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TECHNICAL REPORT
74-44-GP

DESIGN AND OPTIMIZATION OF ELECTROCHEMICAL DEVICE FOR HEATING MILITARY RATIONS

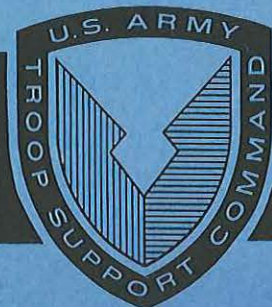
Power Applications, Inc.
Valley Stream, L. I., N. Y. 11580

Contract No. DAAG 17-73-C-0250

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31 December 1973

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760



General Equipment & Packaging Laboratory

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FORWORD

It has long been recognized that it is essential to develop a heating system for the individual ration which can be used by the soldier when on long-range patrol and in desolate or isolated areas where organizational kitchen support or food heating equipment is not available. In a system analysis of heating systems for individual rations in the field, heating with no flames offers some special attractions: no light involved (excellent for use at night), not affected by weather (wind and/or shower), and can be made compact.

The work covered in this report, performed by Power Applications, Inc., Long Island, New York, under Contract No. DAAG17-73-C-0250, represents an investigation of the design and optimization of an electrochemical device for heating military rations. The device is flat in shape and is activated by immersion in water. Two formulations are investigated: an air formulation which requires access to atmospheric oxygen for efficient operation and a non-air formulation which contains the oxidizing agent within the structure. Dr. F. P. Kober was the Principal Investigator, Messrs. S. L. Feld and K. Turk the collaborators in the developmental work for Power Applications, Inc.

The U.S. Army Natick Laboratories Project Officer was Dr. K. H. Hu and the Alternate Project Officer was Dr. L. A. McClaine. Both of them are from the Engineering Sciences Division, General Equipment & Packaging Laboratory.

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ABSTRACT

An electrochemical heating element which is activated by immersion in water was evaluated as a means for heating military field rations. Heating elements measuring 155 cm^2 (24 square inches) and having a dry weight of approximately 30 grams were the basis of the experimental program.

The basic heating element consisted of an anode-cathode-electrolyte/separator sandwich-type thin structure which was connected with an internal current carrying network. Two electrochemical heating element formulations were investigated in detail, i.e., an air formulation which required access to atmospheric oxygen for efficient operation, and a non-air formulation which contained the oxidizing agent within the structure and operated efficiently in any ambient.

Test data are presented which show that heating element performance was essentially independent of activation time (soak time in water), and the temperature of the heating element climbed above 100°C (212°F) in under three minutes, reaching a maximum skin temperature in the range 110°C (230°F) to 122°C (252°F). The heating elements produced 11.6 to 14.1 Kcal (46 to 56 Btu) in the first seven minutes of operation, with a total heat density of 0.68 to 0.70 Kcal per gram (76.4 to 84.8 Btu per ounce). Using the non-air formulation it was possible to heat flex-pack food rations above 77°C (170°F) in eight minutes and above 93.3°C (200°F) in 11 to 15 minutes.

Toxicological test data are given which show the air formulation heating element to be nontoxic and pose no hazards or safety concerns for the user. Based on electrochemical considerations, the non-air formulation can also be anticipated as being nontoxic and completely safe to use.

DESIGN AND OPTIMIZATION OF ELECTROCHEMICAL
DEVICE FOR HEATING MILITARY RATIONS

I INTRODUCTION

Power Applications, Inc. of Valley Stream, N.Y. has developed an electrochemical heat source which upon the addition of water will generate heat. This development is the subject of U.S. Patent No. 3,774,589 (Appendix A). Tests on this heat source, presently called HOT SHEET, conducted by the U.S. Army Natick Laboratories have demonstrated that after immersion in water for ten seconds the HOT SHEET skin temperature reached 190°F in three minutes, and raised the central temperature of the food in contact (5 oz. of ground beef with sauce in flex-pack) from 72°F to 160°F in fifteen minutes. The HOT SHEET formulation evaluated in these tests required exposure to ambient air for efficient reaction to occur.

These initial tests fully demonstrated the feasibility of using the HOT SHEET material as a means of heating military rations. However, it was concluded that improvements in the performance of the HOT SHEET elements were highly desirable. The following areas were pinpointed for improvements and optimization of performance:

1. The rate of release of stored energy should be increased.
2. For field applications, the peak skin temperature must be increased above the presently attainable 190°F.
3. The need for air exposure should be eliminated, or at least minimized, so that the sleeve on the flex-pack can be folded over to minimize heat loss.

In light of these specified areas of improvement the following program objectives have been defined:

1. The skin temperature of the HOT SHEET element shall reach 210°F in three minutes and maintain 190°F - 210°F for the following two minutes (measured at room temperature of 70°F). Also, the device should provide a heat density of at least 3 BTU per gram in total with at least 2 BTU per gram releasable within the five minute heating period.

2. If air is required for operation, the size of the samples for the heating element shall be 4" x 6" and each sample shall be covered by cardboard 4" x 6" with four holes, each with a $\frac{1}{2}$ " diameter opening to provide ample air during the operation.

The following two requirements are in addition to the above stated program objectives.

1. Twenty-five (25) samples representing the best improved electrochemical heating element developed under the program shall be submitted to the Government.
2. The material and supporting supplies being developed shall not possess biological or toxicological effects which could be hazardous from a health or safety standpoint to using personnel.

From the data presented it will become evident that all of these objectives have been met or exceeded. At the same time, the objective or requirement that the device should provide a total heat density of at least 3 BTU's/g with at least 2 BTU's/g releasable within the first five minutes of operation

was found to be only indirectly related to the food heating application. Although formulations were tested which met this requirement, they were not considered the "best formulation" for heating military field rations. In fact, it was necessary to devise new measurement techniques and selection criteria for "best formulation"; and for the purposes of this report an output of total 3 BTU's/g has not been employed as a criterion. All other objectives of the program were found to be salient.

II THEORY OF HOT SHEET OPERATION

Before considering the technical program per se, it is appropriate to discuss the general theory of operation of the electrochemical heat source. The HOT SHEET development is based on the direct conversion of chemical energy into thermal energy (heat) by means of an electrochemical reaction. That converting chemical to thermal energy electrochemically results in high energy conversion efficiency can be seen by examining the basic underlying thermodynamic principles. The total energy inherent in a chemical system or reaction is given by the change in free-energy (ΔF) which is defined by the following relationship:

$$\Delta F = \Delta H - T\Delta S \quad (1)$$

where ΔH is the heat of reaction (or enthalpy) and $T\Delta S$ is the so-called entropy function which defines that portion of the total energy which is unavailable for useful work, i.e., $T\Delta S$ is a direct measure of the inefficiency of a given system. Large entropy functions are associated with reactions involving changes of state, gas formation, large volume changes, etc. Thus, burning reactions, heats of solution, or the more conventional means for generating heat will be of necessity associated with large entropy functions; and the overall conversion efficiency will be well below 100%.

Electrochemical systems, on the other hand, exhibit small changes in entropy under normal operating conditions. The major contribution to the entropy function is non-ohmic polarization which can be greatly minimized through careful system design and choice of components. Rewriting Eq. (1) for an electrochemical system

$$\Delta H = nF (E_r - E_c) + T\Delta S \quad (2)$$

where F is the Faraday, E_r is the reversible system potential, and E_c the operating cell voltage. Thus, it can be seen that if $T\Delta S$ approaches zero, then the energy conversion efficiency of an electrochemical system can be made to approach 100%.

It is now instructive to consider Eq. (2) for the special case where $E_c = 0$, Eq. (2) would now take the form

$$\Delta H = nFE_r + T\Delta S \quad (3)$$

As stated above, $T\Delta S$ arises from non-ohmic polarization which usually manifests itself as internal cell heating. However, if the primary objective is to produce thermal energy (heat) to which $T\Delta S$ will directly contribute the theoretical efficiency for the electrochemical system to produce heat will be 100%. Likewise, the theoretical power efficiency will be 100%. This special case of $E_c = 0$ can be achieved in practice by rendering the internal cell resistance equal to zero. And it will be seen that the HOT SHEET development is in fact a device which allows E_c to approach zero and, therefore, convert chemical to thermal energy at efficiencies approaching 100%.

Perhaps the most common electrochemical energy conversion system or device is the battery which converts chemical energy directly into electrical energy. The basic characteristics of the battery are governed by Ohm's Law,

$$V = I R \quad (4)$$

where V is the voltage, I the current and R the electrical resistance. Furthermore, power is related to the voltage by the relationship,

$$\text{Power} = I V = I^2 R \quad (5)$$

In general, it is these two relationships, Eqs. (4) and (5), which govern the theoretical and practical performance that can be achieved with the HOT SHEET development.

Prior to the development of HOT SHEET, the electrical energy produced by a battery could be converted into heat by connecting the battery directly to an external resistance heating element. The rate at which heat is generated in this external load (resistance heating element), according to Eq. (5) is given by,

$$\text{Power} = dQ = \frac{E_C^2 R_L}{(R_C + R_L)^2} \quad (6)$$

where E_C is the cell or battery voltage, R_C the cell internal resistance and R_L the external load. It can be shown that transfer of power from the battery to the external load is a maximum when $R_L = R_C$, which gives,

$$\text{Power} = \frac{E_C^2}{4 R_C} \quad (7)$$

If, on the other hand, R_C is made to approach zero in the limit, which can be accomplished by providing an internal current carrying path (i.e., internal short circuiting), then all of the power is generated (and dissipated) within the electrochemical cell. Under these conditions it follows from Eq. (6) by means of l'Hopitals rule that the power generated is given by,

$$\text{Power} = \frac{E_C^2}{R_C} \quad (8)$$

Comparison of Eqs. (7) and (8) shows that there is a 25% theoretical limit on transferring power from a battery to an external ohmic resistive load. Conversely, by incorporating the ohmic load internally (internal shorting member) within the electrochemical power cell structure, power in the form of heat can now be generated at a theoretical efficiency of 100%, i.e., theoretically there is no limit to the energy conversion efficiency.

The HOT SHEET development is, in effect, the practical embodiment of Eqs. (7) and (8); consisting in general of a highly efficient electrochemical power cell whereby the elec-

trodes (anode and cathode structures) have been connected internally by means of an electronically conductive shorting member (internal ohmic load). It can be seen, therefore, that HOT SHEET is essentially a combined source of electrochemical power (more specifically current) and a self-contained resistance heating element; this unique combination providing a safe convenient source of electric current which is simultaneously converted to heat by passage through internal resistance elements at conversion efficiencies approaching 100%.

A typical HOT SHEET assembly, therefore, consists of a cathode structure (positive electrode), an anode structure (negative electrode), a porous absorbent separator material placed between the anode and cathode; and shorting members which form internal connections between the two electrodes and, hence, form the internal resistive (ohmic) heating element. Electrochemical reaction and consequent heat generation is immediately initiated by introduction of an electrolyte solution within the cell structure. In those instances where a water soluble electrolyte salt is incorporated directly within the cell structure, heat generation is initiated by the simple addition of water to the HOT SHEET assembly. It is this water activated assembly which is the subject of this technical program.

III EXPERIMENTAL TECHNIQUES

The objectives of the technical program were stated in Sec. I. It can be seen from Sec. II that the optimization of HOT SHEET performance is related to the formulation and assembly of the individual structural components, i.e., cathode structure, anode, separator, shorting members and electrolyte. This technical program is, therefore, designed to evaluate effects of the individual components and assembly parameters on overall HOT SHEET performance. This program will be divided into two parts : a) formulations requiring air for operation, and b) non-air formulations.

Before proceeding to the actual experimental results it is appropriate to consider how the various measurements will be made, i.e., measurements of skin temperature, temperature-time, and BTU per gram.

1. Skin Temperature : (Thermocouple Type T)
attached to surface of element using a high heat transfer silicone fluid (Dow Corning #340 silicone heat sink compound). Thermocouple measurements will be periodically checked using a conventional glass bulb thermometer.

2. Temperature-Time : Automatically recorded using an Esterline-Angus, Model L 1102S (automatic cold junction compensation) time-based temperature recording system.
3. BTU/g :
 - a) Natick method - water calorimeter
 - b) PAI method - copper block calorimeter - allows for measurement of material in sheet form.
 - c) Graphic integration of temperature time curves.

All measurements will be made on samples having dimensions 4" x 6" .

In addition to the measurement of the experimental parameters discussed above, the rise-time to 100°C (212°F) should prove to be an excellent indication of performance optimization, especially with respect to heating of food rations; rise-time, therefore, was carefully noted in all pertinent experiments.

During the course of this study it was found necessary to develop other experimental and measurement techniques, e.g., time-rate of heat generation vs. time, and the corresponding time derivative, and these techniques will be described in the appropriate place in the text.

IV AIR FORMULATION

The HOT SHEET elements which require access to air for operation utilize a so-called air-depolarized cathode structure, i.e., a cathode structure which contains a catalytically active porous carbon structure which reduces oxygen (air) electrochemically. The following structural components will be considered the reference or starting point of the performance optimization studies.

HOT SHEET Reference (air formulation)

Cathode : Darco (Atlas Chem.) S 51-RL
carbon/15% TFE binder
Carbon mix weight - approximately
5.5 g/4" x 6" (0.23 g/in².)

Carbon grid - Exmet 5 Fe 7.4/0
(degreased).

Cathode thickness - 0.023"

Anode : Primary grade magnesium (Dow) - 0.011"

Separator Pad: Webril R-2801 (Kendall Mills) - 0.065"

Salt - greater than 5.7 g/4" x 6" , or 0.238 g/in²

Shorting members: Arrow P-22, ¼" machine staples

Configuration (40) as per drawing

This reference was chosen since it represents the HOT SHEET formulation originally submitted to Natick Laboratories, and any improvements in performance must be judged relative to this reference formulation. Consequently, the experimental program focused attention on the effects of varying component formulations, pretreatment of materials, additives, and methods of heating element assembly. At the same time, it was necessary to determine the effects of water soak time during activation on overall HOT SHEET performance. Except in a few instances to be discussed later all measurements were conducted at room temperature (approximately 70° F) .

IV-1 WATER PICKUP vs. SOAK TIME

The original measurements made at Natick Laboratories used an activation time (water soak time) of ten seconds. There is no reason to assume, however, that a ten second soak yields optimum performance. These experiments were designed to determine the optimum soak time, and the relationship (if any) of water volume and performance. In addition, different thicknesses (densities) of Webril separators were evaluated to determine the least costly material that can still meet

the program performance objectives. All samples used the reference components, but the separator was varied.

<u>Separator</u>	<u>Soak Time</u>	
Webril R-2801	5 sec	35 sec
	10 "	40 "
-2601	15 "	45 "
	20 "	50 "
-2901	25 "	55 "
	30 "	60 "
-2401		

Four (4) separator thicknesses x 12 immersion times
x replication (2) : 96 total experiments in this series.

The results of each of the 96 experiments showed clearly that overall performance (i.e., rise-time and temperature-time dependence) was essentially independent of soak-time (activation time), at least up to one minute. This lack of dependency on soak-time is evident for all of the separator thicknesses evaluated, i.e., for a given separator thickness the performance with a soak-time of five seconds is essentially identical to the performance obtained after a 60 second

soak. Any variations among the data are small, and can be attributed to anticipated statistical spread. Since the temperature-time functionality is independent of soak (activation) time, average performance data are given for each separator thickness (see Table 1). In Table 1 are given representative data for the time from activation (end of soak time) to reach 100°C (rise-time), and the time the HOT SHEET skin temperature remains above 100°C. Also given is the maximum skin temperature reached, and the skin temperature at 3, 5, 7 and 9 minutes after activation.

The fact that HOT SHEET performance (with the R-series Webril materials) is independent of activation time is of considerable practical significance. For example, in field use it is unlikely that activation for a specified period of time could be assured, and this inherent activation time flexibility would afford the user considerable latitude without sacrificing overall performance.

TABLE 1 Soak Time Studies vs. Separator Type

<u>Separator</u>	<u>Time (min) To 100°C **</u>	<u>Time (min) Above 100°C</u>	<u>Maximum Temp.</u>	<u>Skin Temperature (°C)</u>			
				<u>@ 3 min</u>	<u>@ 5 min</u>	<u>@ 7 min</u>	<u>@ 9 min</u>
R-2401	2.35	3.68	110.6 (4.2) *	106	107.25	90	-
R-2601	3.31	5.79	110.75 (5.5) *	96.4	109.6	107	100
R-2801	3.02	6.0	114.35 (5.4) *	100.6	113.0	110.6	100
R-2901	3.25	7.43	113.75 (6.04) *	96.8	109.9	112.2	107.8

Note : * Refers to time after activation at which maximum temperature is reached.

 ** Time from the end of soak period in minutes.

Further examination of the data in Table 1 indicates definite differences in performance among the four separator thicknesses evaluated, differences especially with respect to rise time and the period of time the skin temperature remains above 100°C. It must be concluded, therefore, that the separator thickness and possibly the salt and water content, and salt/water ratio affect the overall heat generating characteristics. The general properties of the four separator materials are listed in Table 2. As can be seen from these data, the salt and water content vary as a function of thickness, whereas the salt/water ratio remains relatively constant (except for the R-2601 samples which will be discussed subsequently).

The rise times obtained with the R-2401 and R-2801 either meet or exceed the program objectives of reaching a skin temperature of 100°C (or above) within three (3) minutes after activation. Moreover, the time over which the skin temperature is maintained is also well within the program objectives. The differences in rise-time can be attributed to the fact that with increasing separator thickness the internal resistance is increased, at the same time increasing the diffusion path and distance over which ionic species and re-

TABLE 2 R - SERIES SEPARATOR CHARACTERISTICS

<u>Separator</u>	<u>Weight</u>	<u>Dry</u> <u>Thickness</u>	<u>Av. Salt</u> <u>Content</u>	<u>Av. Water</u> <u>Pickup</u>	<u>Salt/Water</u> ⁽¹⁾
R-2401	120 g/yd ²	0.035 "	9.69 g.	21.41 g.	0.397
R-2601	160 g.	0.045	20.79	30.25	0.639
R-2801	200 g.	0.065	14.82	36.22	0.409
R-2901	250 g.	0.085	15.12	40.16	0.376

Note (1): These values are at or above a saturated NaCl solution.

action products must migrate during the course of electrochemical reaction.

Also, a longer period of time is required to heat the increased volume of electrolyte solution. This is especially evident with the R-2901 material which shows a significantly slower average rise-time, particularly when compared with the R-2401 material. It should also be noted that the time over which the skin temperature remains above 100°C increases with increasing separator thickness and electrolyte volume. Before proceeding to a discussion of the R-2601 material, it should be pointed out that no further work was done with the R-2901 separator. Its substantially higher cost per sq. yd. did not warrant devoting any additional time in improving its performance characteristics (rise-time); and was considered only in the light of academic interest.

From the data in Table 2, it can be seen that the salt content of the R-2601 material is considerably greater than for any of the other separators, whereas the volume of water absorbed during activation is in line with the materials. Inadvertently, the R-2601 separator samples were overloaded with electrolyte salt during preparation, and the salt built

up on one surface of the separator. It is now believed that built-up salt deposit caused a retardation in the rate of dissolution upon activation with water and a subsequent decrease in the rate of diffusion of electrolyte; hence the slower rise-time to 100°C. Even under these circumstances, 8 of the 24 experiments run with the R-2601 material (or 33%) exhibited rise-times to 100°C of under three minutes, with the fastest being 2.5 minutes. Consequently, it can be concluded that the R-2601 material is inherently capable of exhibiting a rise-time to 100°C at or below the specified 3.0 minute cut-off. At the same time, the average temperature-time profile for the R-2601 indicates a total heat output close to or in excess of that of the R-2801 material which is more costly by approximately 30%.

Because of the potential cost savings in using the R-2601 material, it appeared worthwhile to work to improve the rise-time characteristics without reducing the total heat output (BTU's/g). The same logic prevailed in the case of the R-2401 which exhibited fast average rise-time of 2.35 minutes. Based on the data already obtained, experiments were conducted to determine the performance of the R-2401 and R-2601 materials at various salt/water ratios, and it was

found that by reducing the salt buildup on the R-2601 (i.e., lower the salt/water ratio) the rise-time was substantially and reproducibly reduced below 3 minutes.

Even at this early point in the experimental program, the following general conclusions could be drawn:

1. Performance for a given separator material is independent of soak (activation) time -- up to one minute.
2. Rise-time to 100°C becomes more rapid with decreasing separator thickness (Webril R-series).
3. Time over which skin temperature is maintained above 100°C (a measure of total heat output - BTU's/g) increases with increasing separator thickness (electrolyte volume).

Of the four separator materials used, the R-2801 appeared to give the best overall performance in terms of rise-time, maximum skin temperature and time above 100°C and, consequently, was chosen for some of the following experiments. However, it appears that the performance of the R-2401 and R-2601 can be improved; and the ultimate use of either of these materials would

afford meaningful cost savings. The ultimate choice of separator and "best formulation" was based on differential calorimetry measurements.

IV-2 ANODE PRETREATMENT AND CONFIGURATION

The purpose of these experiments was to determine whether pre-treatment, preparation or configuration of the Mg anode sheet in any way affected the heat generating characteristics. Primary grade magnesium was used in all the experiments. Other alloys were also evaluated, such as AZ-31 and AZ-61, as part of the calorimetry studies (Subsequent Section).

The experimental data are tabulated in Table 3. The data represent in each case the average of two experiments. The temperature-time profiles differ little from those obtained with the previous experiments with the R-2801 separator given in Table 1. In general, it can be concluded that anode pre-treatment or configuration are not significant factors in the performance of the heating element. Consequently, all future experiments will use magnesium anode material in the "as received" condition.

TABLE 3 EFFECTS OF ANODE TREATMENT OR CONFIGURATION

<u>Anode</u>	<u>Time (min) to 100°C</u>	<u>Time (min) Above 100°C</u>	<u>Maximum Temp. (°C)</u>	<u>@ 3 min.</u>	<u>Temperature (°C)</u>		
					<u>@ 5 min.</u>	<u>@ 7 min.</u>	<u>@ 9 min.</u>
HCl Etch	2.5	5.0	113.75 (4.0)	108.75	111.5	103	92.25
Base Etch	2.5	4.5	114 (4.25)	107.25	113.25	104	90.0
Wirebrushed Surface	2.75	5.75	112 (4.75)	103.5	112	106.75	96.75
Perforations 100-150 (0.030" d)	2.5	6.0	113.25 (5.0)	105	113.25	108	97.25
4" x 6" Sheet	2.25	5.0	116.25 (4.5)	110.25	115.75	104	89
Two Strips 2" x 6"	2.5	5.0	113 (4.25)	106.25	111.75	102.25	89
Four Strips 1" x 6"	2.75	4.75	111.25 (4.5)	103.25	110.25	102.5	91

Note: Cathode = Darco S 51-RL; R-2801 - Salt/Water = 0.4 - 0.6;

All samples activated by 30 second soak in water.

The rise-times for these experiments were somewhat faster than previously obtained with R-2801. Rechecking of individual experiments strongly indicates that this improvement in the rise-time is not attributable to the various anode treatments, but more likely, to the separator and salt/water ratio which averaged somewhat higher (0.5) than the previous experiments. These data did show, however, that improvements in performance using the R-series separators could definitely be achieved.

IV-3 CATHODE FORMULATION

As mentioned previously, the cathode utilizes an active carbon catalytic surface, and various sources of active carbon were evaluated. Likewise, additives to increase catalytic activity for oxygen reduction were also evaluated. Conductivity of the carbon surface and the most suitable conductive grid was included in this series of experiments.

1. Carbon

- a. Darco G-60
- b. PWA (Pittsburgh)
- c. Nuchar carbons
- d. Additions of Cabot conductive carbons

2. Additives (take best materials from above).
 - a. Electrolytic MnO_2 (Lavina # 6680 and 6681)
 - b. Permanganate
 - c. Black and doped NiO
3. Grid evaluation
 - a. Screens (staked)

The activity of the catalytic carbon surface of the cathode structure could greatly alter the heat generating time-temperature profile. Until now, Darco S51-RL activated carbon (Atlas Chemical Co.) has been used exclusively. However, without experimental comparative data there is no reason to assume that this carbon provides the "best" cathode structure. Therefore, other so-called activated carbons were evaluated to determine their electrochemical activity.

Darco G-60 was evaluated as a HOT SHEET cathode since at one time it found extensive use as a fuel cell air-depolarized cathode. However, it should be noted that in the fuel cell the cathode operates at a $\text{pH}=15$, and is usually associated with a noble-metal catalyst. As a cathode structure in a HOT SHEET element, the Darco G-60 was found to show only minimal activity. The highest temperature attained was

only 50°C, this temperature having been reached some 7 - 10 minutes after activation. In light of this poor performance, no further work was conducted with Darco G-60.

Pittsburgh PWA activated carbon was found to have extremely high activity as a cathode structure in the HOT SHEET element. Consequently, a more detailed evaluation of this cathode material was undertaken. The PWA cathode was evaluated with the four Webril separator materials, at three different soak times (10, 30 and 60 seconds). All experiments were duplicated and the results averaged. These data are given in Table 4.

With respect to rise-time to 100°C the PWA formulation appears to favor somewhat the shorter soak time, but for all practical purposes, the overall performance can be considered as being independent of soak (activation) time. What is striking, however, is the significant improvement in rise-time when compared to the Darco S51-RL samples without any apparent decrease in total heat output. In fact, all separator materials including R-2901 exhibited average rise-times and temperature-time profiles well within the prescribed program objectives.

TABLE 4 PERFORMANCE, PWA CATHODE

<u>Separator</u>	<u>Time (min)</u> <u>To 100°C</u>	<u>Time (min)</u> <u>Above 100°C</u>	<u>Maximum</u> <u>Temp. (°C)</u>	<u>@ 3 min.</u>	<u>Temperature (°C)</u>		
					<u>@ 5 min.</u>	<u>@ 7 min.</u>	<u>@ 9 min.</u>
R-2401	1.83	2.75	113 (3.0)*	111.8	99.4	77.7	-
R-2601	2.75	5.75	111.7 (4.75)*	103	110	105.6	96.8
R-2801	2.41	5.25	113 (4.33)*	106.5	112.3	104	91
R-2901	3.0	6.25	116.5 (5.3)*	101	115.9	111.6	101.6

Note: * Refers to time in minutes after activation at which maximum temperature is reached.

One possible explanation for the improved rise-times can be seen from the separator characteristics given in Table 2. The average water pickup during activation of the element made with PWA cathodes is lower than with the elements made with Darco S51-RL cathodes. Apparently, less water is absorbed by the PWA structure. Hence, there is a smaller volume of water to heat which could explain the faster rise-times. Also, it is conceivable that since less water is absorbed by the cathode structure, less of the structure is "flooded" providing more active sites for the electrochemical reduction of oxygen (air), i.e., an inherently more electrochemically active cathode. In any event, the use of the PWA cathode does appear to yield meaningful improvements in overall performance.

Other so-called activated carbons were also evaluated (e.g., the Nuchar carbons and other Pittsburgh carbons), but none showed the activity of the PWA or Darco S51-RL. At the same time, various additives (listed above) were also evaluated, and it was found that any "foreign" substance added to either PWA or Darco resulted in decrease of performance. Therefore, it was concluded that the carbon must be used in a pure unadulterated form, with PWA probably being the best material for the intended application.

The physical or chemical property(s) which renders the carbon electrochemically active has still not been identified. At first, it was believed that activity was related to electronic conductivity. As a point of reference the Darco S 51-RL is less conductive than the PWA by several orders of magnitude, yet performance is nearly the same. Also, samples were tested in which Cabot Corp. Vulcan XC-72 R, a highly conductive carbon, was mixed with the Darco S 51-RL. Although electronic conductivity was now comparable to the PWA there was no discernible difference in performance. Thus, it must be concluded that conductivity per se is not the primary factor in determining electrochemical heat generating activity.

It has been proposed that catalytic carbon activity is related to the number and density of organic surface groups, or the free electron spin density at the surface. Carbon suppliers usually refer to this parameter as "volatile content", and give some indication of its level through measurement of the Iodine Number. It would prove desirable to ultimately pinpoint and define the source of carbon activity, but for the purposes of this investigation a phenomenological approach to carbon cathode activity must be pursued.

Currently, the cathode structure utilizes an expanded metal (Exmet) steel grid to provide support and electrical continuity. Although the Exmet material is quite suitable it is a relatively expensive material. Other grid materials were evaluated with the objective of lowering costs without adversely affecting performance.

It was immediately found that metallic aluminum grids were not suitable for this application. The use of aluminum grids always yielded a very slow rise time (greater than 10 minutes to 100°C) , a lower maximum temperature, and a prolonged heating time. It was concluded, therefore, that emphasis would be placed on steel based materials.

Because the major objective of this study was lowering of material costs, woven wire screens were evaluated (staked and unstaked). Of the many screen sizes and types evaluated, Data for the most promising are given in Table 5.

Staked steel screens were definitely superior to the unstaked screens tested. In the case of the PWA cathode performance with these staked screens was, indeed, comparable to performance obtained with the Exmet grid. In addition, the 25 x 25 mesh gave a faster rise-time than the 32 x 32

TABLE 5 CATHODE GRIDS

<u>Structure</u>	<u>Time (min) To 100°C</u>	<u>Time (min) Above 100°C</u>	<u>Maximum Temp. (°C)</u>	<u>@ 3 min.</u>	<u>Temperature (°C)</u>		
					<u>@ 5 min.</u>	<u>@ 7 min.</u>	<u>@ 9 min.</u>
PWA-R2801 25x25 mesh Staked (0.007")	2.5	6.2	114 (5.4)*	102	113.5	108.5	98.5
PWA-R2801 32x32 mesh Staked (0.009")	2.7	7.5	115 (6.3)*	103	110	114	111
Darco-R2801 25x25 mesh Staked (0.007")	3.4	7.0	115 (6.2)*	96	112	114.5	108.5
Darco-R2801 32x32 mesh Staked (0.009")	6.0	3.4	102 (8.4)*	83	98	101	101

Note: * Refers to time in minutes after activation at which maximum temperature is reached.

mesh structure. Temperature-time for the PWA - 25 x 25 mesh was found to be quite reproducible, and this structure was singled out for further testing. If this screen type does in fact prove suitable for use with the food heating application, its use would afford a cost saving over Exmet of more than 50%/ft² .

IV-4 CALORIMETRY STUDIES

All measurements discussed thus far have been in the form of temperature-time curves, i.e., the skin temperature of the HOT SHEET element as a function of time. It is now believed that this type of measurement is not a true indication of food heating capability, but at best a qualitative or semi-quantitative indication of performance improvements. A more definitive measure of food heating ability is the time rate of BTU's produced.

Consequently, considerable effort was devoted during this program to develop reproducible experimental procedures for measuring:

1. Total BTU's (BTU/g)
2. BTU's over a given time-frame
3. Time rate of BTU's produced

Items 1 and 2 above were based on conventional calorimetry, with two types of calorimeters being evaluated. The first type to be evaluated was a copper block calorimeter in which the heating element was mounted against a pre-weighed copper block, and the temperature rise in the copper block recorded with a thermocouple probe. The total system was then enclosed in an insulated container. However, this type of calorimeter gave only marginal reproducibility because of heat losses to the surroundings. It was found that this system could not be made adiabatic while still allowing even moderate air access to the heating element being tested.

Because of the difficulties encountered with the copper block calorimeter, a water calorimeter as suggested by Dr. Kwoh Hu of the U.S. Army Natick Laboratories was used. The system is enclosed in a Dewar flask, thus giving reproducible adiabatic conditions. The HOT SHEET sample to be measured is placed around the inside circumference of an aluminum can which is immersed in the water; air access to the element is provided by two tubes projecting into the sample holder. Using this type of water calorimeter, heat losses to the surroundings are small and can be neglected; and it is these measurements that are given in this Report.

A reproducible means has also been developed to measure the time rate of BTU's produced. The HOT SHEET element is placed on a balance and the change in weight is measured as a function of time as well as the temperature-time functionality. The weight loss with time is proportional to the amount of water being evaporated and, as will be shown, the first derivative of the weight with respect to time plotted as a function of time (dw/dt vs. t) provides a direct quantitative assessment of the time-rate of BTU's produced.

These two types of measurements differ markedly in their significance. Total BTU's measured under adiabatic steady-state conditions yields the total heat generating capability inherent in a given formulation. Since the experimental conditions are highly controlled, total BTU's provides a means for assessing the relative heat generating capabilities among various materials and formulations.

But in terms of the food heating application, the rate at which heat is being generated under non-equilibrium conditions is more relevant. Consequently, the rate of water evaporation as a function of time was measured. These values can then be converted into BTU/t values. More mean-

ingful is the first derivative with respect to time (dw/dt vs. t), which allows for direct comparison of various formulations under conditions approaching those encountered in the food heating application. Since these rate measurements are run in contact with ambient air which has a high heat transfer coefficient U , these data must be considered as an upper limit. Admittedly, the heat transfer coefficient at the surface of the food flex-pack would certainly be somewhat lower than in air, but it is felt that the conditions are sufficiently close to be directly relevant to the food heating application. The importance of the heat transfer coefficient and integration of the HOT SHEET element into the food pack was discussed in detail in the original Proposal for this study, and was the subject of PAI's proposed phase II. The importance of the heat transfer coefficient will become even more evident after reviewing the rate data.

The total BTU measurements were made in a one liter Dewar-type container which was loaded with 680 g of water. The sample to be measured was placed around the inside surface of an aluminum can having dimensions of 4.75" h x 2.5" d.

The sample was activated and the can then immersed in the calorimeter and the system closed. Two small diameter tubes provide air access in and out of the sample can. Temperature was measured by means of a thermocouple placed between the surface of the HOT SHEET and the inside surface of the sample can, and a second thermocouple placed in the water. The temperature rise reaches equilibrium within 1.25 - 1.5 hours with periodic stirring.

Total BTU's and BTU's/g are calculated as follows :

$$\text{BTU} = \sum_i N_i C_{pi} \Delta T, \quad (9)$$

where N_i is the weight of the i -th component, C_{pi} its specific heat, and ΔT the temperature rise of the system at equilibrium. Rewriting Eq. (9) for the calorimeter system,

$$\text{BTU} = \left[N_1 C_{p1} + N_2 C_{p2} + N_3 C_{p3} + N_4 C_{p4} \right] \Delta T, \quad (10)$$

where (1) is the water in the calorimeter, (2) is the aluminum sample can, (3) is the stainless steel liner, and (4) is the HOT SHEET sample after activation. In this manner, all the heat generated is accounted for. Several of

the above factors are constants of the system, and can be considered collectively.

$$\text{BTU} = \left[2.7965 + (3.9685 \times 10^{-3}) (W_4) \right] \Delta T, \quad (11)$$

where W_4 is the weight in grams of the water retained by the HOT SHEET sample after activation. All values of total BTU's are based on Eq. (11); and the BTU/g are obtained by dividing this value by the dry weight of the HOT SHEET sample. These values are tabulated in Table 6.

From the data shown in Table 6, it appears that more total heat is generated with use of primary magnesium, but it should be noted that the samples of AZ -31 had a thickness of 0.010" while the primary measured 0.011" . Therefore, the differences in total BTU's must be attributed to this difference in available active anode material ($\text{prm}/\text{AZ-31} = 1.11/1.00$) . The values given in the Table are essentially in this ratio. All magnesium samples had a thickness of 0.011" regardless of the alloy, and the primary grade and Az - 31 were used interchangeably.

TABLE 6 CALORIMETRY : TOTAL BTU

<u>Separator</u>	<u>Cathode</u>	<u>Anode</u>	<u>Total BTU</u>	<u>BTU/g.</u>
R-2801	Darco	AZ-31	93.96	2.86
		Prim.	93.96	2.65
	PWA	AZ-31	96.89	2.89
		Prim.	92.50	2.41
R-2601	Darco	AZ-31	79.28	2.56
		Prim.	93.96	2.95
	PWA	AZ-31	70.47	2.36
		Prim.	88.09	2.86
R-2401	Darco	AZ-31	73.41	2.66
		Prim.	76.34	2.65
	PWA	AZ-31	67.53	2.22
		Prim.	70.47	2.29
P - 17	Darco	AZ-31	67.53	2.21
		Prim.	76.34	2.46
	PWA	AZ-31	73.41	2.29
		Prim.	82.22	2.89
P - 18	Darco	AZ-31	76.34	2.12
		Prim.	85.15	2.41
	PWA	AZ-31	79.28	2.22
		Prim.	85.15	2.40

There does appear to be a general trend that the Darco S 51-RL formulation provides more total heat output than the PWA structure. It should be remembered, however, that these calorimetry measurements are done under controlled highly limited air access conditions, conditions which can be designated as "low rate". This is not an unexpected result since battery experience has shown that S 51-RL yields higher efficiencies than PWA at low current densities, but that PWA is the more suitable structure at high current densities. These differences in performance as a function of current density became readily evident from the derivative of the rate data (i.e., dw/dt vs. t). Therefore, the use of total BTU data (or even BTU/g) per se could prove misleading in choosing the "best formulation" for the food heating application. Nonetheless, these data are an excellent indicator for determining relative performance among various formulations and component combinations.

From the values of total BTU and BTU/g, R-2801, 2601 and P-17 must be considered as the most promising. Since the differences between R-2601 and R-2801 are, indeed, small, preference must be given to R-2601 on the basis of material cost. By the same token, since the P-17 separator represents

a significant cost reduction over the R-series separators, this material is worthy of further evaluation.

As stated previously, perhaps more meaningful than the calorimetric data is the time rate of heat generation as a function of time, i.e., $d \text{ (BTU)}/dt$ vs. t . The following logic prevailed in the measurement of this derivative function. The heat being generated manifests itself in two ways :

1. To raise the temperature of the HOT SHEET element
2. To evaporate water contained within the HOT SHEET element.

The first contribution is essentially linear and, thus, adds a constant to the derivative. For the purposes of comparative analysis this constant can be neglected. The second contribution, the evaporation of water, manifests itself as a decrease in sample weight which can be readily measured as a function of time. If this change in weight with time is to be completely accurate then it would be necessary to add a correction due to the formation of magnesium hydroxide from oxygen derived from air, according to the equation,



This formation of Mg(OH)_2 would add weight to the sample as a function of time, thus making the net weight of water evaporated greater than actually measured. It is unlikely that the formation of hydroxide with time is constant, but here again, for the purposes of comparative analysis, this term is considered constant and can be neglected.

In light of these assumptions and neglected correction factors, the plot of dw/dt vs. t (where w is the measured weight loss of the sample) is a direct measure of the rate of BTU generation as a function of time. These rate data together with calculations of BTU's generated over the time span of interest, i.e., 5 to 7 minutes, provide a more accurate means of discerning the so-called "best formulation" for the food heating application. The BTU's generated in 5 to 7 minutes are obtained by integrating the differential rate data and correcting for sample heating and formation of Mg(OH)_2 . The hydroxide correction factor is found from Eq. (12). Analysis indicates that within the first seven minutes of operation about half of the original Mg is reacted. With a starting weight of Mg of 8.1g the correction of hydroxide

formation is found to be 5.67 g. The BTU's generated over the first seven minutes of operation (incorporating the above corrections) are tabulated in Table 7. Also included are representative data for BTU's generated in the first 20 minutes of operation (Table 8).

Before analyzing and discussing these data it is instructive to briefly calculate the heat required to raise a typical flex-pack of food (4.5 oz. or 128 g.) from ambient (70°F) to 160°F or even 170°F. The total heat required can be calculated from Eq. (13), i.e.,

$$\text{BTU} = C_p (W) \Delta T, \quad (13)$$

where C_p is the specified heat of the food, W its weight, and ΔT the temperature rise from ambient. Since food plus sauce is predominantly water, it seems reasonable to assume a specific heat (C_p) of 1 cal/g/°C. Based on this assumed value for C_p , it would require to raise the temperature of the food from 70°F - 160°F (21°C - 71°C), 25.31 BTU. Likewise, 28.35 BTU would be required to raise the same food temperature to 170°F (77°C).

TABLE 7 BTU GENERATED IN SEVEN MINUTES

<u>Separator</u>	<u>Cathode</u>	<u>Anode</u>	<u>BTU (7 min)</u>	<u>BTU/g</u>
R-2801	Darco	AZ-31	51.22	1.52
		Prim.	55.94	1.65
	PWA	AZ-31	56.4	1.69
		Prim.	59.65	1.64
R-2601	Darco	AZ-31	48.04	1.64
		Prim/	53.15	1.52
	PWA	AZ-31	52.04	1.65
		Prim.	52.26	1.68
R-2401	Darco	AZ-31	42.28	1.66
		Prim.	43.58	1.49
	PWA	AZ-31	45.48 (1)	1.40
		Prim.	44.97 (2)	1.48
P - 17	Darco	AZ-31	38.79	1.38
		Prim.	39.71	1.32
	PWA	AZ-31	40.36	1.43
		Prim.	46.66	1.44

Notes: (1) After 5 minutes

(2) After 6 Minutes

TABLE 8 BTU GENERATED: SCREEN BASED CATHODE

<u>Separator</u>	<u>Cathode (1)</u>	<u>BTU</u>	<u>BTU/g.</u>
R-2801	Darco	45.51	1.27
	PWA	50.10	1.31
R-2601	Darco	44.34	1.48
	PWA	53.0	1.55
R-2401	Darco	40.0	1.48
	PWA	45.1	1.58
P - 17	Darco	43.87	1.35
	PWA	45.90	1.57

Notes : (1) Cathodes made with 25 x 25 mesh staked screen

 (2) Anode: AZ - 31

After 20 minutes

R-2801	PWA	65.97	1.91
R-2601	PWA	49.83	1.68
R-2401	PWA	39.90	1.38
P - 17	PWA	43.98	1.59

In light of the calculations above, all formulations evaluated generate more than sufficient heat in 7 minutes to raise the food at least to 170°F from ambient. However, examination of the data in Tables 7 & 8 strongly indicate that the "best" formulation for the food heating application is PWA - R-2601 - AZ-31 (or primary). Without doubt, the PWA cathode offers a significant improvement in high rate heat output when compared with Darco S 51-RL. Although the Darco cathode does generate more total heat over the long-term its time rate of heat output proved inadequate for the present application. Consequently, all subsequent work stressed the use of the PWA cathode structure.

With respect to the separator materials, the data indicate that the use of the Webril R-2601 offers the best trade-offs in terms of time rate of heat generation, total heat output in 7 and 20 minutes, and cost. Consequently, the R-2601 material was used as the separator in the present definition of "best formulation". As discussed previously, the experimental results show that primary grade and AZ-31 can be made interchangeably. Thus, the "best formulation" for the purposes of further experimentation was defined as :

Cathode : PWA
Separator: R-2601
Anode : AZ-31 or Primary Grade

Let us now consider the "best formulation" in terms of the food heating application. It has been shown that it requires 28.35 BTU's to heat 4.5 oz. of food from room-temperature to 170°F. The PWA - R-2601 "best formulation" yields greater than 52 BTU's in the first seven (7) minutes of operation, more than sufficient to heat the food. In fact, only some 54% of the total heat generated in the first seven minutes of operation need be transferred to the food to raise its temperature to 170°F. Hence, heat transfer from the HOT SHEET to the food will be an important consideration in the food heating application.

The above definition of "best formulation" was independently arrived at by Dr. Kwoh Hu of Natick Laboratories in food heating experiments. At the same time, these experiments vividly demonstrated the importance of heat transfer consideration when the HOT SHEET element is used to heat military field rations. For example, by heating the food pack from two sides simultaneously using two 3" x 4" elements

instead of the single 4" x 6" element, a significant improvement in food heating was achieved. These data are shown in Table 9 and should be compared with the original Natick food heating experiments mentioned in the Introduction. It should be noted that the flex-pack cover was provided with four half-inch holes to allow for some air access to the heating elements.

TABLE 9 NATICK FOOD HEATING TESTS

4.5 oz. of Food - Flexpack

<u>Time (minutes)</u>	<u>Food Temperature</u>
0	75° F
4	100
6	130
8	145
10	156
14	168
15	168

In lieu of more definitive studies to ascertain the optimum heating element size and configuration for integration into the food heating pack, samples consisting of two 4" x 3" elements connected by a flexible screen will be delivered as part of this contract.

IV-5 AIR FORMULATION: TOXICITY EVALUATION

Since the intended application for the HOT SHEET element is heating of military field rations, it is appropriate to determine whether the heating element represents a toxicological hazard, however small. The areas of major concern are:

1. Acute oral toxicity
2. Primary and abraded skin irritation
3. Eye irritation

Before proceeding to the actual test data consideration should be given to the chemical components comprising the HOT SHEET elements, and the reaction products produced during the process of heat generation. All chemical constituents comprising the air formulation of HOT SHEET have been discussed in detail and extensive literature references and citations show that

none of these materials either individually or in combination pose any toxicological hazard. Therefore, any concern for toxicity must be given to the reaction products.

The reactions and reaction products must be divided into three classes : a) electrochemical, b) hydrolysis, and c) corrosion. Each class will be considered individually.

Electrochemical Reaction

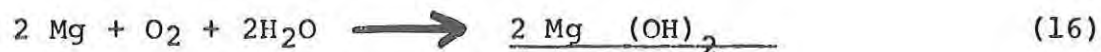
Air Cathode :



Anode :



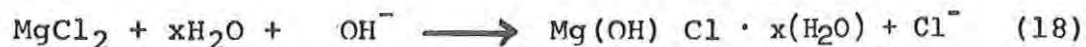
Net Electrochemical Reaction :



For the food heating application the magnesium hydroxide (which is sold commercially as an antacid) is the predominant product.

Corrosion Reaction

The MgCl_2 hydrolyzes almost instantaneously and will be discussed below. The corrosion reaction produces a small amount of hydrogen gas, and this gas combined with moist air can sometime cause the semblance of an odor -- but in actuality the material is odorless.

Hydrolysis Reaction

Thus, from all of the possible reactions the products are magnesium hydroxide, hydrated magnesium hydroxy chloride (both highly insoluble), and a very small amount of hydrogen gas.

HOT SHEET "best formulation" samples were submitted to Food and Drug Research Laboratories, Inc., East Orange, N.J. The results of these tests are given in Appendix B, and show conclusively that the air formulation HOT SHEET elements pose no toxicological hazard, and can, therefore, be considered as completely safe.

IV-6 LIMITED AIR STUDY

Before proceeding to any formal study of HOT SHEET performance under conditions of limited air access, it was decided to obtain some "feel" for the limits for heating food. These limits were established by actually heating the 4.5 oz. flex-pack furnished by Natick Labs. Also, because of the superior results obtained by Dr. Hu with heating the food sample from both sides simultaneously this approach was taken in establishing food heating limits.

Two conditions for food heating were evaluated :

(1) HOT SHEET elements totally exposed to air, and (2) heating element completely enclosed with the flex-pack, thus totally limiting the accessibility of air to the element. The HOT SHEET element consisted of two 2" x 5" elements connected by an integral R-2601 separator. Thus, the element could be wrapped around the food and allow for heating from both sides simultaneously, ten square inches of HOT SHEET per side with a total of 20 sq. in. The food heating results are shown in Table 10.

TABLE 10 FOOD HEATING TESTS ; FLEX - PACK

I - Air Access Condition (Two Sides)Central Food Temperature (1)

<u>Heating Time</u>	<u>° C</u>	<u>° F</u>
0 minutes	22	71.6
1 "	47	116.6
2 "	68	154.4
3 "	75	167.0
4 "	82	179.6
5 "	87.5	189.5
6 "	91	195.8
7 "	93	199.4
8 "	94.5	202.1
9 "	95	203.0
10 "	96	204.8

II - No Air Condition (Enclosed in Flex-Pack)

0 minutes	22	71.6
5 "	35	95.0
8 "	44	111.2
12 "	53	127.4
15 "	57.5	135.5
20 "	62	143.6
25 "	69.5	157.1
30 "	74.5	166.1
35 "	77 (Stable)	170.6

Note : (1) Thermocouple Probe.

These data, as mentioned above, represent "limits" under conditions of complete air exposure, and total air limitation, i.e., the air available within an enclosure with only very limited air replenishment from the outside. These data do show that the HOT SHEET element is inherently capable of raising the central temperature of the food above 200°F in under eight (8) minutes. The data also show that even under conditions of no air accessibility the central food temperature can still be raised to 170°F, but at the considerable expense of heating time. From these two experiments it can be concluded that the degree of air accessibility affects the rate of heat generation without significantly altering the total heat output. At the same time, since the rate of heat output is affected, the rate of heat transfer to the food is also changed. Consequently, an optimum trade-off situation must be found between air accessibility and rate of heat output (rate of heat transfer to the food).

Experiments were conducted in an effort to determine the optimum trade-off between the limits of total air accessibility and no-air. HOT SHEET elements (6" x 4") were tested in which the air cathode side was backed with cardboard.

Different levels of air accessibility were evaluated by placing holes in the cardboard backing. The degree of air access was varied by changing the percent open area, i.e., the percent of air cathode area directly exposed to air; the variables being hole size and number of holes. The heat output data are shown in Table 11. All samples evaluated consisted of PWA-R-2601-AZ 31, with both screen and Exmet being tested as cathode grid. Since no differences were observed between screen and Exmet, screen will be used in all subsequent HOT SHEET formulations because of its appreciably lower cost. The samples for which data are shown in Table 11 differ only in the extent to which the air cathode structure is exposed to ambient air.

From the data shown in Table 11 it is possible to define three general types of HOT SHEET operation: a) no air access, b) limited air access, and c) total air access. Operation of the heating element remains essentially constant over a wide percentage of open area exposure regardless of the size of the openings (e.g., 3% - 30%) . Even with the use of spacers which assumedly provide a volume of air to the cathode, BTU output still remains in the range of 40-42 BTU's after 5 minutes, and 46-49 BTU's after 7 minutes. It must be

TABLE 11 LIMITED AIR STUDY

<u>Size of Hole</u>	<u>No. of Holes</u>	<u>% Open Area</u>	<u>Total BTU's</u>	
			<u>5 minutes</u>	<u>7 minutes</u>
1/16 in	90	1 %	39.51	47.49
1/16 "	207	2 %	40.46	47.67
1/8 "	60	3 %	40.38	49.05
3/16 "	30	3 %	40.05	47.30
3/16 "	44	5 %	40.60	45.73
1/4 "	15	3 %	43.19	49.77
1/4 "	25	5 %	41.08	47.60
1/4 "	35	7 %	40.96	46.09
1/2 "	4	3 %	42.48	48.04
1/2 "	6	5 %	42.18	48.39
1/2 "	9	7 %	43.03	48.60
1/2 "	11	9 %	43.83	49.18
1/2 "	12	10%	42.34	48.27
<u>Controls</u>				
-	-	0 %	33.62	37.47
-	-	100 %	49.48	54.61
Slits of varying dimensions:		15 %	42.18	47.95
		20 %	41.11	47.67
		25 %	40.75	46.70
		30 %	42.02	46.53

concluded, therefore, that by limiting air access to the heating element (air formulation) - irrespective of the degree of air limitation - the rate of reaction (i.e., dBTU/dt) is diminished; and, hence, food heating time would be increased somewhat. For efficient high rate operation the air formulation HOT SHEET elements should be totally exposed to air if heating time is to be optimized.

The data and conclusions demonstrate the desirability of an efficient non-air HOT SHEET formulation for the food heating application. The non-air formulation is discussed in detail in Sec. V. However, before proceeding to a discussion of non-air formulations, it is appropriate to consider HOT SHEET operation at various temperatures, especially low temperatures. Although operation at low ambient temperatures was not an objective of this program, efficient operation at low ambient temperatures has important ramifications for widespread military field applications.

IV-7 LOW TEMPERATURE MEASUREMENTS

From a practical point of view it would be highly desirable if the HOT SHEET elements would operate efficiently at ambient temperatures below room temperature (70°F). Even though these measurements were not part of the planned program samples using both Darco S 51-RL and Pittsburgh PWA cathodes were evaluated at an ambient temperature of approximately 50°F (10°C). The purpose of these initial low temperature measurements was to identify problem areas, if in fact they manifested themselves.

Both Darco S 51-RL and PWA samples (6" x 4") were made with R-2401, R-2601 and R-2801 separator materials. Prior to activation, the test element and the water were allowed to come to equilibrium inside the cold chamber (5°C - 10°C). Once the samples equilibrated, they were soaked (activated) for 30 seconds. The test data are given in Table 12.

The heat generating performance for both Darco S 51-RL and PWA at an ambient of 5°C - 10°C was found to be essentially identical to that obtained at room temperature. Thus, from these preliminary data, no problem areas for operation of HOT SHEET elements at low temperature are anticipated.

TABLE 12 LOW TEMPERATURE PERFORMANCE

<u>System</u>	<u>Time (min) To 100°C</u>	<u>Time (min) Above 100°C</u>	<u>Maximum Temp. (°C)</u>	<u>@ 3 min.</u>	<u>Temperature (°C)</u>		<u>@ 9 min</u>
					<u>@ 5 min.</u>	<u>@ 7 min.</u>	
<u>R-2401</u>							
S51-RL	2.0	2.5	108 (3.0)	108	92	66	46.5
PWA	2.25	2.25	109 (3.75)	107	104	80	59
<u>R-2601</u>							
S51-RL	3.0	3.0	106 (4.0)	100	105	92	76
PWA	2.25	5.25	115 (4.0)	104	112.5	103	85
<u>R-2801</u>							
S51-RL	3.5	6.0	111 (5.75)	86	110	110	101
PWA	3.25	6.75	108 (4.0)	94	95 (1)	101	105

Note (1): Water condensed on sample in cold chamber

(2): Average Salt content ; R-2401 = 7.64 g; R-2601 = 9.42 g; R-2801 = 14.74 g.

More extensive measurements at low temperature, including measurement of BTU/g should be made to establish performance even at -20°C .

Although these low ambient temperature tests must still be considered as preliminary, they show rather dramatically that operation at low temperature presents no problems. Even the rise-time (to 100°C) is unaffected indicating that sufficient internal heating to efficiently sustain the reaction is produced immediately upon activation. There is definite indication, therefore, that the HOT SHEET elements are suitable for use over a wide range of ambient temperature conditions.

V NON-AIR FORMULATIONS

Based on the results obtained with the air-formulation studies, the desirability of a non-air formulation is manifest. Recalling the theory presented in Sec. II, any cathode-anode combination can in principle be used within the HOT SHEET concept. However, in order to minimize the experimental effort it was decided to utilize all of the air-

formulation technology which proved readily applicable to a non-air structure. Consequently, the Mg (AZ-31) anode, R-2601 Separator, NaCl electrolyte salt, and a shorting member configuration previously described were retained for the non-air studies. Moreover, these components have been shown not to impart any toxicity or hazard to the heating element, and attention, therefore, could be devoted solely to the cathode formulation and structure.

Of the myriad cathode materials and formulations compatible with aqueous electrochemical systems, it was decided to emphasize the use of manganese dioxide (MnO_2) as the cathode oxidizing agent. This compound, MnO_2 finds widespread use as a so-called cathode depolarizer in the common "dry cell"; and offers perhaps the best trade-offs among performance, hazard-free operation and handling, and cost.

The HOT SHEET element differs markedly from the common dry cell in one very significant way, i.e., HOT SHEET demands high sustained rates of reactions, whereas dry cells are suitable for low rate discharge. Therefore, if MnO_2 were to prove useful as a cathode structure for HOT SHEET its formulation must be capable of sustaining high rates of reaction.

The reaction rate at the cathode structure is a function of: a) inherent reactivity of the MnO_2 , b) electrolyte accessibility, and c) electronic conductivity. A number of MnO_2 samples were evaluated for reactivity including naturally occurring ores and synthetic manganese dioxides. For the purposes of HOT SHEET it was found that the natural ore materials were more than adequate, while affording substantial cost savings over synthetic materials. An ore material containing 74% by weight MnO_2 (A Man Co., Inc., Phila, Pa.) was chosen for the HOT SHEET non-air formulation studies.

In an effort to insure electrolyte accessibility an inert porous inorganic filler - Fullers Earth - was added to the MnO_2 . Fullers Earth is capable of absorbing many times its weight in liquid, and its presence in the cathode mix would insure sufficient electrolyte to sustain the high rate electrochemical reaction. In addition to the 20 x 20 mesh screen as a grid, a small amount of Cabot XR-72 highly conductive but otherwise inert carbon was added to impart additional electronic conductivity to the cathode mix. It was now necessary to determine the optimum ratios of MnO_2 /Carbon/Fullers earth.

HOT SHEET elements were fabricated using MnO_2 cathode structures in which the ratios of Cabot carbon and Fullers earth were varied. In all cases the anode was AZ-31 (0.010") and the separator Webril R-2601 with salt. The weight of the samples averaged 1.25 g/in^2 . All samples were activated by immersing in water for 30 seconds - one minute. The rise-time to 100°C and the maximum skin temperature attained was measured, as was the total BTU output at 5 minutes and 7 minutes. These data are shown in Table 13.

These data indicate that the "best formulation" of MnO_2 /Cabot/F.E. is 10g/2g/1g, and that the ratio of Cabot/F.E. is extremely critical in terms of overall performance and reproducibility. It should be noted that the MnO_2 non-air structures in general, and especially the 10/2/1 formulation exhibit extremely fast rise-times to 100°C ; a particularly important feature for the food heating application.

At the same time, the maximum skin temperature attained is comparable or better than that attained with the air formulations; and well above the objectives of the program. Moreover, the BTU output is in the same range as the air-formulations, but with considerably faster rise-times.

TABLE 13 NON-AIR CATHODE FORMULATIONS

<u>MnO₂</u>	<u>Weight (g)</u>		<u>Time to</u>		<u>Total BTU's</u>	
	<u>Cabot</u>	<u>F.E.</u>	<u>100°C</u>	<u>Max.Temp.</u>	<u>@ 5 min.</u>	<u>@ 7 min.</u>
10	1.5	2.0	2 min.	120°C	36.14	39.16
10	1.5	1.5	1.4	115	28.45	32.7
10	1	2	4.2	114	22.9	28.03
10	2	1.5	2.5	117	33.8	39.6
10	2	1	1.1	120	42.57	46.21
10	2	0.5	1.5	119	32.27	38.26
10	1.5	1	2.4	114	33.44	39.86
10	2	1.25	1.4	121	41.23	45.1
10	2.0	1.1	2.5	107	38.66	43.14
10	2.5	1	2.2	120	29.39	33.68
10	2	1	1.3	117	40.59	46.36
10	2	1	1.3	122	41.02	45.9
10	2	1.5	1.9	118	29.79	33.4
10	1.5	0.5	3.1	116	38.14	43.27

Because the non-air formulations operate efficiently in the absence of air, the need for holes in the food packaging can be eliminated. Thus, heat losses to the ambient are minimized or even eliminated, and a high percentage of the heat produced is transferred directly to the food. If this is indeed the case, then the food should be heated faster with the non-air formulation than with the air formulations.

HOT SHEET samples (non-air) were constructed of two 3" x 4" elements connected by a flexible screen. The elements were placed around the food so as to heat from two sides simultaneously. The elements were activated in water (30 sec to 1 minute), and the food and elements were placed in the flex-pack which was completely closed, i.e., no access to ambient air. In one case the central food temperature was measured as a function of heating time (Run 1), and in other instances the temperature at the extremities of the food pack were measured vs. time (Run 2). These measurements are shown in Table 14.

In Run 1, the heating elements were removed at the end of 15 minutes and allowed to stand exposed to room temperature of 68°F. After 20 minutes of stand, the central food temperature was still above 145°F showing that the food and sauce was thoroughly heated with the non-air elements.

TABLE 14 FOOD HEATING: NON-AIR ELEMENTS

<u>Heating Time</u>	<u>Run 1 (1)</u>	<u>Run 2 (2)</u>
2 minutes	108.5°F	78.8
4 "	137.3	108.5
6 "	169	131
8 "	191	152
10 "	199	166
12 "	204	182
14 "	206	187
16 "	206	191
18 "	-	195

Notes: (1) Central food temperatures

 (2) Food temperature at extremities of the pack .

The data in Table 14 are to be compared with the data in Table 10. It can be seen that the non-air formulation is comparable to the air formulation under ideal conditions (free air access), and considerably better than air formulations when run in limited air. The results with the non-air formulation must be considered as being highly successful with respect to food heating, while affording appreciably greater use flexibility in that the need for air has been eliminated.

Experience with the non-air formulation is not as extensive as with the air formulations, and further experimentation is justified to ascertain the optimum overall formulation, mode of construction, and reproducibility. Also, because the non-air formulation data were obtained at the end of this program, there was insufficient time for evaluation of toxicity. However, based on the electrochemistry of the non-air system a non-toxic completely safe structure can be anticipated. Nevertheless, toxicity testing must be undertaken at some future date. But even at this point, the non-air formulation has proven an effective means for heating military field rations quickly and efficiently, with no toxicological or other hazards to be anticipated. At the same time, the weight of the non-air formulation is essentially identical to that of the air formulation.

VI SUMMARY, CONCLUSIONS AND SUGGESTED FOLLOW-ON STUDIES

This program emphasized two areas of investigations: 1) optimization of the air-formulation, and 2) demonstration of feasibility and optimization of non-air formulation HOT SHEET heating element. With respect to the program objectives stated in Sec. I, both areas of investigation (i.e., air and non-air formulations) have resulted in HOT SHEET elements which meet or exceed these objectives. It has been a further objective of this program to determine a "best formulation" for the heating element, and because of the progress made in both areas of air and non-air it is necessary to define two "best formulations"; and both types of samples have been submitted to U.S. Army Natick Laboratories.

Best Formulations:

Air -	Cathode :	PWA - Screen
	Separator :	R-2601 (NaCl)
	Anode :	AZ-31 or Primary Mg
Non-Air -	Cathode :	MnO ₂ /Cabot/F.E. = 10/2/1
	Separator :	R-2601 (NaCl)
	Anode :	AZ-31 or Primary Mg.

It should be noted, however, that because of the many inherent advantages to the user the non-air formulation should be emphasized and form the basis of any continuing effort or further evaluation.

The general performance characteristics of the HOT SHEET elements are summarized below :

1. Overall performance is essentially independent of activation time (soak time) in water - from 5 seconds to one minute.
2. Rise-time to 100°C is under three minutes, and in the case of the non-air formulation is under 1.5 minutes.
3. Maximum skin temperature of the heating element is in the range of 110° - 122°C.
4. Total BTU's produced is in excess of 42 BTU's in five minutes, and 46-56 BTU's in seven minutes.
5. The total BTU output inherent in the heating element is 2.7 - 3.0 BTU's/g; albeit this result has been shown to be not

directly germane to the food heating application. The measurement of dw/dt vs. t is more relevant to the heating of military rations.

6. The air-formulation has been certified as non-toxic and poses no hazards or safety concerns to the user. The non-air formulation must still be tested, but based on the electrochemical reactions no difficulties are anticipated.
7. Using the air-formulation with free air access, the flex-pack food rations can be heated above 170°F in less than 10 minutes. Under conditions of limited air access, the food heating time is increased by at least 35 - 50%.
8. Using the non-air formulation, it is possible to heat the flex-pack food to above 170°F in 8 minutes, and above 200°F in 11 - 15 minutes.

9. Based on preliminary experiments, operation of the heating element at low ambient temperatures (down to 0°C) is comparable or equivalent to operation at 20°C (room temperature).

It is apparent that the feasibility and practicality of heating military rations has been well demonstrated with both the air and non-air formulation heating elements. There is no doubt, however, that the non-air formulation is of greater interest because of its ability to operate over a wide range of field and use conditions. Optimization of the non-air formulation HOT SHEET element should now be straightforward, and the following studies are immediately suggested. These studies would emphasize and anticipate the variety of conditions that the user might conceivably encounter.

Non-Air Studies

1. Performance vs. soak time (5 seconds - one minute).
2. Performance as a function of ambient temperature, and temperature of the water to be used for activation.

Ambient temperature: -40°C to $+40^{\circ}\text{C}$

Water temperature: 0°C to $+40^{\circ}\text{C}$

It would also be instructive to evaluate the use of melted snow for activation of the heating element.

3. Toxicity testing of the non-air formulation.

In the original proposal which resulted in this program, it was stressed (Phase II) that integration of the HOT SHEET element into the food package was an essential part of the overall study. Although some food heating studies have been made as a part of the present program -- studies which proved the efficacy and practicality of the heat element for this application -- there is no reason to assume that the present element size and configuration is optimum, optimum in terms of heat transfer per unit time and cost. Obviously, the objective of the package-element integration study would be to minimize the size and thus the cost of the heating element. Furthermore, by minimizing the size of the heating element, storage of the elements, especially in large quantities would be greatly facilitated.

This heating element - package integration study is in effect an investigation of the so-called heat transfer coefficient U of the total system. Although U is a complex

function of various system parameters, in essence it is dependent on the geometry, heat transfer contact surface, and the materials across which heat is transferred. Since the food packaging per se must remain a constant of the system, this study would be concerned primarily with the geometry and construction of the HOT SHEET element itself. One area of investigation, for example, would be the use of an insulating backing on the heating element which would minimize heat losses to the surroundings while at the same time optimize heat transfer to the food. This type of HOT SHEET insulation is now possible since the heating element is now independent of air access.

In summary, the HOT SHEET formulation optimization program is now essentially complete, with the result being a non-air formulation showing considerable promise as a practical, efficient and safe means for heating military rations. The suggested follow-on studies would result in an optimum heating element geometry and configuration for integration into the flex-pack food package. Because of the substantial technological base already available, these follow-on studies would require an absolute minimum of time and effort for successful completion.

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APPENDIX A

United States Patent [19]

Kober

[11] 3,774,589

[45] Nov. 27, 1973

[54] SELF CONTAINED ELECTROCHEMICAL
HEAT SOURCE

[75] Inventor: Frederick P. Kober, Bayside, N.Y.

[73] Assignee: Chem-E-Watt Corporation, Valley
Stream, N.Y.

[22] Filed: Aug. 30, 1971

[21] Appl. No.: 175,846

[52] U.S. Cl. 126/263, 44/3 A, 132/36.2 B,
136/86 A

[51] Int. Cl. F24j 1/04, F24j 3/04

[58] Field of Search 136/86 A, 111, 161;
126/263; 132/36.2 B; 44/3 R, 3 A, 3 C;
204/197; 219/224

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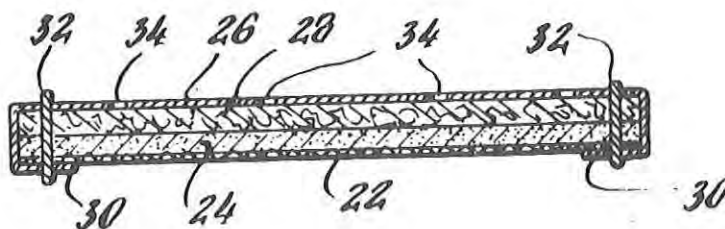
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[57] ABSTRACT

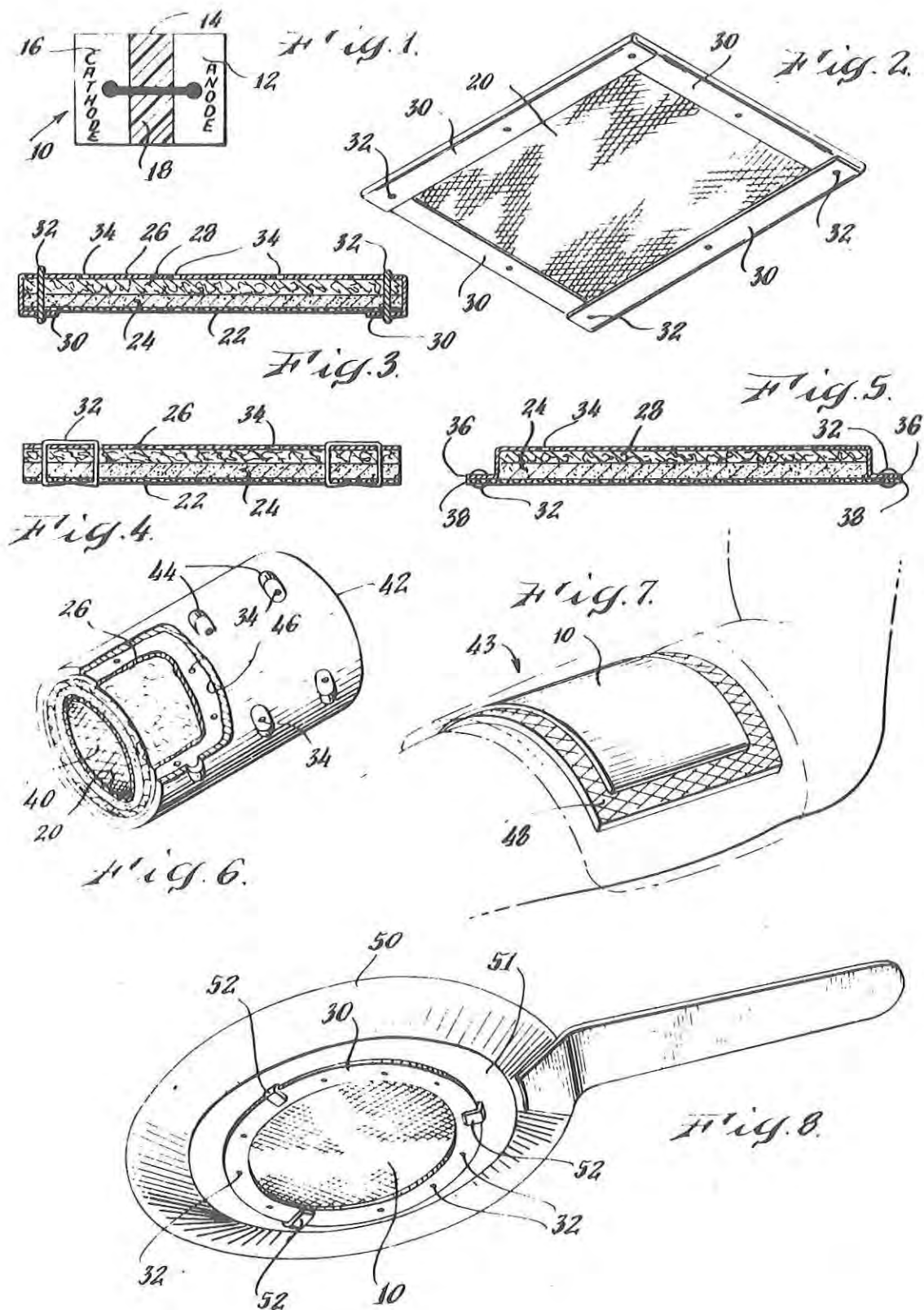
An electrochemical heat source is described wherein an electrochemical cell is provided with an electrical shorting member which is connected to the anode and cathode electrodes of the cell to enable the electric energy of the cell to be dissipated as heat. A safe non-toxic electrochemical heater for hair waving, hot compresses and similar uses is described wherein an anode in the form of a foil of aluminum or aluminum alloys is spaced by a non-conductive separator from an air depolarized activated carbon electrode. An electrolyte of a solution of table salt is employed to activate the heater. Various configurations and sandwich structures are described.

10 Claims, 8 Drawing Figures



Patented Nov. 27, 1973

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SELF CONTAINED ELECTROCHEMICAL HEAT SOURCE

This invention relates to an electric heat source generally and more specifically to a disposable self contained electrochemical heat source for use in hair waving devices, hot compresses and similar heating applications

BACKGROUND OF THE INVENTION

Several heat sources for permanent wave setting of hair have been proposed. In one such device an electric current is passed through a resistance wire to heat a closely adjacent tress of hair. Another device employs a solution in place of the resistance wire so that the electric current may heat the solution which vaporizes and thus both heats the tress of hair as well as provide fluid for hair absorption. The U.S. Pats. to Durham et al. Nos. 2,118,177 and Gentile, 2,055,099 are illustrative of such so-called "electrolytic" heaters. Disadvantages with such electrolytic heating devices reside in their need for a low voltage power supply and an inherent danger if the low voltage electrodes are inadvertently shorted.

Still another heating device utilizes the heat generated during a reaction of particular chemical materials. The U.S. Pat. to Pazul No. 2,725,060 is exemplary of this type of heater. As described in the Pazul patent, an aluminum foil is employed in a sandwich pad structure with an absorbant cotton sheet which was impregnated with dry stannous chloride. The structure is enclosed with aluminum foils and is suitably pierced to enable water to be introduced for activation of the pad. The water dissolves the stannous chloride and the solution migrates into contact with the aluminum to initiate a chemical reaction which generates heat. Many other exothermic heating pads have been proposed and utilize different materials; see for example U.S. Pat. Davis et al. No. 2,132,681.

The exothermic type of heating devices have disadvantages such as potential explosions, noxious fumes, toxicity and corrosive materials that may be injurious to persons. Control of the exothermic reactions is more complicated as illustrated by the reaction delaying chemicals described in the Pazul patent.

SUMMARY OF THE INVENTION

In a heating device in accordance with the invention an electrochemical cell such as may be employed in a battery is provided with a substantially integrally contained electrical conductor which is connected between anode and cathode electrodes of the cell to form a direct electrical short circuit. When the cell is activated, it produces an electrochemical reaction which converts chemical energy directly into electrical energy. The short circuit provided by the electrical conductor enables the cell to convert this electrical energy in a highly efficient manner into heat.

The electrochemical heating device of this invention dispenses with the need for external electrical power sources such as are required by electrolytic heaters. In fact, the short circuited construction of the electrochemical heating device provides a self contained structure which is safe to handle and free of voltage hazards. The internal voltage generated by the shorted electrochemical cell functions as a driving force to maintain a generation of heat. Hence, catalytic initiators, often employed in exothermic heating pads, may

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be dispensed with and the hazards associated with exothermic heaters are advantageously avoided.

An electrochemical heating device in accordance with the invention may be formed of non-toxic materials in a safe structure and may be advantageously stored for long time periods. For example, in one sandwich structure embodiment for an electrochemical heating device a cathode is formed of an activated carbon air electrode and the anode is formed of a metallic foil of aluminum or alloys thereof. A porous non-conductive separator is placed between the anode and cathode and is impregnated with table salt to form a sodium chloride aqueous electrolyte by the simple addition of water. The anode and cathode are electrically shorted to one another by employing metallic fasteners such as a staple applied through the structure to contact both electrodes. An electrical short may also be formed with a strip of the anode foil which is wrapped around the separator to contact the cathode. This electrochemical heater provides a safe and controllable source of heat with relatively inexpensive components.

It is, therefore, an object of this invention to provide a self-contained heating device which may be non-toxic and safe to handle and can be advantageously controlled to provide heat for a wide variety of applications such as permanent hair waving, body heating compresses and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of an electrochemical heating device according to the invention.

FIG. 2 is a perspective underside view of an electrochemical heating device in accordance with the invention.

FIG. 3 is a cross-section of the electrochemical device shown in FIG. 2.

FIG. 4 is a cross-section of an electrochemical heater with another embodiment for a short circuiting element in accordance with the invention.

FIG. 5 is a cross-section of an electrochemical heating device with still another embodiment for a short circuit element in accordance with the invention.

FIG. 6 is a perspective of an electrochemical heating device in accordance with the invention for use as a hair curler.

FIG. 7 is a perspective view of an electrochemical heating device in accordance with the invention for heating of a medical hot compress.

FIG. 8 is a perspective view of an electrochemical heating device in accordance with the invention for heating of a food pan.

DESCRIPTION OF THE EMBODIMENTS

With reference to the schematic illustration of FIG. 1 an electrochemical heating device 10 is shown formed of an anode 12, a separator 14, a cathode 16 and an integrally contained shorting member 18. The anode is an electrochemically oxidizable substance which is electrically conductive and may be made of commonly available metals and their alloys such as for example magnesium, Mg; tin, Sn; aluminum, Al; zinc, Zn; and iron, Fe.

The cathode 16 is an electrochemically reducible substance which is conductive. The cathode need not itself be a reducible substance but may provide an electrochemically active surface upon which another material, e.g. oxygen on an activated carbon air electrode,

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is reduced. Cathode materials may be formed of a wide variety of substances such as for example manganese dioxide; metadinitrobenzene; silver chloride, AgCl; silver oxide, Ag₂O; copper fluoride; copper chloride and air depolarized cathode structures of the carbon and metal types.

The separator 14 is formed of a non-conductive porous material such as cotton, felt or bibulous papers which enable ions of an electrolyte to freely pass between the anode and cathode.

An electrolyte formed of an ionically conductive medium is placed within the separator 14. The electrolyte may be an aqueous salt solution such as table salt, NaCl or may be selected from a host of many well known other electrolyte materials compatible with the selected anode and cathode materials.

The shorting element 18 is formed of an electrical conductor which is sized to support the short-circuiting current produced when the electrochemical heating device is activated. The shorting element further is integrally contained as part of the structure.

FIGS. 2 and 3 illustrate a sandwich structure cotton an electrochemical heating device 10 in accordance with the invention wherein an activated carbon air electrode 20 is employed as a cathode. The air electrode 20 is formed in a manner that is well known in the art. The air electrode 20 includes a screen 22 which may be formed of a metal such as nickel or iron and serves as a contacting electrode with a layer 24 of activated hydrophobic carbon. A metallic electrically conductive anode foil 26, formed of a chemically non-toxic material such as magnesium, aluminum, zinc or their commercially available alloys, is wrapped around a cotton separator layer 28 to contact the metal screen 22 with peripheral edges 30. Fasteners 32, such as rivets or staples, are employed to secure a connection between the anode 26 and cathode 20. The resulting electrical shorting element is formed by both the overlapping edges 30 and the fasteners 32 which thus also provide a mechanical connection of the parts of the heater.

The separator layer 28 is impregnated with a dry salt such as sodium chloride or alternatively the salt may be dispersed in dry form between the anode and cathode. The anode foil 26 is suitably apertured at a variety of areas 34 to enable water to penetrate the space between the anode and cathode and form a salt electrolyte.

Activation of the electrochemical heater 10 involves the simple step of applying water. As soon as the water has formed an electrolyte solution with the salt an electrochemical cell is formed whose output voltage is determined by the materials employed for the anode and cathode. The shorting path provided by the edges 30 and fasteners 32 then enables the electrical energy to be converted to thermal energy at an efficiency approaching 100 percent.

The thermal power generated is directly proportional to the square of the current and the internal resistance of the cell. One may thus control the current flow by selecting the thickness of the separator 28 and control the thermal power. The current flow also may be controlled by varying the resistance or cross-sectional area of the shorting element. For example, as shown in FIG. 3, the shorting path can be determined solely by the number and type of fasteners 32 (e.g. staples) which electrically interconnect the anode 26 to the cathode 20 without the use of an overlapping edge 30 shown in

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FIG. 3. Alternatively, a shorting element 18 such as shown in FIG. 5 may be used. In the structure of an electrochemical heater 10 as shown in FIG. 5 a peripheral edge 36 of the anode 26 is brought in registration with a correspondingly shaped edge 38 of the screen 22 and connected together either with a fastener 32 or spotwelds or other convenient means.

In the structure of FIG. 5 the contact of peripheral edges 36 and 38 provide an electrical short circuit of the cell. The electrical shorting conductor may thus be conveniently formed into an integral part of a self contained electrochemical heater and provides an efficient conversion of the chemical energy into heat.

The electrochemical heating device exhibits an advantageous flexibility in that it may be conveniently adapted to a variety of shapes. The thickness of the cell can be reduced to form a flexible structure that can fit in the recess of a hair heat protective cylinder 42 as shown in FIG. 6 or adapt to the contours of a body area for a hot compress 43 as shown in FIG. 7.

The hair heat protective cylinder 42 is formed of a plastic material and is provided with apertures 44 extending into a centrally located recess 40 into which an electrochemical cell such as shown in FIGS. 2 and 3 is placed. The aluminum foil anode electrode 26 is located adjacent to the cylinder wall 46 to enable the air electrode 20 to remain exposed to air. After insertion of the electrochemical heater 10 into recess 40 and submersion into water the heat is transferred through the cylinder wall 46 onto a person's hair that is wrapped around the cylinder to receive a permanent wave. Apertures 44 serve to enable the water electrolyte to provide water for hair absorption. After the chemical energy has been dissipated the electrochemical heater 10 may be removed from recess 40 and replaced by another so that the cylinder 42 can be re-used.

The hot compress 43 shown in FIG. 7 utilizes a cotton or other suitable water absorbent material 48 which is placed in contact with the body area to be treated (a forearm in FIG. 7). A flexible electrochemical heater 10 is located over the cotton compress 48 which may have been previously wetted. The electrochemical heater also may have been filled with liquid electrolyte or the water for formation of an electrolyte can be absorbed from the wetted cotton compress 48. A suitable string or other fastening device (not shown) may be employed to hold the hot compress 43 in place over the body area to be treated. The water electrolyte advantageously prevents overheating since excessive temperatures would cause a boiling off of the water. The aluminum or aluminum alloy anode and activated carbon depolarized air cathode electrode and table salt electrolyte form a non-toxic safe selfcontained localized heater suitable for such medical purposes.

In the arrangement shown in FIG. 8 an electrochemical heater 10 of enlarged surface area is shown removably mounted to the bottom 51 of a food pan 50. Adjustable clips 52 retain the heater 10 which is of circular shape for adequate heating of the pan 50.

The electrochemical heater 10 shown in FIG. 8 may be such as shown in FIG. 2 and 3 with an overlapping anode edge 30. The anode electrode is placed adjacent to the bottom 51 of the pan 50 while the air cathode electrode 20 is exposed to air even when the pan 50 rests on clips 52. After the heater 10 is mounted to the pan, the latter's bottom 51 is quickly dipped into water

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to wet the electrochemical heater 10 which is then activated to commence heating of the pan 50 and food placed therein.

The electrochemical heater as thus described may take a variety of forms. For example the electrochemical heater may be formed in an enclosed structure which includes an anode and a cathode and a liquid electrolyte. The anode and cathode may be externally accessible for connection to a separate shorting member. When the shorting member is connected in contact between the anode and cathode electrochemical heating is commenced in the manner as described with respect to the previous embodiments.

Having thus described an electrochemical heater its many advantages may be appreciated. It may be formed of non-toxic non-hazardous materials suitable for heating applications in medical or food related fields. The electrochemical heater may be stored for long time periods and can be readily activated by the simple addition of water where a dry electrolyte material is enclosed. The aluminum or aluminum alloy foil anode and air cathode electrochemical heater may be activated with table salt solution. The electrochemical heater may be controlled by sizing as desired. For example, in a thin sandwich structure form the heater can be cut with scissors to a desired size and shape. The amount of heat produced can be controlled by limiting the quantity of water supplied to the porous separator. A wide variety of materials may be employed in selecting a desired electrochemical heater.

What is claimed is:

1. A self contained electrochemical heat source without electrical terminals comprising

an electrochemical cell structure formed of a generally thin electrically conductive first member made of an electrochemically active oxidizable material and a generally thin electrically conductive second member made of an electrochemically active non-metallic reducible material, said first and second members having material for forming an ionically conductive electrolyte located therebetween, said first and second members being further selected for forming an electric heating current producing electrochemical couple capable upon electrical interconnection of the members of heating the electrochemical cell structure to a temperature which is sufficiently high for forming said self-contained heat source; and

a multiple of discrete electronically conductive elements extending between the electrochemically active oxidizable first member and the electromechanically active reducible second member for electrical contact therewith, said electronically conductive elements being spaced and selected to conduct an electric heating current between the first oxidizable member and the second reducible member for a uniform heating of the electrochemical cell structure during activation of the electrochemical cell.

2. An electrical heating source comprising

a sandwich shaped thin electrochemical cell structure including an anode and a cathode said anode being formed of a foil shaped material selected from the group consisting of aluminum, aluminum alloys, magnesium and magnesium alloys, said cathode being formed of an activated carbon depo-

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larized air electrode, a non-conductive separator located between the anode and cathode;

a multiple of discrete electrically conductive metal fastening elements pierced through the anode and cathode and electrically connected thereto to form a mechanically integral electrochemical cell structure;

said metal fastening elements being spaced from each other and selectively sized to further provide a desired conversion rate of electrochemical energy into heat upon electrolyte activation of the cell structure.

3. The electric heating source as claimed in claim 2 wherein said electrochemical cell further includes an electrolyte material formed of table salt to provide an ionizable table salt electrolyte upon the addition of water to the electrochemical cell.

4. The electrochemical heat source as claimed in claim 1 wherein the electronically conductive elements are in the form of mechanical metal fasteners extending through the oxidizable first member and the reducible second member to fasten hereto and retain the electrochemical cell into a thin sandwich shaped structure.

5. The electrochemical heat source as claimed in claim 1 wherein the electronically conductive elements are metallic conductors extending through the first and second members to electrically connect thereto and form a corresponding number of generally uniformly distributed discrete shorting points between the first and second members for a uniform heating of the electrochemical cell structure.

6. A self contained electrochemical heating source comprising an electrochemical cell structure formed of a generally thin electrically conductive first member made of an electrochemically active oxidizable material and a generally thin electrically conductive second member made of an electrochemically active non-metallic reducible material, said first and second members being selected to provide a substantial electrochemical driving voltage to convert electrochemical energy to heat, said first and second members being further selected for forming an electric heating current producing electrochemical couple capable upon electrical interconnection of the members of heating the electrochemical cell structure to a temperature which is sufficiently high for forming said self-contained heat source, a porous non-conductive separator interposed between the first and second members and formed of a material selected to retain an electrolyte, a plurality of discrete electronically conductive elements in contact with the first and second members for electrical contact therewith, said elements being spaced and selected to conduct a controlled electric heating current between the first oxidizable member and the second reducible member upon the introduction of an electrolyte into the porous separator to enable an electric heating of the sandwich structure.

7. The electrochemical heating source as claimed in claim 6 wherein the discrete electronically conductive elements are structured to mechanically fasten the first and second members into a thin sandwich shaped structure.

8. The electrochemical heating source as claimed in claim 7 wherein said first and second conductive members are formed with conductive peripheral segments extending outwardly from the porous separator, and with discrete electrically conductive elements being lo-

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cated to extend through said extending peripheral segments.

9. The electrochemical heating source as claimed in claim 6 wherein said elements are formed of electrically conductive metal fasteners operatively applied through said first and second members and said separator to retain the sandwich structure relationship and

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provide said electrical heating.

10. The electrochemical heating source as claimed in claim 6 wherein said discrete elements are metal staples extending through the first and second conducting members.

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APPENDIX B

Material: "Hot Sheet" Electro Chemical Heating Element

Company: Power Applications Inc. OE 4029-1181
Valley Stream, N.Y. 30 November 1973

Assay: Water extraction of spent heating element and determination of dissolved solids.

Authorized: 2 October 1973 Received: 8 November 1973

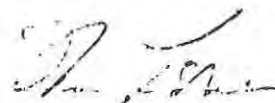
Procedure & Results: The heating element was immersed in water for 30 seconds, removed and placed in a Pyrex pie plate, covered and allowed to react. The contents became hot and remained so for about 25 minutes. In one hour the contents had cooled to room temperature. The corroded element was cut into small pieces after the metal staples were removed. All was placed in a glass beaker and digested with 200 ml of distilled water on a hot plate for 30 minutes. It was then filtered with suction and washed with water. The filtrate was clear and colorless.

The following data was obtained. The weight of the element was 28.7 grams. The volume of extract was 278 ml. A 15 ml aliquot upon drying at 110°C gave 0.523 grams of colorless crystals. Therefore, the total amount of salts in the extract was 9.7 grams representing 3.5% w/v of the extract.

Reviewed & Approved by:



HOWARD S. HARPEL, PH.D.
Director



THEODORE LEVENSON, PH.D.
Chief Chemist

Material: "Hot Sheet" Electro Chemical Heating Element

Description: Clear Colorless Liquid OE 4029-1181
Date 3 December 1973

Company: Power Application Inc.
Valley Stream, N.Y.

Purpose: Classification Under the Federal Hazardous Substances Act.

Assay: Primary Skin Irritation Study

Authorized: 2 October 1973 Received: 19 October 1973

Procedure: This study was performed using six albino rabbits. The procedure was that described under 16 CFR 1500.41.

Results: Scoring of the effects produced by the test material is shown in the attached chart.

The test material produced no erythema or edema to the intact or abraded skin sites in any of the animals.

Conclusion: "Hot Sheet" Electro Chemical Heating Element, as tested is not a primary irritant in accordance with the criteria as specified in 16 CFR 1500.3.

Reviewed & Approved by:



HOWARD S. HARPEL, PH.D.
Director



MARTIN MOLDOVAN, M.T.

PRIMARY SKIN IRRITATION IN RABBITS

WITH
Power Applications Inc.
"Hot Sheet" Electro Chemical Heating Element

RESULTS

		Exposure Time (Hours)	Exposure Unit (Value)					
			1	2	3	4	5	6
Erythema and eschar formation:								
Intact Skin	24		0	0	0	0	0	0
" "	72		0	0	0	0	0	0
Abraded Skin	24		0	0	0	0	0	0
" "	72		0	0	0	0	0	0
Subtotal			0	0	0	0	0	0
Edema formation:								
Intact Skin	24		0	0	0	0	0	0
" "	72		0	0	0	0	0	0
Abraded Skin	24		0	0	0	0	0	0
" "	72		0	0	0	0	0	0
Subtotal			0	0	0	0	0	0
Total			0	0	0	0	0	0
Score			0	0	0	0	0	0

Average = 0

Material: "Hot Sheet" Electro Chemical Heating Element

Description: Clear Colorless Liquid

Company: Power Application Inc.
Valley Stream, N.Y.

OE 4030-1181
3 December 1973

Assay: Acute Oral Toxicity Study

Purpose: To determine the acute oral toxicity in mice

Authorized: 2 October 1973

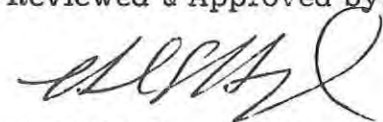
Received: 9 November 1973

Procedure & Results: Five groups of albino mice consisting of five males and five females in each group were set aside and observed for a period of one week to assure normalcy. The animals were then starved for 24 hours. Doses at levels as indicated in the table below were determined for each animal and administered directly into the stomach by means of a stomach tube. Following this the animals were allowed food and water ad libitum during a fourteen day observation period.

Dosage Level ml/kg	No. Rats Dosed															Mortality After 14 days
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	
2.5	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0/10
5.0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0/10
10.0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0/10
20.0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0/10
40.0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0/10

Conclusion: "Hot Sheet" Electro Chemical Heating Element, as tested in mice has an acute oral LD₅₀ greater than 40.0 ml/kg.

Reviewed & Approved by:



HOWARD S. HARPEL, PH.D.
Director



MARTIN MOLDOVAN, M.T.

Material: "Hot Sheet" Electro Chemical Heating Element

Description: Clear Colorless Liquid OE 4030-1181
3 December 1973

Company: Power Application Inc.
Valley Stream, N.Y.

Assay: Rabbit Eye Irritation Study

Purpose: To determine the deleterious effects of the test material to the rabbit eye.

Authorized: 2 October 1973 Received: 9 November 1973

Procedure: Six albino rabbits were employed in this eye irritation study.

The method employed was patterned after that of Draize, et al.

("Dermal Toxicity". J. H. Draize, Ph.D., Chief, Skin Toxicity Branch. Appraisal of the Safety of Chemicals in Foods, Drugs and Cosmetics, Association of Food and Drug Officials of the United States. pp. 46-59, 1959).

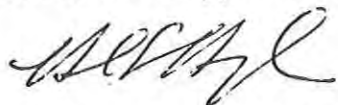
The test material was applied by placing 0.1 ml into the conjunctival sac. Application was made into the right and left eye of each of six test animals, the left eye was washed 30 seconds after the instillation of the test material.

Results: Scoring of the effects produced by the test material is shown in the attached charts.

The test material produced no corneal, iridial or conjunctival effects in any of the animals at the 6, 24, 48, 72 and 96 hour observation periods to either washed or unwashed eyes.

Conclusion: "Hot Sheet" Electro Chemical Heating Element, as tested in both washed and unwashed rabbit eyes is not an ocular irritant.

Reviewed & Approved by:



HOWARD S. HARPEL, PH.D.
Director


MARTIN MOLDOVAN, M.T.

Eye washed 30 sec. after instillation of the test material.

Rabbit Eye Irritation Study
Individual Daily Scores

OE 4030-1181

Date: 3 December 1973

Client: Power Application Inc.

Material: "Hot Sheet" Electro Chemical Heating Element

Hours:

Rabbit No.	Item	Tissue	Reading	6	24	48	72	96		
1 left eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		
2 left eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		
3 left eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		

See attached sheet for "Scale for Scoring Ocular Lesions."

Eyes washed 4 seconds after
instillation of test material

Rabbit Eye Irritation Study
Individual Daily Scores

Client: Power Application Inc

OE 4030-1181

Material: "Hot Sheet" Electro Chemical Heating Element

Date: 3 December 1973

Hours

Rabbit No.	Item	Tissue	Reading	6	24	48	72	96		
4 left eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		
5 left eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		
6 left eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		

See attached sheet for "Scale for Scoring Ocular Lesions."

Rabbit Eye Irritation Study
Individual Daily Scores

Eyes unwashed

OE 4030-1181

Client: Power application Inc.

Date: 3 December 1973

Material: "Hot Sheet" Electro Chemical Heating Element.

Hours:

Rabbit No.	Item	Tissue	Reading	6	24	48	72	96		
1 right eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		
2 right eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		
3 right eye	A	Cornea	Opacity	0	0	0	0	0		
	B	Cornea	Area	0	0	0	0	0		
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0		
	C	Iris		0	0	0	0	0		
		(2) Iris Total = (C) x 5		0	0	0	0	0		
	D	Conjunctiva	Redness	0	0	0	0	0		
	E	Conjunctiva	Chemosis	0	0	0	0	0		
	F	Conjunctiva	Discharge	0	0	0	0	0		
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0		
		Totals Added = (1 + 2 + 3)		0	0	0	0	0		

See attached sheet for "Scale for Scoring Ocular Lesions."

eyes unwashed

Rabbit Eye Irritation Study
Individual Daily Scores

OE 4030-1181

Client: Power Applications Inc.

Date: 3 December 1973

Material: "Hot Sheet" Electro Chemical Heating Element

Hours:

Rabbit No.	Item	Tissue	Reading	6	24	48	72	96	
4 right eye	A	Cornea	Opacity	0	0	0	0	0	
	B	Cornea	Area	0	0	0	0	0	
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0	
	C	Iris		0	0	0	0	0	
		(2) Iris Total = (C) x 5		0	0	0	0	0	
	D	Conjunctiva	Redness	0	0	0	0	0	
	E	Conjunctiva	Chemosis	0	0	0	0	0	
	F	Conjunctiva	Discharge	0	0	0	0	0	
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0	
		Totals Added = (1 + 2 + 3)		0	0	0	0	0	
5 right eye	A	Cornea	Opacity	0	0	0	0	0	
	B	Cornea	Area	0	0	0	0	0	
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0	
	C	Iris		0	0	0	0	0	
		(2) Iris Total = (C) x 5		0	0	0	0	0	
	D	Conjunctiva	Redness	0	0	0	0	0	
	E	Conjunctiva	Chemosis	0	0	0	0	0	
	F	Conjunctiva	Discharge	0	0	0	0	0	
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0	
		Totals Added = (1 + 2 + 3)		0	0	0	0	0	
6 right eye	A	Cornea	Opacity	0	0	0	0	0	
	B	Cornea	Area	0	0	0	0	0	
		(1) Cornea Total = (A x B) x 5		0	0	0	0	0	
	C	Iris		0	0	0	0	0	
		(2) Iris Total = (C) x 5		0	0	0	0	0	
	D	Conjunctiva	Redness	0	0	0	0	0	
	E	Conjunctiva	Chemosis	0	0	0	0	0	
	F	Conjunctiva	Discharge	0	0	0	0	0	
		(3) Conjunctiva Total = (D+E+F)x2		0	0	0	0	0	
		Totals Added = (1 + 2 + 3)		0	0	0	0	0	

See attached sheet for "Scale for Scoring Ocular Lesions."

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		6. PERFORMING ORG. REPORT NUMBER
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) An electrochemical heating element which is activated by immersion in water was evaluated as a means for heating military field rations. Heating elements measuring 155 cm ² (24 square inches) and having a dry weight of approximately 30 grams were the basis of the experimental program. Continued on reverse side.		

19. Key Words

	Link A Role Weight	Link B Role Weight
Design	8	
Optimization	8	
Devices (Electrochemical)	9	10
Electrochemical power generation	9	10
Heat Processing	4	4
Thermal Processing	4	4
Military Rations	4	4
Tests		8
Feasibility		8
Heat Transfer		9
Hot Sheet		10

20. Abstract (Continued)

The basic heating element consisted of an anode-cathode-electrolyte/separator sandwich-type thin structure which was connected with an internal current carrying network. Two electrochemical heating element formulations were investigated in detail, i.e., an air formulation which required access to atmospheric oxygen for efficient operation, and a non-air formulation which contained the oxidizing agent within the structure and operated efficiently in any ambient.

Test data are presented which show that heating element performance was essentially independent of activation time (soak time in water), and the temperature of the heating element climbed above 100°C (212°F) in under three minutes, reaching a maximum skin temperature in the range 110°C (230°F) to 122°C (252°F). The heating elements produced 11.6 to 14.1 Kcal (46 to 56 Btu) in the first seven minutes of operation, with a total heat density of 0.68 to 0.70 Kcal per gram (76.4 to 84.8 Btu per ounce). Using the non-air formulation it was possible to heat flex-pack food rations above 77°C (170°F) in eight minutes and above 93.3°C (200°F) in 11 to 15 minutes.

Toxicological test data are given which show the air formulation heating element to be nontoxic and pose no hazards or safety concerns for the user. Based on electrochemical considerations, the non-air formulation can also be anticipated as being nontoxic and completely safe to use.