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CHEMICAL PATIENT BLANKET PREHEATERS

Final Report

Contract No. DAAD05-74-C-0723

By
P. W. D. Mitchell
C. T. Davey

The Franklin Institute Research Laboratories
Benjamin Franklin Parkway
Philadelphia, PA 19103

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U. S. ARMY LAND WARFARE LABORATORY
Aberdeen Proving Ground, Marylan 21005

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Under Work Assignment No. 6 of Contract DAAD05-74-C-0723 by the Franklin Institute Research Laboratories (FIRL) for the U.S. Army Land Warfare Laboratory, two prototype systems were developed for preheating patient blankets. A number of methods of producing heat were investigated including two commercial products. Several of the methods investigated show promise with some developmental work. The prototypes developed are a two chemical system in which mixing of two normally separated chemical components are

mixed when heat is desired, and a pyrotechnic mix which is ignited by mechanical or electrical activation. Prototypes of these devices have been demonstrated to operate at low temperatures and fill the requirements for the preheater as defined by the sponsor.

FOREWORD

This report is submitted in compliance with contractual requirements as directed by the U.S. Army Land Warfare Laboratory, Aberdeen Proving Ground, Maryland under Contract No. DAAD05-74-C-0723. Mr. J. L. Baer, Chief Applied Chemistry Branch, served as Technical Supervisor for the work.

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AD-784195

1. INTRODUCTION

In the treatment of injured military or civilian personnel, particularly in the case of shock, keeping the victim warm is essential. Due to delays in rescue, victims sometimes are required to be kept warm for long periods of time. In cold regions, such as the Arctic where -60^{o} temperatures together with 30 knot winds are not uncommon, the problem of providing warmth to the victims becomes more difficult since, in this case, heat must be generated as well as retained.

Any device for providing this heat must do so at a moderate rate without the production of noxious gases and without the requirement of elaborate generators.

Heat generators considered for the task of preheating blankets or sleeping bags for injured personnel under Arctic conditions were investigated. The organo-metallic reactions were considered first as being a prime area for investigation. Literature survey and previous experience with triethyl aluminum (TEA) had disclosed hazards which made experimental progress very slow. In fact, this area of investigation was limited due to the need for working in an inert atmosphere and with precaution against contact of TEA with air. Under air contact, the material immediately reacts violently producing a pyrophoric reation. It was felt that materials like TEA would have been undesirable under field conditions where personnel may inadvertently come into contact with the material and air at the same time.

For the safety reasons cited above, efforts were concentrated on other means of producing heat, both short and longer term. Items investigated were as follows:

a. A solid fuel hand warmer
b. A flat battery pack
c. Several pyrotechnic materials

d. A chemical device with two isolated mixes.

From these investigations, the two part chemical mix and the pyrotechnic mixes emerged as potentially usable heat sources.

2. CONCLUSIONS

A. A pyrotechnic composition contained in sand and ignited electrically is capable of generating a sustained amount of heat suitable for the heated blanket requirements.

B. A two component chemical system when mixed will generate heat at a moderate rate without the production of noxious gases and can be activated at temperatures as low as -60°. One component consists of a mixture of calcium oxide and calcium hydroxide, the other is a mixture of clay and phosphoric acid. The relative proportions of the reactants in each component can be varied to give versatility in heating rates. This system has shown promise for the desired application.

C. Insufficient work has been done to evaluate the triethyl aluminum system suggested in the work order.

D. Several of the interim systems studied briefly during the course of this project phase are believed to be worth further effort in maintaining heat under Arctic conditions.

3. THEORETICAL

Many chemical reactions are exothermic. Common ones are those involving heats of oxidation, heats of solution, heats of hydration, heats of neutralization of acids by bases and heats of phase changes. Probably the most exothermic are oxidation reactions such as the burning of hydrocarbons, coal, etc. and to a lesser degree, the burning of oxygenated hydrocarbons such as, for example, alcohols, ketones, esters and carbohydrates. In particular, the "burning" of such metals as aluminum, magnesium, sodium and zinc and of their alkyl derivatives such as triethyl aluminum (TEA) and triisobutyl aluminum (TIBIA) is capable of producing exceptionally large amounts of heat. As contrasted with hydrocarbons, which require preheating for reaction with air to occur, the metal alkyls are mostly spontaneously inflammable in air. This reaction when controlled has been used in a prototype chemical heater (U.S. Patent No. 3,261,347, 19 July 1966) in which TEA was suitably contained in an oxygen-free atmosphere until air was allowed in through vents of controlled size. The highly corrosive and pyrophoric nature of the metal alkyls is a major drawback to their use in chemical heating systems.

Various chemical heating devices are commercially available and these involve either the addition of water, a drawback at sub zero temperatures, or the mixing of a two component system. An example of the latter is a product called "Medi Heat," manufactured by the Chemi-Temp Corp. of Lodi, N.J. This product cannot be activated at sub zero temperature because the liquid component freezes solid. Even when activated at 20°C, the heat output is rather poor. An ingenious electrical heater made by the Chem-E-Watt Corp. of Valley Stream, N.Y. also requires water for activation.

Any chemical heater for sub zero temperatures must therefore involve reactants which do not freeze at low temperatures or which dispense with the need for a liquid reactant such as the metal alkyls or the pyrotechnic materials.

Previous work at FIRL in a totally different area (dental cements) had shown the highly exothermic nature of the reaction of metal oxides, such as zinc oxide, with phosphoric acid. The products are solids and non-toxic, a useful property for the chemical blanket.

Part of our effort was, therefore, devoted to development of a heating system from the less expensive calcium oxide and/or calcium hydroxide with phosphoric acid.

4. EXPERIMENTAL

4.1 Sleeping Bag Evaluation

Of primary interest to any heating method to be used under Arctic conditions are the thermal characteristics of the bag itself. Without estimates of the energy and power required from the heating source, there would be little guidance for the heat source designer and developer. It is for this reason that evaluation instrumentation was developed. This equipment is shown schematically in Figure 1.

A commercial sleeping bag was purchased early in the program to be used until a GI bag could be obtained. This commercial bag weighed about 6 pounds. The bag was conditioned at very low temperatures using dry ice in an ice chest. A low temperature was maintained outside a section of the bag while a light bulb was activated on the inside with various power levels. Current through and voltage across the light bulb was measured and input power maintained. The temperature inside an air pocket in the bag in which the light bulb was located and the outside temperature were measured continuously. Outside temperature was maintained at about $-60^{o}C$, and the bag was allowed to stabilize at this outside temperature. The results of measurements at power input of 20 and 75 watts are shown in Figure 2.

The comfort zone of temperature was taken to be about $20^{o}C$, $(68^{o}F)$. Viewing Figure 2, it can be seen that a power of about 75 watts would cause a rise rate of about $3^{o}C$ per minute. To heat from $-30^{o}C$ to $+20^{o}C$ represents a $50^{o}C$ change which would require about 16 minutes. The heat energy to accomplish this is 72,000 joules (watts/seconds) or 17 Kg calories or 68.4 BTU.

The curve for 20 watt power input leveled off at about $15^{o}C$ where presumably the power supplied equaled the losses. This level of heat input evidently would not be adequate under these conditions.

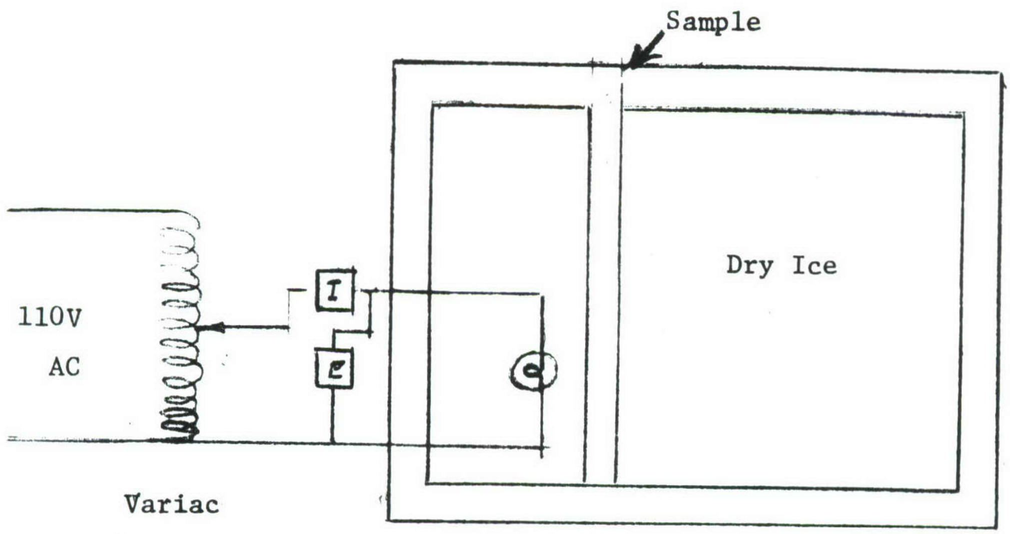

Figure 1. Equipment for Evaluation of Sleeping Bag Insulation

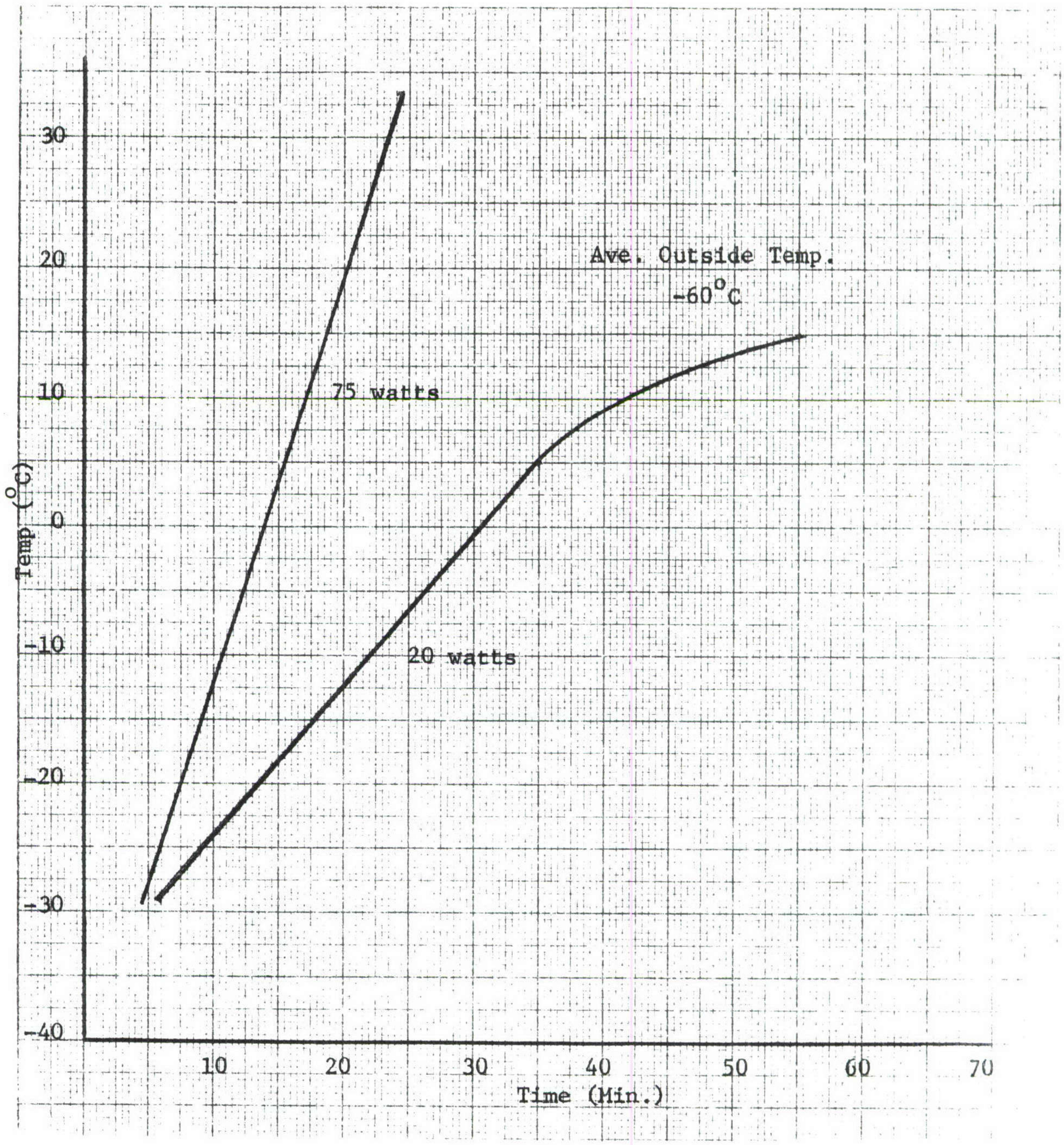

Figure 2. Thermal Characteristics of Commercial Sleeping Bag

4.2 Army Down-Filled Bag

An Army down-filled bag designed especially for Arctic use was obtained from Natick Laboratories. Measurements of the type run on the commercial bag were made to assess the energy requirements.

Dry ice was placed in direct contact with the surface of the bag. A 75 watt electric bulb (not lit) was placed inside a 12 ounce cylindrical tobacco can in the space normally occupied by the person. The bag rested on the surface of a laboratory work bench. A styrofoam chest was placed over the dry ice.

Temperature was measured at the interface of the dry ice and bag in the air space surrounding the tobacco can. Temperature decay is indicated in Figure 3. The equilibrium temperature appeared to be about $-20^{\circ}C$.

After equilibrium was reached, power was applied to the lamp (approximately 75 watts). In ten minutes the inside temperature had reached $+28^{\circ}C$. The area of concern here was on the order of one square foot. Energy input to achieve this temperature rise was 45,000 joules or 42.8 BTU.

The GI sleeping bag showed considerable improvement in insulation over the commercial bag. The 48° temperature rise in 10 minutes achieved with 75 watt input compares with about 31° temperature rise in 10 minutes in the commercial bag. In addition, during the tests of GI bag, the dry ice was in direct contact with the bag. In the test of the commercial bag, this was not the case. The heat required to bring the entire GI bag to temperature is about 43 BTU per square foot or roughly 1000 BTU total. To maintain the bag at a reasonable comfort level with outside temperatures very low (say $-60^{\circ}C$) and without a person in the bag, the power level required is estimated to be on the order of 10 watts per square foot of bag area or about 200 to 300 watts. A person inside the bag would, of course, generate some minimum level of heat during normal respiration process.

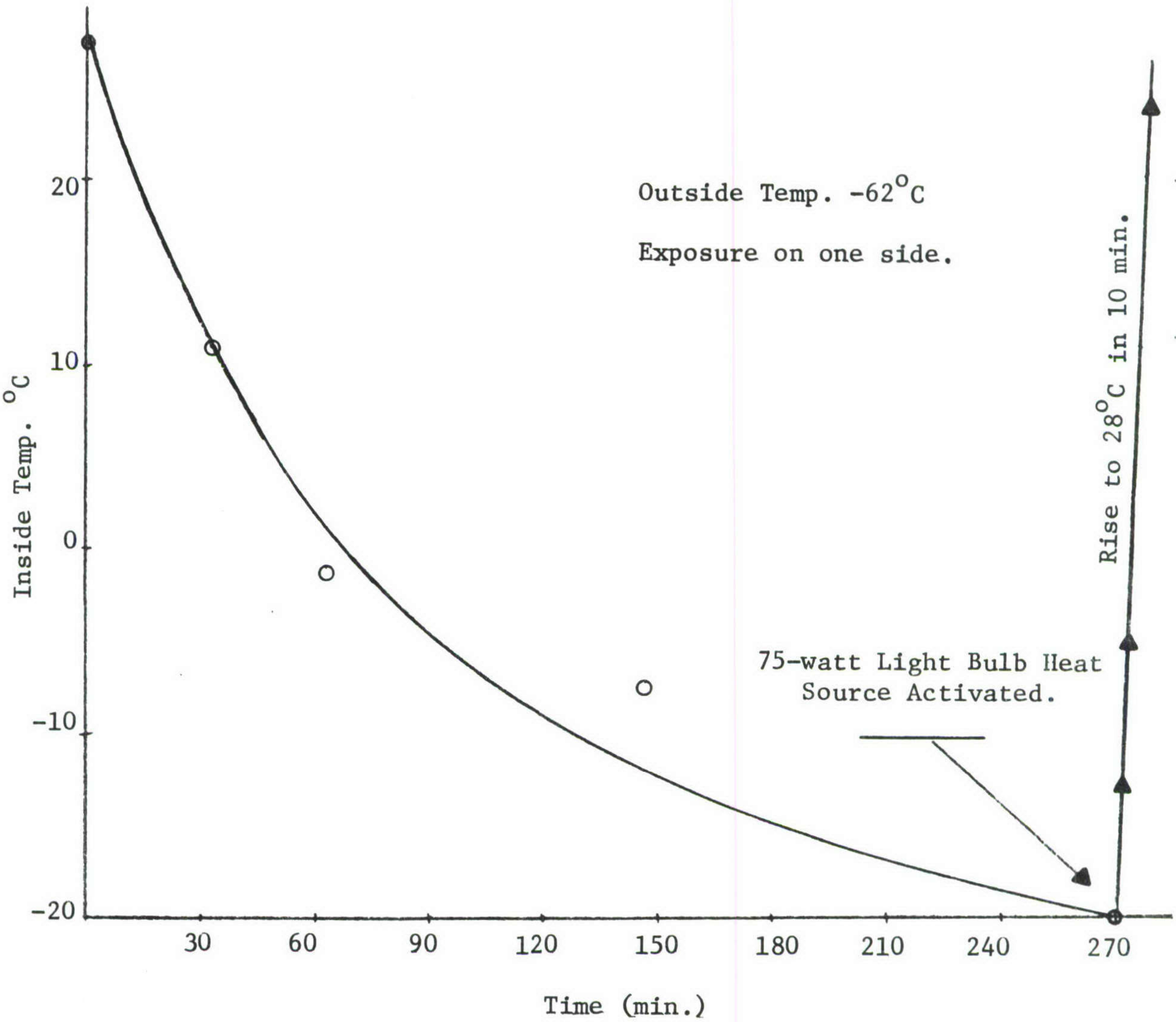

Figure 3. Temperature Decay and Rise Inside Army Sleeping Bag

4.3 Description of Heat Producers and Results

Solid Fuel Sticks: Pyrotechnic sources evaluated under this task included solid fuel sticks that are normally used in pocket hand warmers. These warmers and fuel sticks are available at a cost of less than five cents per stick from K-mart stores (Stock No. K501). They are lighted with a match, placed in a fiberglas lined metal container, and allowed to burn. It is claimed that they last up to 10 hours and produce comfort to the hands under cold weather conditions.

During laboratory evaluation drawbacks for this application were evident. Those tried went out often. Some burned for several hours--none for the 10 hours claimed, and generally they were considered to be unreliable. The need to light them with a match is not desirable. They are not recommended for consideration as a patient blanket preheater in their present state of development.

The long-term performance of these devices, if it could be confirmed, might make them desirable for providing sustained heat. Heat output, remote lighting, comparison with needed heat, improved reliability and better packaging are needed to examine these heat sources further. For the sustaining heat of 200 to 300 watts discussed above, several of these devices might efficiently provide the needed heat.

Pyrotechnic Delays: A commercial pyrotechnic delay cord is now available from Ensign Bickford Co. Timeline is a heat producer which burns as slowly as 10 seconds per inch and is claimed to operate from $-65^{\circ}F$ to $200^{\circ}F$. Samples were requested for evaluation and received in late May, too late to be evaluated experimentally for the purposes of this development. The pyrotechnic composition is encased in a metal tube and in the sample cursorily tested was shown to generate too much heat too rapidly to be in direct contact with the blanket or bag. Integration of the heat from this material might be a solution to the rapid blanket preheating needed.

Electrical Source: The Polaroid Camera battery, which is currently supplied with each Film Pack for the XL70 camera, produces 2 watt hours of electrical energy. This packet is of obvious advantage in heat production and control and may also be competitive with other systems in cost. Application would be similar to that of an electric blanket insert. While no detailed experimental work was carried out on this battery, it appears that it would be of interest in supplying sustaining heat to make up heat losses once the bag is brought up to temperature by chemical or pyrotechnic means.

Pyrotechnic Heat Pack: A pyrotechnic heat pack was developed. The heat producer consists of a powdered iron-oxidizer wafer which is ignited by a piece of heat paper and an electric match. This pyrotechnic train is housed in a metal film can. Two models of this unit were constructed and tested. The difference was in the manner in which the very high temperature of the pyrotechnic composition was moderated by integrating heat sinks. In one design steel blocks were used astride the heat disk. In the other, the film can was filled with white sand around the match, heat paper and heat disk.

When the match was ignited with a miniature electromagnetic generator (hell box), the case temperature reached about 200°F and remained at a high temperature for 10 to 20 minutes in a room-temperature atmosphere. Only a fine wisp of smoke was observed to emanate from the can.

The heat pack appears to be a feasible approach to the heating problem. The advantages of such a system are that it may be electrically or mechanically activated (with an electric match or a friction fuse starter). Some control may be applied to such a system by segmenting the total heat supply and igniting portions as required. There is only a need to supply an electrical pulse or to pull a friction igniter to begin heat production. A rigid or flexible package may be used with proper design. There is no need to make direct contact with the heat package in order to activate it.

Chemical Mix Bag: Commercial heat products were purchased for testing. As discussed in Section 3, the Medi Heat unit was evaluated and found to generate enough heat to appear warm to the touch at room temperature but not at sub-zero temperatures.

A second candidate, the Chem-E-watt unit, operated by an electro-chemical reaction and required water for activation. It also produced some heat at room temperature. Based upon the liquid components required in both of these commercial systems, neither is likely to be useful at Arctic temperatures.

A mix of FIRL origin, described in Section 4.4, was tested in the same manner and with the same equipment described earlier for testing the sleeping bags.

The chemical heating pad was placed inside the inner wall of the Army sleeping bag. The bag was placed flat on a styrofoam sheet. Dry ice was piled on the top surface of the bag and a styrofoam chest placed over the dry ice so that the edge of the chest gasketed against the bag. Thermometers were placed at the ice-to-bag and heat generator-to-bag interfaces. The system reached equilibrium in about four hours with the inside temperature at -30^{o}C and the dry ice interface at -65^{o}C.

The first and second trial with the chemical mixes failed. The first trial resulted in the bag tearing when activation was attempted. In the second trial, proper heat generation was not achieved when the constituents were found to be too hard to mix well. Adjustments in the mix were brought about by introducing ethanol to the mix. After "soaking" to reach the -30^{o}C inside temperature the mix was activated and achieved a temperature of 130^{o}F within a minute of activation. The following temperature-time history was recorded: 3 min, 120^{o}F; 10 min. 110^{o}F; 15 min. 85^{o}F; 23 min. 70^{o}F; 28 min. 60^{o}F; 1 hour and 23 min. 0^{o}F.

This mix is considered to have considerable promise as a suitable method of preheating a blanket or sleeping bag for personnel.

4.4 Chemical Investigations

A. Cupric Chloride - Aluminum System

A novel chemical heater has been described by W.R. Hydro and B. Wilten in Edgewood Arsenal Report No. EA-SP-1200-9 (June '72). This heater employs the reaction of aluminum powder and 30% cupric chloride solution whereby Al displaces Cu exothermically. Ethylene glycol can be added to the $CuCl_2$ solution to lower its freezing point.

This system was evaluated and found to react exothermically as described. Al foil can be used instead of powder to give a slower reaction. A solution of $CuCl_2.2H_2O$ (5g;0.0293 mole) in ethylene glycol (5 mls) was made up in a pyrex test tube and immersed in 200 mls of water contained in a Dewar flask and at 23^{o}C. Al foil (0.79g; 0.0293 mole) was added and a slow reaction started as shown by the bubbling of the contents. 0.2 mls. of water were added and a vigorous reaction took place; the bath water temperature rising to 28^{o}C in 3 minutes. Further addition of 0.2 mls. of water caused no additional heat to be generated. Total heat developed = 1000 calories for 0.79g of Al foil. Another piece of 0.79g Al foil added to the above solution followed by 1 ml of water again gave a vigorous reaction with bath temperature rising to 32^{o}C in 2 minutes.

Although the reaction gives off a substantial amount of heat, the copious evolution of gas, presumably hydrogen, makes it unsuitable for the desired application.

B. Phosphoric Acid - Lime Systems

Phosphoric acid (H_3PO_4) is readily available in various strengths and is one of the cheaper inorganic chemicals. It dissolves exothermically in water and reacts exothermically with CaO and $Ca(OH)_2$ to give insoluble salts (cements) containing calcium phosphate, $Ca_3(PO_4)_2$ and water.

$$3\ Ca(OH)_2 + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6H_2O$$

$$3\ Ca\ O + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3H_2O$$

Quick lime also reacts exothermically with water:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

These factors enable one to devise systems where the production of water can be eliminated altogether if desired by reducing the amount of $Ca(OH)_2$ relative to phosphoric acid and adding CaO to absorb the water (itself a heat producing reaction of no mean value -- 1.5 K cals/g). From consideration of the above equations, it will be seen that the reaction products are completely inocuous and even the reactants are not too bad. Phosphoric acid, for example, is an ingredient of coca cola.

In all the following experiments, 85% phosphoric acid was used.

1. 10 ml of acid contained in a small beaker was floated in 200 mls of water at 20°C contained in a Dewar flask. 5g of $Ca(OH)_2$ were stirred in. After 5 minutes, the temperature had risen to 32°C where it remained.

Hence, heat generated = 1400 calories

2. Reaction modification with clay. The above reaction is rather rapid so phosphoric acid was mixed with ball milled "Speedi-Dri" (an Attapulgite clay) to give a pliable mixture and this mixed in with calcium hydroxide in a polyethylene bag. This mixture warmed up at a moderate rate and stayed at a comfortably hot temperature for about 15 minutes. The experiment was repeated with satisfactory results using the following measured amounts.

Phosphoric acid	20 mls	mixed together
Clay	15g	

19g of the above mixture were squeezed into 5g of $Ca(OH)_2$ contained in the polyethylene bag.

3. Low Temperature Experiments. The above clay-acid mixture when cooled to -50°C became too hard to be worked. Phosphoric acid similarly cooled to -50°C was also found to become exceedingly viscous at -50°C but did not solidify. When mixed 50:50 by volume with ethanol, the viscosity was much less at -50°C.

50 mls of phosphoric acid were mixed with 50 mls of ethanol and 75g of clay stirred in.

a. 17G of this mixture were then mixed with 5g of $Ca(OH)_2$ at room temperature. Heat was developed at a moderate rate and after reaction a dry white powder (calcium phosphate) was obtained.

b. 22G of the mixture were cooled to $-50^{o}C$ in an acetone dry ice bath. At this temperature the mixture could still be squeezed into $Ca(OH)_2$ powder (5g) and the temperature of the reactants rose from $-50^{o}C$ to $65^{o}C$. This showed that the system will work at sub zero temperatures.

c. Experiment (b) was repeated at $-70^{o}C$ and still worked satisfactorily.

4. Room Temperature Prototype. For room temperature operation, a prototype heater was made using an empty "Medi-Heat" bag and clamps.

First, 30g of clay and 40 mls of phosphoric acid were mixed to a pliable clay in the lower part of the bag (some gas - H_2S is given off). Then the lower half of the bag was sealed off with a clamp and 15g of $Ca(OH)_2$ placed in the top half which was then closed with a clamp.

The middle clamp was removed and the contents mixed by kneading. A very good heat-generation followed and the bag did not blow up. In a later replication, however, a bag did burst indicating the need for careful control of the ingredients. Comfortable heat was still present in the bag after 30 minutes. At this time, the bag was opened and contained a free flowing white powder.

C. Experiments with CaO

30g of calcium oxide were added to 200 mls of water in a Dewar flask at $22^{o}C$. The final temperature of $52^{o}C$ was reached in 10 minutes which is equal to 6000 cals from 30g or 200 cals/g of CaO.

Unfortunately, although the reaction between CaO and water involves the cheapest of materials, it is a reaction difficult to control, and appears to be autocatalytic. Thus CaO mixed with excess 50% aqueous ethanol (low temperature solution) remains quiescent for 15 minutes and then rapidly warms up and boils. Also, CaO mixed with moist clay slowly warms and then gets out of control.

D. Experiment with CaO and $Ca(OH)_2$ and Phosphoric Acid

The useful composition of acid and $Ca(OH)_2$ already described above tends to generate a little steam and to remove this and also perhaps create more heat, CaO was mixed in.

The following equation indicates the best composition to eliminate water production:

$$3\ Ca(OH)_2 + 6\ CaO + 2\ H_3PO_4$$

$$\rightarrow\ Ca_3(PO)_2 + 6\ Ca(OH)_2.$$

Material	Moles	g	1/20 Scale
$Ca(OH)_2$	3	222	11g
CaO	6	336	16g
H_3PO_4	2	230.6 (of 85%) (140 mls)	7mls

11g of $Ca(OH)_2$ and 16g of CaO were mixed with 10 mls of 85% phosphoric acid rendered powdery by mixture with a suitable amount of clay. This warmed-up nicely and stayed warm for about 30 minutes. The upper temperature was lower than before, probably because too much clay was used.

30G of clay were mixed with 40 mls of phosphoric acid to give a pliable clay. This was then squeezed into a mixture of 10g of $Ca(OH)_2$ and 15g of CaO. This time plenty of heat was generated (more than the $Ca(OH)_2$ only composition). Although the bag temperature rose above $100^{o}C$, there was only a slight pressure development. This mixture is considered to be a good one and seems to work well in the "Medi-Heat" container. Tailoring of the mix during engineering development may nevertheless be necessary.

The compositions as shown above were used to make up demonstration heaters for activation at room temperature. For making a number of bags, it is easiest to mix up the two component mixtures in large amounts beforehand and then weigh them out for packaging. Typical recipes are given below:

Component A: Place 100g of $Ca(OH)_2$ and 150g of CaO in a can with reasonably airtight lid and roll until well mixed. It will keep indefinitely in the absence of moisture.

Component B: Mix 300g of ball milled "Speedi-Dri" with 400mls of 85% phosphoric acid. Total weight equals 965g. This can be accomplished manually or mechanically to achieve a dough-like consistency. It should be matured in an airtight jar with room for expansion as some swelling occurs for an hour or two due to gas evolution. There is also a small exothermic reaction.

For a 1 foot square bag, 75g of Component A and 290g of Component B should give good heating.

The bag material must be resistant to phosphoric acid and not become brittle at $-60^{\circ}C$. Neither material used so far meets these requirements but Mylar is considered to be a likely satisfactory candidate.

E. Method of Release of Heat Producing Components

So far, the general make-up of the "Medi-Heat" system has been copied. However, there are alternatives which might be much better. For example, the clay and acid, as one component, could be made up in sausage links, the cases being of an easily ruptured material and the links embedded in the CaO-$Ca(OH)_2$ mixture, all being contained in a bag. One could then generate heat when desired and at various rates by bursting the links at intervals.

F. Low Temperature Operation

This requires the addition of, for example, ethanol to the clay-acid component to prevent it becoming too stiff at low temperatures. The possible drawback of this is that it means the introduction of a solvent which can vaporize (and expand the bag) should the contents get above their boiling point. However, this drawback is not regarded as likely to produce any serious problems. Pre-heating bags could easily be specifically marked and color coded for temperate (intermediate climatic) use and for Arctic (extreme cold climatic) use.

G. Types of Clay

Ball milled Attapulgite clay is satisfactory but there are a number of modifications of this clay which might be better in terms of being more efficient moderators of the reaction and better adsorbents for a given weight. This would enable reductions in the heating mixture weight to be made. Incidentally, some clays are very much less satisfactory for the system. A sodium bentonite which was used (when the Speedi-Dri supply ran out) gave poor results. Samples of "Attagels" made by Engelhard Minerals are on hand now for further trials.

H. Materials Costs

All chemicals are in the "very cheap" category and are also readily commercially available. A relatively small mix suitable as a competitor for "Medi-Dri" would use 30g of clay, 40 mls of 85% phosphoric acid, 15g of calcium oxide, and 10g of calcium hydroxide at a total cost at current prices (June 1974) of no more than 4 cents.

I. Temperatures Generated

A bag made of the above mixture and activated at room temperature gave the following performance as measured by a thermometer over which the activated bag was folded:

Time (mins.)	Temperature (^{o}C)
1	105
10	105
15	102
25	80
35	65

5. RECOMMENDATIONS

A. The ability to generate heat inexpensively at a controlled level over an extended period of time in a small bag after a simple mixing process merits further refinement and development for extensive military and commercial applications.

B. In addition to the heat source for an Arctic patient blanket pre-heater, this system should be considered for pre-heating batteries for quick start under Arctic conditions, for heating frogmen or others obliged to work in very cold water, or for construction or repairmen operating under low temperature conditions, just to name a few.

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Commander U.S. Army Natick Laboratories ATTN: STSNL-CCP Dr. Malcolm C. Henry Natick, Massachusetts 01760	3
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