide. The calcium peroxide can be provided as a mixture with calcium hydroxide and an acid wherein the amount of acid is equivalent in molar terms to the calcium hydroxide. The acid can be selected from the group comprising oxalic acid, citric acid and malic acid. The acid can comprise succinic acid. The alkali carbonate can be sodium carbonate. The reducing agent is provided as a powdered composition. The reducing agent can comprises aluminum. The reducing agent can include aluminum compound with a chemical structure containing a sulphur atom. Alternatively, the reducing agent can comprise sodium metabisulphite or ascorbic acid. The reaction is as follows [14]:

$$3CaO_2+3Na_2CO_3+2Al=3CaCO_3+2NaAlO_2+4NaOH$$

The powdered solids mixture can be placed in small water-porous reaction bags conveniently made from non-woven or woven fibre, ideally fabricated so that it does not disintegrate in use. A reaction bag can typically be produced from a rectangular sheet of such fibrous material arranged in a two-ply fashion, say of 10 cm×20 cm, whereby to define a bag, conveniently divided into a number of smaller pockets, the two sides of the material being stitched, heat treated, glued or otherwise fastened together [14].

Similar works were investigated by the authors [15], where liquid and solid reactants are combined to produce heat. The reactants include quicklime (CaO), sodium hydroxide, cobalt, chromium, iron, iron hydroxide, magnesium, manganese, magnesium chloride, molybdenum, tin oxide (II), titanium, sodium, calcium hydroxide, sulfuric acid, nitric acid, and metallic sodium. The reactants generate an oxide reacting with oxygen at room temperature in the form of a metal or a metallic compound and have an exothermic characteristic.

In the study of powder mixtures of flameless heaters, special attention is given to containers that have special considerations in carrying out exothermic reactions. For example, the authors of the work investigated a device which has a disposable tray with an upper com parchment which contains a food product and a lower compartment which has two reagents which are separated from each other by one or more watertight partitions and also having one axis with radial blades to tear said watertight partitions and a control knob visible outside of the tray and, moreover, having at least one screen equipped with orifices which are crosswise to said axis. Outwardly they look like in Figure 1.

The authors of the patent [16] describe a heating device that generates heat by the oxidation of a metal, activated by the addition of water. The reactants are a mixture of aluminum, copper sulfate, potassium chlorate, and calcium sulfate, which generates flammable or corrosive gases. In the work [17] shows a self-heating device using a sealed container holding calcium oxide and water. The calcium oxide and water are kept separate by a sealed pouch. A tearing element affixed to the pouch opens the pouch and the container, allowing water to contact the calcium oxide, starting the exothermic reaction to heat the food. Author of patent [18] also describes a self-heating container using three heating packs based on a calcium oxide reaction. For reactions using sodium hydroxide with hydrochloric acid. Although this reaction produces more heat per weight of heater material than the hydration of calcium oxide discussed above, it requires the handling of a strong acid. The inventors also describe the oxidation of iron powder to produce heat, but this reaction is muted by water.

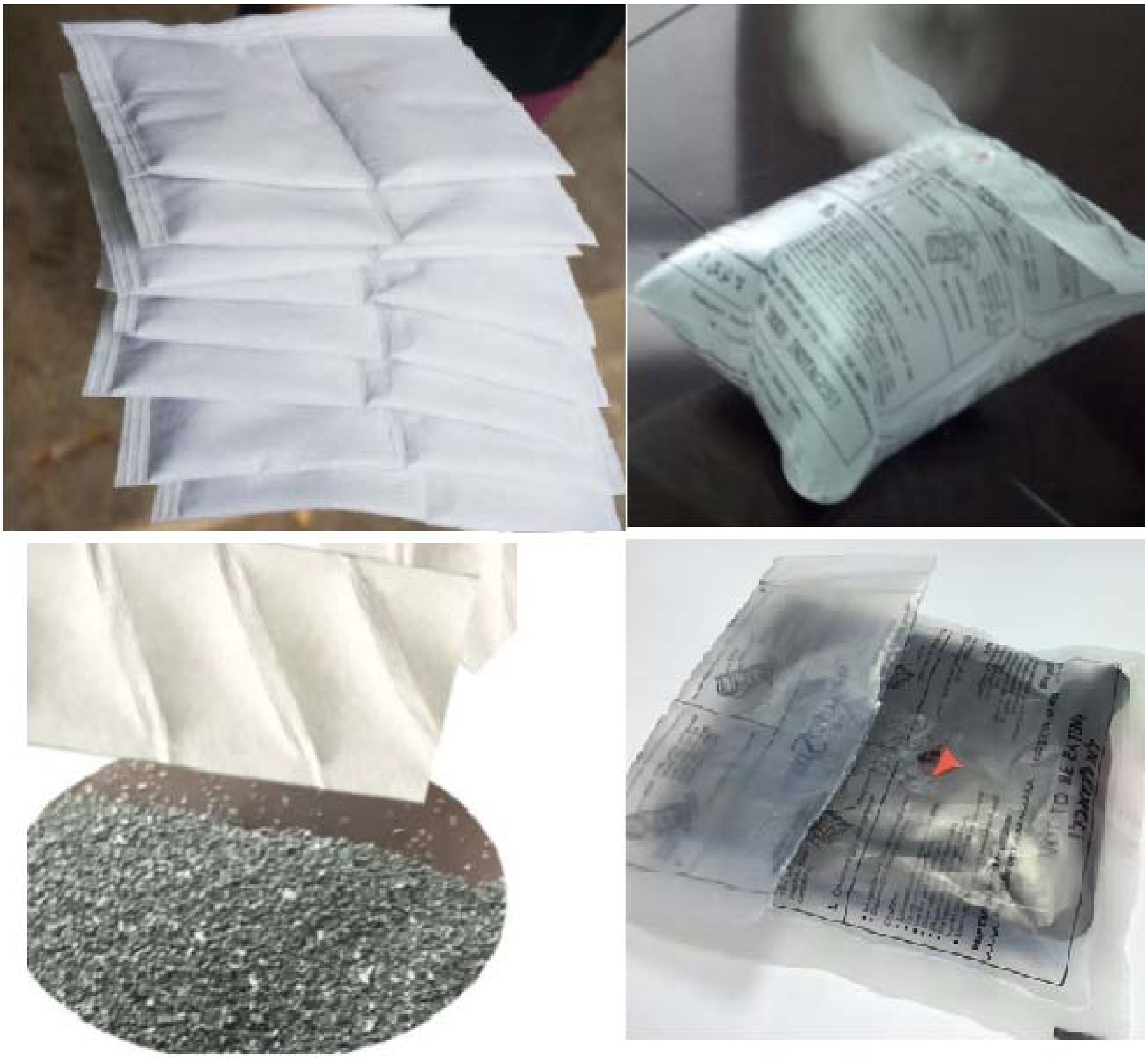

Fig. 1. Different types of flameless heaters [1, 10].

Conclusion

These analysis of various literary data shows how relevant the study and determination of the exothermic compositions for food heating. A literature search also shows that the technical task for devices and devices using heat produced by exothermic chemical reactions is to equip them with compounds characterized by:

- on the one hand, high heat generation, which is achieved by using in the exothermic mixture only those ingredients that release heat as a result of the reaction;
- on the other hand, by stable and continuous heat release in the range of specified temperatures, which is achieved by introducing additional ingredients regulating the reaction rate, as a rule, in the direction of its slowing down.

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ПОРОШКОВЫЕ СМЕСИ ДЛЯ БЕСПЛАМЕННЫХ НАГРЕВАТЕЛЕЙ

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Аннотация
В статье приводится обзор литературы по основным группам порошковых смесей для осуществления экзотермической реакции для беспламенных нагревателей. Рассматривается использование порошковых смесей разного состава для создания безопасных и высокоэффективных нагревателей в области химических источников тепла. Указаны особенности свойств порошковых смесей в зависимости от структурных особенностей композитов.

Ключевые слова: беспламенные нагреватели, экзотермическая реакция, порошковые смеси, источники теплопередачи, самонагреватели.

ЖАЛЫНСЫЗ ҚЫЗДЫРҒЫШТАРҒА АРНАЛҒАН ҰНТАҚТЫ ҚОСПАЛАР

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Аннотация
Мақалада экзотермиялық реакцияларды жүзеге асыратын, жалынсыз қыздырғыштарға арналған ұнтақты қоспалардың негізгі топтары бойынша әдебиеттік шолу келтірілген. Қауіпсіз, тиімділігі жоғары қыздырғыштарды алу мақсатындағы құрамы әртүрлі ұнтақ қоспаларды химиялық жылу көздері саласында пайдалану қарастырылған. Ұнтақты қоспа қасиеттерінің оны құрайтын композиттердің құрылымдық ерекшеліктеріне тәуелділігі көрсетілген.
Түйін сөздер:жалынсызқыздырғыштар, экзотермиялық реакция, ұнтақты қоспалар, жылу беру көздері, өздігінен қыздыру.