

July 1, 1969

M. MEKJEAN

3,453,416

HEAT STORAGE APPARATUS

Filed Nov. 20, 1967

Sheet 1 of 4

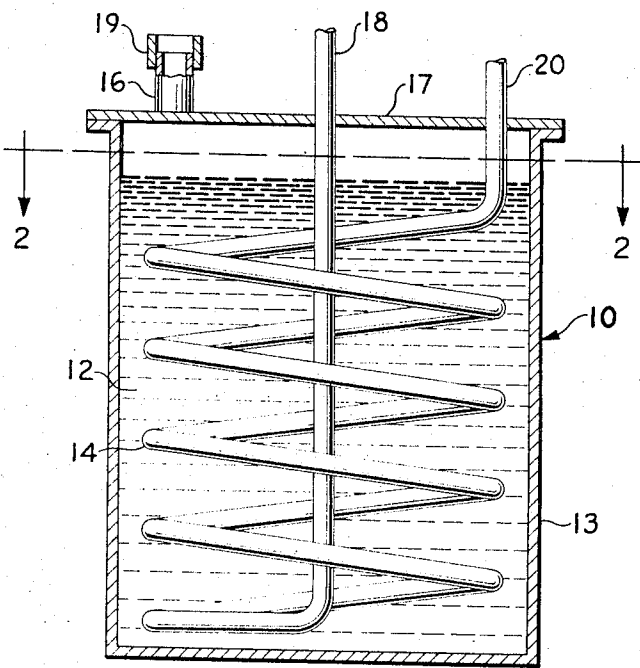


Fig. 1

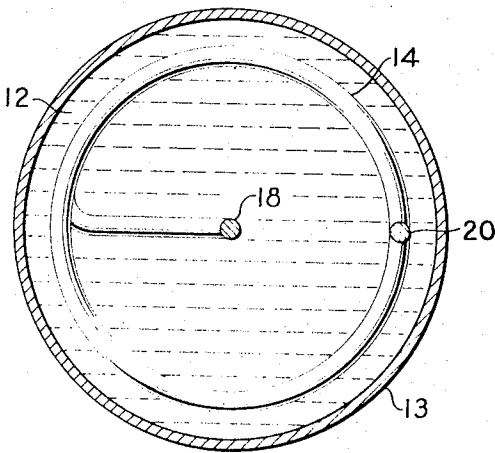


Fig. 2

July 1, 1969

M. MEKJEAN

3,453,416

HEAT STORAGE APPARATUS

Filed Nov. 20, 1967

Sheet 2 of 4

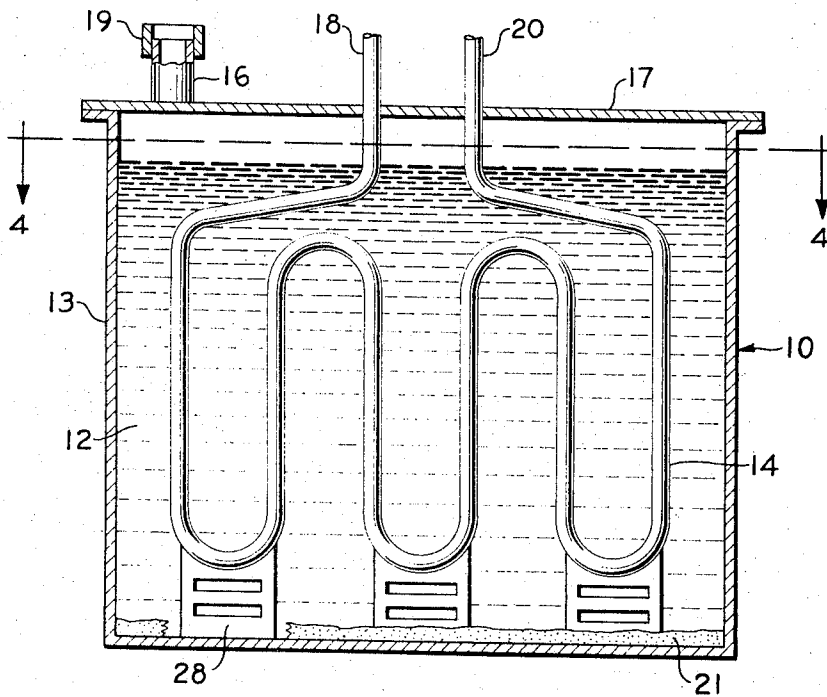


Fig. 3

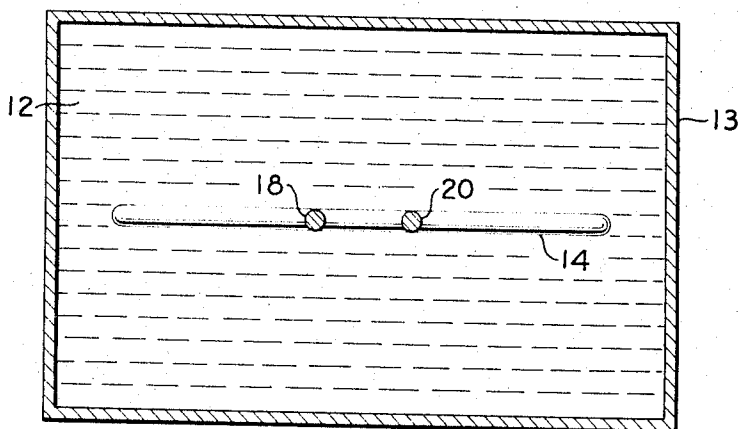


Fig. 4

July 1, 1969

M. MEKJEAN

3,453,416

HEAT STORAGE APPARATUS

Filed Nov. 20, 1967

Sheet 3 of 4

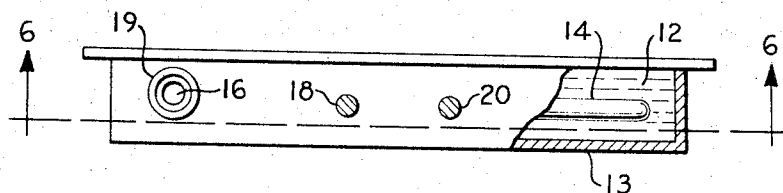


Fig. 5

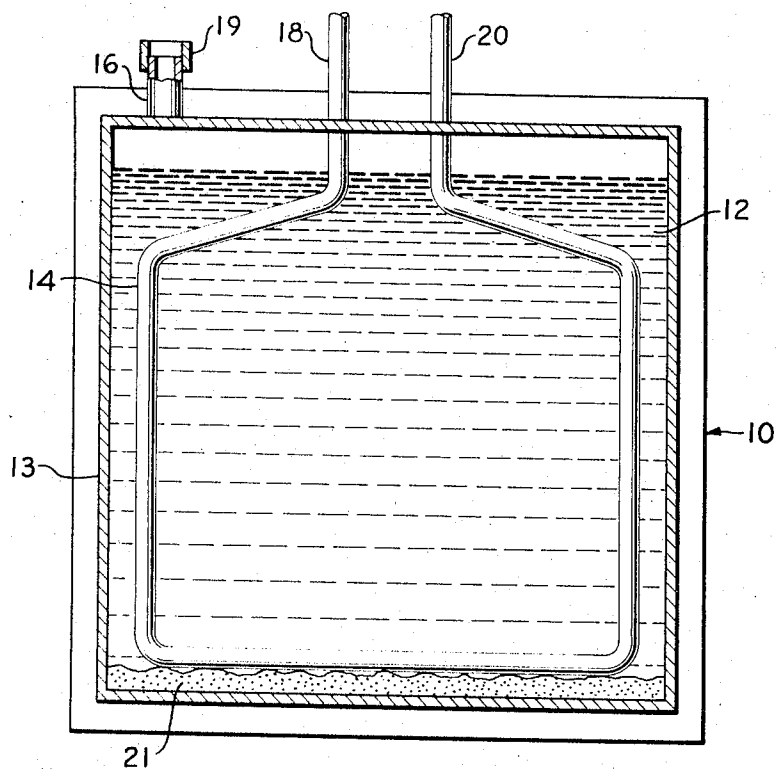


Fig. 6

July 1, 1969

M. MEKJEAN

3,453,416

HEAT STORAGE APPARATUS

Filed Nov. 20, 1967

Sheet 4 of 4

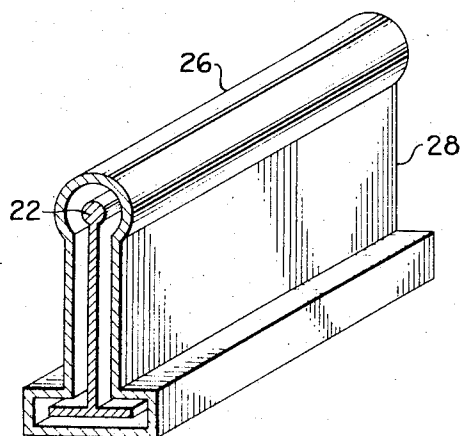


Fig. 7

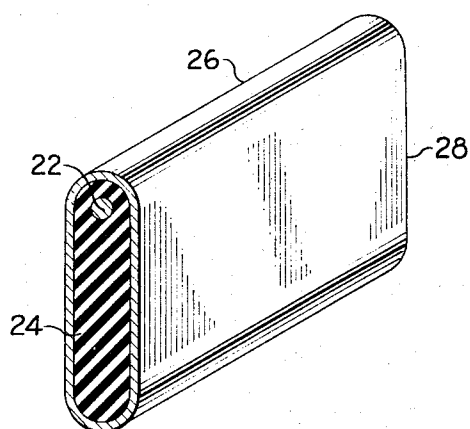


Fig. 8

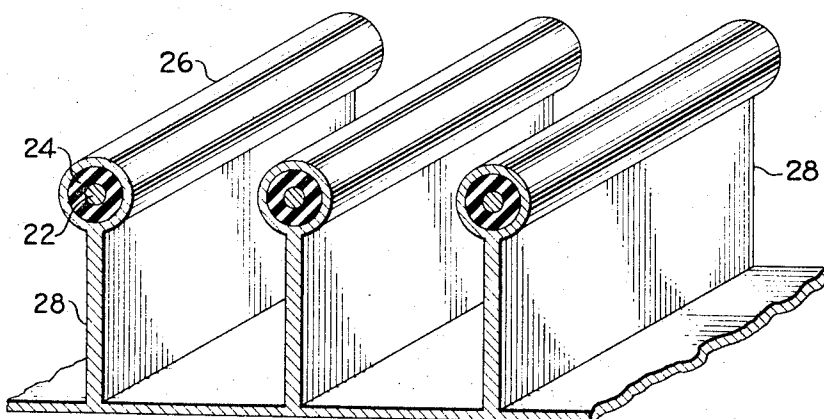


Fig. 9

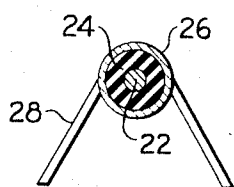


Fig. 10

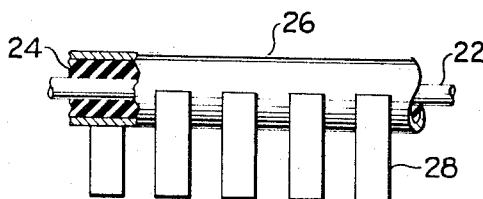


Fig. 11

United States Patent Office

3,453,416

Patented July 1, 1969

1

3,453,416

HEAT STORAGE APPARATUS

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Continuation-in-part of application Ser. No. 366,471,
May 11, 1964. This application Nov. 20, 1967, Ser.
No. 684,180

Int. Cl. H05b 3/06, 3/50
U.S. Cl. 219—530

9 Claims

ABSTRACT OF THE DISCLOSURE

A heat storage apparatus having a container, a substantially anhydrous alkali metal hydroxide heat storage medium in said container, and electrical resistance heaters positioned within said heat storage medium above the bottom of said container. The electrical resistance heaters are provided with a protective sheathing or cover of a material such as gold, zirconium, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and alloys thereof containing a substantial percentage of the recited metals. Likewise, an iron-aluminum alloy provides an operable sheathing material.

This application is a continuation-in-part of copending application Ser. No. 366,471 filed May 11, 1964, now U.S. Patent 3,356,834.

This invention relates to electric heaters. More particularly it relates to electric heaters utilized in heating a heat storage medium.

It has recently been discovered that a composition comprising a major proportion of an alkali metal hydroxide and a minor proportion of modifiers therefor can be utilized as the heat storage medium in a heat storage reservoir. An example of such a heat storage medium is a substantially anhydrous alkali metal hydroxide bath composition comprising a major proportion of sodium hydroxide, and minor proportions of sodium nitrate and sodium chromate. Although several means of heating this type of heat storage medium have been proposed and may be utilized, it has been found that the utilization of off-peak electric power, converted directly into heat is an extremely efficient and economical way. Immersion electrodes may be utilized to heat the storage medium described above. When such a system is utilized, however, special electrical equipment is often demanded. Also, when electrodes are utilized, one or both of them may have to be replaced from time to time. To avoid the replacement of electrodes and the utilization of special electrical equipment, electrical resistance heating elements have been suggested for use in heating heat storage medium in the reservoir. Generally, the heating elements known to the prior art are not satisfactory and may fail after a time under the conditions present in an alkali metal hydroxide bath, especially at the temperatures to which the bath is subjected, i.e., from about 140 to 1500° Fahrenheit.

In accordance with this invention it has been found that an improved heating element in a heat storage unit comprising an electrical resistor means covered with a protective sheathing material will minimize undesirable effects of the alkali hydroxide heat storage medium at temperatures from about 140 to 1500 degrees Fahrenheit. In addition, it has been surprisingly found that the heating elements of the invention, when employed under the conditions described, i.e., as heaters for the heat storage medium, are capable of operating at higher temperatures than when they are utilized as heaters outside the heat storage medium. Thus, they are able to add heat to the medium at a very satisfactory rate.

2

For example, a heating element within the scope of the invention, e.g., Nichrome resistor in an insulating material and sheathed with nickel, heated outside the heat storage medium, may only reach a maximum temperature of about 1000 degrees Fahrenheit before it begins to deteriorate. On heating this element in the heat storage medium disclosed supra, a temperature much higher than that obtainable in the atmosphere may be obtained, i.e., temperatures in the range of 1500 degrees Fahrenheit.

In pure sodium hydroxide, a temperature of about 2450 degrees Fahrenheit may be produced. Thus, about twice the amount of heat may be produced in the presence of a heat storage medium as may be produced in the atmosphere.

Other aspects and features of the invention will appear from the following description and the accompanying drawing in which:

FIG. 1 is a central vertical section of a heat storage reservoir;

FIG. 2 is a horizontal section along 2—2;

FIG. 3 is a central vertical section of a heat storage reservoir having a modified heating element therein;

FIG. 4 is a horizontal section along 4—4;

FIG. 5 is a partially broken away plan view of a modified heat storage reservoir;

FIG. 6 is a vertical section along 6—6;

FIGS. 7, 8 and 9 are perspective views which illustrate various modifications of the heating element;

FIG. 10 is a vertical sectional view of another heating element; and

FIG. 11 is a partially cutaway side elevation of part of the heating element of FIG. 10.

In the drawings heat storage reservoir 10 contains heat storage medium 12 and electric heating element 14. Filling orifices 16 allows the heat storage medium to be added to the reservoir and sealed therein by coupling means 19. This coupling means may be connected to a bellows means (not shown) which prevents atmospheric air from entering the reservoir 10. In another embodiment, the coupling means 19 may be connected to a breather system (not shown) which permits free access by oxygen to the heat storage material. The breather assembly may be equipped with a device to remove carbon dioxide and water from the air before entry into the heat storage reservoir 10. Likewise, the heat storage reservoir 10 may be equipped with internal or external conduit means through which a heat transfer fluid such as water may be heated for direct supply of steam to an apparatus or for heat transfer to an area or medium to which it is desired to supply heat. Reservoir 10 comprises walls 13 and cover 17 which are constructed of any suitable material such as American Iron and Steel Institute 1020 or lower steel classification or ductile iron. Terminals 18 and 20 of the heating element protrude from reservoir 10 through cover 17. These terminals are connected to a source of electricity (not shown). These areas where terminals 18 and 20 pass through cover 17 are sealed by known means to prevent air or other contaminants from entering reservoir 10. It is to be understood that in FIGURES 1-6, only diagrammatic illustrations of the various configurations of heat storage reservoirs 10 and of heating elements 14 are shown. Other configurations can be readily adapted to the invention, the only requirement being that the configuration of the heating element be such as to allow the medium to heat efficiently and prevent the distortion of the walls of the reservoir 10 due to the expansion of the medium when it is heated. In FIGURES 7, 8, 9 and 10 various modified heating elements are shown having resistor 22 encompassed by insulating material 24 sheath 26 and having extensions 28 or protrusions 28 of, or from, the sheathing 26.

In operation the heat storage medium 12 will be heated by the electric heating element 14 to a desired temperature up to about 1500 degrees Fahrenheit at which temperature the heating element is turned off. Air may be passed over the reservoir, or a liquid heat transfer medium such as water may be passed in heat transfer relationship with the heat storage medium, to extract heat and supply it to the desired area or medium to be heated.

The medium 12 cools at a slow rate and in most cases reheating of the medium is not required for about 24 hours.

During the operation of the reservoir over a long period of time heat distribution in the element may become uneven due to by-product 21 buildup at the base of the reservoir which may cover part of the heating element. This buildup reduces the efficiency of the element 14. FIGS. 7-11, illustrate various structures which can be utilized to cause the heat created in resistor 22 to be more efficiently and uniformly distributed throughout the cell, especially to the bottom thereof, and to prevent burn-outs of the heater. FIGURES 7-11 illustrate the adaption of types of extensions 28 attached to or made part of the heating element. FIGURE 7 shows an inverted T, FIG. 8 is an illustration of an oval, FIG. 9 shows a segmented extension and FIG. 10 shows an extension containing fins thereon.

These protrusions, or extension, affixed to, or part of the covering material may be placed at the bottom or over the entire surface of the element. It is to be understood that the metal and alloy covering materials set forth herein are corrosion resistant in the medium at temperatures from 140 to about 1500 degrees Fahrenheit. Some of these metals are oxidized to form films on their surface that are substantially insoluble in the medium. It is preferred that the oxide film be completely insoluble in the medium, but films having a solubility not in excess of 500 parts per million of medium at 480 degrees centigrade are satisfactory.

Further, the metals and alloys that are utilized as covering material should have a melting point above the highest temperature obtainable by the alkali metal hydroxide bath. The thickness of the resistors and the covering materials are standard in the art and can be determined by referring to handbooks available to the art, such as Chemical Engineers Handbook, third edition, published by McGraw-Hill Book Company, New York, page 417 (1950). Examples of suitable sheathing or covering materials are cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, their alloys containing a substantial percentage of the recited metals, and zirconium, gold, and ferro-aluminum alloys. Some of the examples of alloys are nickel steels including all percentages of Ni-Fe and up to 4 percent copper; cobalt alloys containing varying percentages of nickel, iron, silicon, chromium and others; nickel alloys containing varying percentages of cobalt, chromium and others; nickel alloys containing up to 80 percent copper; and nickel-molybdenum steel and the like. In all of the above alloys, the carbon content is below 0.3 percent by weight. Many of the preferred alloys are sold under trademarks such as Haynes Stellite Alloy No. 3, 6, 93 and 157 manufactured by Haynes Stellite Co., Hastelloy Alloy A, B, C, D, F and X manufactured by Haynes Stellite Co., Monel K, KR, R and S manufactured by International Nickel Co. and Spang Chalfant 1, 2 and 3 manufactured by National Supply Co. The compositions of the above alloys are further described in Metals Handbook, 1948 edition, published by "The American Society of Metals," Cleveland, Ohio, in Metals Handbook, eighth edition, volumes I and II published 1962-64 by "American Society for Metals," Metals Park, Novelty, Ohio, and Chemical Engineers Handbook, second edition published by McGraw-Hill Book Co., New York, 1941, pages 2108 through 2129.

These materials may be utilized to protect other good heat conductors which may form part of the protrusion

28, up to the melting point of the conductor; e.g., the disclosed coatings may be used to protect copper, silver or aluminum heat conductors.

The substantially anhydrous heat storage media of this invention comprise either a neutral or an oxidizing system containing a major proportion by weight of an alkali metal hydroxide and a minor proportion by weight of an additive which will not produce a reducing system in combination with the alkali metal hydroxide. A corrosion inhibitor may also be added to this composition in an amount of from 0.1 to about 25 percent of the composition by weight.

The corrosion inhibitors found to be acceptable in the heat storage system described in the preceding paragraph are selected from the group consisting of alkali metal and alkaline earth metal chromates, dichromates, phosphates, pyrophosphates, manganates, permanganates, tetraborates, borates, iron particles and mixtures thereof such as potassium dichromate, sodium permanganate and so forth. By utilizing these inhibitors, corrosion of metals in contact with the alkali metal hydroxide and inorganic non-reducing salt is substantially reduced to give a long life to the reservoir, the heating element and the medium.

Examples of alkali metal hydroxides that may be utilized in this invention are the hydroxides of potassium, sodium, lithium, rubidium, cesium, and mixtures thereof.

The additives which, when combined in a minor proportion with an alkali metal hydroxide, produce a neutral system are those compounds such as alkali metal and alkaline earth metal sulfates, phosphates, halides, carbonates, stannates, silicates, fluosilicates, fluoborates, tetraborates, metaborates, aluminates, bismuthates, borates, molybdates, tungstates, vanadates, and mixtures thereof, e.g., sodium carbonate, sodium sulfate, potassium sulfate, lithium carbonate, and the like. From 1 to about 45 percent by weight based on the alkali metal hydroxide containing system may consist of these neutral additives.

Examples of oxidizing additives which may be utilized in the heat storage media of the invention are alkali metal and alkaline earth metal, nitrates, nitriles, manganates, permanganates, chlorates, iodates, perchlorates, persulfates, chromates, dichromates, hypochlorites, oxides (e.g., perborates, MnO_2 , SnO , SnO_2 , TiO_2 , MoO_3 , CrO_3 , V_2O_5 , P_2O_5 , WO_3) and mixtures thereof. From 1 to about 45 percent by weight based on the alkali metal hydroxide containing system may consist of these oxidizing additives.

Examples of resistor element materials are Chromel A (78 percent nickel, 20 percent chromium, 2 percent manganese maximum and about 0.06 percent carbon) manufactured by Hoskins Manufacturing Company, Detroit, Mich.; Tophet A (80 percent nickel, 20 percent chromium) manufactured by Wilbur B. Driver Co., Newark, N.J.; Nichrome IV (80 percent nickel, 20 percent chromium) manufactured by Driver Harris Co., Harrison, N.J.; and so forth.

From the description it is seen that utilization of an insulation material between resistance heater element and the heater sheath is preferred, primarily to prevent short-circuiting and subsequent loss of the heater. However, in unusual designs, the insulation material may be dispensed with, as in using silicone-carbide sintered cylindrical rods which may be permitted to glow within the space provided in an open chamber or axially-parallel tube, which chamber protects them from direct contact with the heat storage medium. Of course, air, gas or other substance intermediate heater and tube may be considered to be the insulator.

Examples of insulation material that may be used between the resistance heater element and the sheathing material are magnesium oxide, zirconium oxide, zirconium silicate, titanium dioxide, beryllium oxide, calcium oxide. Such materials have specific heats in the range of 0.01 to

0.30 and are solids throughout the entire temperature range employed within the heat storage composition.

It is apparent that the specific illustrations shown above have been given by way of illustration and not by way of limitation, and that the structures above described are subject to wide variation and modification without departing from the scope or intent of the invention. For example, it is also possible to provide heating elements that will pass through the heat storage media. That is, one terminal will be on the upper side of the heat reservoir and the other terminal will be at the lower side of the heat storage reservoir. It is to be further understood that not just one heating element per reservoir needs to be utilized but that many such heating elements may be employed depending upon the size of the heat storage reservoir and the temperatures desired. Also, it is to be understood that the protective sheathing materials above described, which are in direct contact with the heat storage medium, may be utilized as cladding materials over more thermally conductive metals such as copper, silver or aluminum up to the melting point of these materials.

What is claimed is:

1. A heat storage apparatus, comprising:

- (a) a container;
- (b) a substantially anhydrous alkali metal hydroxide heat storage medium in said container; and
- (c) a heating element positioned within said heat storage medium above the bottom of said container, comprised of an electrical resistor covered with a material selected from the group consisting of zirconium, gold, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, alloys thereof, and ferro-aluminum alloys, said material being electrically insulated from said resistor by insulative means.

2. The apparatus of claim 1 in which the electrical resistor is sheathed with an alloy selected from the group consisting of:

- (a) iron in combination with aluminum;
- (b) nickel in combination with a member of the group consisting of iron, copper, cobalt, chromium, molybdenum, silicon and mixtures thereof; and
- (c) cobalt in combination with a member of the group consisting of nickel, iron, silicon, chromium, tungsten and mixtures thereof.

3. The heat storage apparatus of claim 1, wherein said covering material is selected from the group consisting of cobalt, cobalt alloys, nickel, and nickel alloys.

4. The heat storage apparatus of claim 3, wherein said alloys contain less than three percent carbon.

5. The apparatus of claim 1 in which said electrical resistor is covered with a sheathing of nickel.

6. The apparatus of claim 1 in which said electrical resistor is covered with a sheathing of a nickel-iron alloy containing from 1 to 50 percent iron.

7. The apparatus of claim 1 in which said electrical resistor is covered with a sheathing of a nickel-iron-copper alloy containing about 70 percent nickel, from 0.1 to 4 percent copper, and the remainder being iron.

8. The apparatus of claim 1 in which said electrical resistor is covered with sheathing of a nickel-copper-aluminum-silicon alloy containing about 90 percent nickel, 3 percent copper, 1.5 percent aluminum and 10 percent silicon.

9. The apparatus of claim 1 in which said electrical resistor is covered with a sheathing of a cobalt-chromium-tungsten alloy.

References Cited

UNITED STATES PATENTS

1,802,695	4/1931	Bennett	165—133
2,181,484	11/1939	Harris	338—236 X
2,469,801	5/1949	Vogel et al.	338—240 X
2,649,532	8/1953	Woodman	219—316
2,697,130	12/1954	Korbelak	13—23 X
2,911,513	11/1959	MacCracken	219—530 X
2,936,741	5/1960	Telkes	126—400 X
3,170,227	2/1965	Richmond et al.	165—142 X
3,213,263	10/1965	Steenbergen	219—205
3,356,834	12/1967	Mekjean	219—530

FOREIGN PATENTS

471,505	1937	Great Britain.
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VOLODYMYR Y. MAYEWSKY, *Primary Examiner*.

U.S. Cl. X.R.

126—400; 165—142; 219—316, 378, 439, 540, 553; 338—59, 243