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(54) **Title:** POROUS OXYGEN ACTIVATED HEATER

(57) **Abstract:** An substrate heater includes at least a wet porosity of between 15-35% to allow for sufficient electrolyte solution and porosity for access of a reducing agent within the substrate and oxygen.

TITLE OF THE INVENTION

POROUS OXYGEN ACTIVATED HEATER

CROSS REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to U.S. Provisional Application No. 61/583,410 filed on January 5, 2012, and to U.S. Provisional Application No. 61/583,418 filed on January 5, 2012, both of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[002] The invention relates to a porous heater that uses oxygen (generally atmospheric oxygen) as a source of a chemical reactant for an exothermic reaction.

BACKGROUND OF THE INVENTION

[003] Portable flameless heaters are currently used in a variety of applications, such as heating comestible, medical, and consumer items.

[004] Some heaters utilize the reaction of magnesium and water to produce heat. While such a heater produces a sufficient amount of heat, hydrogen gas is product of the exothermic reaction. This can generate safety, transportation, storage, and disposal concerns. In addition, the exothermic reaction requires water, which can be tiresome to constantly carry around.

[005] Other heaters utilize the heat from the reaction of "quicklime" (calcium oxide) and water. While this reaction does not generate hydrogen as a byproduct, it still is based upon using water as a reactant. Accordingly, this type of heater also requires a user to constantly have a sufficient amount of water. Furthermore, the specific energy of the system is low (approximately 1.2 kJ per gram of calcium oxide), making it a suitable, but ineffective, alternative to the magnesium and water heaters.

[006] In addition to the water-based heaters described above, it is known to utilize oxygen-based heaters. Oxygen-based heaters, such as those described in U.S. Pat. Nos. 5,984,995, 5,918,590 and 4,205,957, have certain benefits over water-based heaters.

[007] First, oxygen-based heaters do not require the addition of water to generate heat. Second, because oxygen-based heaters generate heat only in the presence of oxygen, the exothermic reaction can be stopped by simply preventing oxygen access. In addition, some such heaters allow for the exothermic reaction to be restarted at a later time by re-introducing oxygen. Furthermore, since oxygen is abundant in the atmosphere, these heaters do not require mixing of components or additional reactants (as oxygen from the atmosphere is the only missing reactant).

[008] The assignee of the present invention has provided oxygen-base heaters and various packages for same. *See, e.g.*, U.S. Pat. No. 7,722,782, issued on May 25, 2010; U.S. Appl. Ser. No. 12/376,927, filed on February 9, 2009; U.S. Appl. Ser. No. 12/874,338, filed on September 2, 2010; U.S. Appl. Ser. No. 61/583,418, filed on January 5, 2012; U.S. Appl. Ser. No. 61/714,526, filed on October 16, 2012; U.S. Appl. Ser. No. 61/716, 226, filed on October 19, 2012; U.S. Appl. Ser. No. 61/716,279, filed on October 19, 2012; and, U.S. Appl. Ser. No. 61/716,906, filed on October 22, 2012, all of which are incorporated herein by reference.

[009] These disclosed heaters and packages are successful at providing an oxygen based heater and/or package for same.

[010] Since these heaters typically are a porous composite structure and rely on the reaction of atmospheric oxygen with a chemical constituent of the heater composite, the porosity of the composite heater is an important feature for providing an efficient and effective heater.

[011] The present invention is directed to providing a heater that has sufficient porosity so as to be efficient and effective without compromising performance, as well as other benefits.

SUMMARY OF THE INVENTION

[012] In one aspect of the present invention, the present invention is directed towards an oxygen based heater with a wet porosity of approximately 15-35%. The heater may also include a dry porosity of approximately 60%.

[013] In another aspect of the present invention, the present invention is directed towards a heater with the wet porosity of approximately 15-35% in a package.

[014] The dry porosity refers to the porosity of the heater sheet before the electrolyte is introduced, and the wet porosity refers to the porosity of the sheet after electrolyte has been added. The organization of the components within the heater sheet to achieve these porosity ranges is an important attribute to ensure that the heater includes the right micro-environment for the oxygen initiated reaction to occur and these porosity ranges are an indication of establishing the right microstructure.

[015] If the dry or wet porosity is too small, oxygen diffusion to the reaction sites is reduced and, therefore, the heater performance is reduced.

[016] On the other hand, if the dry porosity is too high, the integrity of the heater sheet is compromised and this can impact the ability to manufacture and handle the sheet.

[017] Similarly, if the wet porosity is too high, the performance of the heater sheet will be reduced due to a lack of electrolyte to support the reaction.

[018] Accordingly, the present invention is also directed at providing a heater with a wet porosity sufficient to reach a desired temperature in an acceptable amount of time.

[019] These and other benefits should be apparent to those of ordinary skill in the art in view of the present disclosure.

[020] It is to be understood that the aspects and objects of the present invention described above may be combinable and that other advantages and aspects of the present invention will become apparent to those having ordinary skill in the art upon reading the following description of the drawing and the detailed description thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[021] The present invention will become more fully apparent from the following description and appended claims, taken in conjunction with the accompanying drawings. Understanding that the accompanying drawings depict only typical embodiments, and are, therefore, not to be considered to be limiting of the scope of the present disclosure, the embodiments will be described and explained with specificity and detail in reference to the accompanying drawings as provided below.

[022] Figure 1 is a graph showing the temperature after 5 minutes for various heaters according to the present invention.

[023] Figure 2 is a graph showing the time it takes various heaters according to the present invention to achieve a 100 °F temperature rise (starting from a 40 °F temperature).

[024] Figure 3 is a graph showing the time it takes heaters according to the present invention to reach their respective maximum temperatures.

[025] Figure 4 is a side cutaway view of an embodiment of a heater according to the present invention in a package.

DETAILED DESCRIPTION OF THE DRAWINGS

[026] While this invention is susceptible of embodiment in many different forms, there is shown in the drawings and will herein be described in detail one or more embodiments with the understanding that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the invention to the embodiments illustrated.

[027] Reference throughout this description to features, advantages, objects or similar language does not imply that all of the features and advantages that may be realized with the present invention should be or are in any single embodiment of the invention. Rather, language referring to the features and advantages is understood to mean that a specific feature, advantage, or characteristic described in connection with an embodiment is included in at least one embodiment of the present invention. Thus, any discussion of the features and advantages, and similar language, throughout this specification may, but does not necessarily, refer to the same embodiment.

[028] Various composite heaters were prepared by forming sheets of material using a standard mixing and rolling process developed by the and with the formulation shown in Table 1. The heater includes Zn as a reducing agent. The heater also includes carbon treated with $KMn0_4$ as a promoter and a polytetrafluoroethylene as a binding agent that holds the chemical constituents together and allows for a flexible composite heater to be made. A

preferred carbon is Ketjenblack KB300J produced by AkzoNobel Polymer Chemicals, and a preferred polytetrafluoroethylene is a powdered polytetrafluoroethylene such as Laurel Product's Marzon-10. Other chemical constituents could be included and still fall within the scope of the present invention. For example, the heater may also include additives to improve stability such as indium, bismuth, stannates, or silicates.

[029] Table 1

Sheet Formulation	g	w/w %
Zn	3375	81.70%
$KMnO_4$	1.9	0.04%
Carbon	268.1	6.49%
polytetrafluoroethylene	486	11.76%
Total	4131.0	100.0%

[030] The properties of the produced composite heaters are shown in table 2. The dry porosity is determined by calculating the theoretical density of the components in the dry heater sheet and then subtracting the apparent density from the theoretical density. The difference is then divided by the theoretical density to determine the dry porosity.

[031] Table 2

Sheet Properties	Weight, g	Thickness (inches)	Thickness (cm)	Volume	Apparent Density g/cm3	Dry % Porosity
Max	30.34	0.050	0.127	15.77	2.00	64.3%
Min	28.20	0.048	0.122	15.14	1.79	60.0%
Average	29.13	0.049	0.124	15.43	1.89	62.3%

[032] The composite heaters were activated with various amounts of a 20%> (by weight) potassium chloride solution and assembled into pouches. The different amounts of the electrolyte solution are shown in Table 3. The use of the various amounts also resulted in different wet porosities, also shown in Table 3. The wet porosity is determined by calculating the free volume in the dry heater sheet, subtracting the volume of activator solution added to the sheet to determine the final free volume and then dividing by the sheet volume.

[033] Table 3

	% Porosity	Free Volume, cm^3	Activator Solution Weight, g	Total Liquid Volume, cm^3	Final Free Volume, cm^3	Final Wet Porosity
Group A	61.9%	9.37	4.9	4.3	5.09	33.6%
Group B	61.9%	9.37	6.4	5.5	3.83	25.3%
Group C(a)	60.9%	9.23	8.0	7.0	2.27	15.0%
Group C(b)	63.6%	10.03	7.8	6.7	3.29	20.8%
Group D	63.6%	10.03	9.2	8.0	2.02	12.8%
Group E	62.8%	9.90	10.88	9.46	0.44	2.8%

[034] The performance of each of the composite heaters was evaluated in a standard eight ounce water bag test in which the temperature of water is monitored during the heating process.

[035] The parameters of the test that were measured are as follows: the temperature rise in five minutes; the time to raise the water temperature by 100 °F from an initial temperature of 40 °F; the time to reach the maximum temperature; and, the maximum temperature achieved. In these tests, the 140 °F desired temperature was chosen as a desired temperature because a temperature of 140 °F is a desired temperature for a comestible when heated from a cold temperature. As used herein "desired temperature" means a temperature that is chosen and which represents a temperature sufficient to achieve the purposes of the heater (i.e., heat a comestible, boil water, melt ice, etc.).

[036] Figures 1-3 illustrate the effect of wet porosity on the performance of heater pouches.

[037] More specifically, Fig. 1 shows the temperature rise in five minutes for various composite heaters. As shown and demonstrated by Fig. 1, the lower the porosity, the slower the temperature rise (in the initial five minutes). This indicates a lack of oxygen access to reaction sites within the composite heater. By increasing the wet porosity, it is believed there is more access to the reaction sites within the heater structure leading to a faster rate of reaction and higher temperature at five minutes.

[038] The effect of wet porosity on the time that it takes for a heater pouch to achieve a 100 °F temperature rise in an eight ounce water bag test is shown in Fig. 2. As shown, in the range of 15-35% wet porosity there is only a small impact on the time to 100 °F rise.

However, lowering the wet porosity to less than 10% greatly increases the time needed to achieve the same temperature rise. This effect is believed to also indicate a reduced oxygen access to reaction sites leading to a slower reaction rate and thus, a longer time for the temperature rise. As a result, it is believed that more than approximately 12 minutes to reach the desired temperature was unacceptable. An "acceptable time" would be a time in which the heater reaches the desired temperature (and thus can sufficiently perform its desired function).

[039] Finally, the effect of wet porosity on the time it takes to reach the maximum water temperature in the test is shown in Fig. 3. As is demonstrated in Fig. 3, the time to maximum increases as the wet porosity decreases. This trend is believed to reflect the lower access to reaction sites due to a decrease in available porosity in the heater sheet.

[040] As shown in Fig. 4, heater 6 may be disposed inside of package 5. Such package 5 may be a pouch comprising first sheet 9 and second sheet 12. Second sheet 12 includes a plurality of openings 14 forming oxygen access portion 11. Disposed over at least oxygen access portion 11 may be flap 8 (or other similar structure capable of selectively opening and preferably re-closing). Flap 8 may include adhesive 10 to secure flap 8 over oxygen access portion 11 when the production of heat is not desired or no longer desired. As shown, package 5 may include side 7 without any openings 14; however, the depicted package is merely a representative package which selectively prevents oxygen access to heater 6 to control an exothermic reaction between heater 6 and atmospheric oxygen.

[041] Heater 6 is made according to the present invention, and as disclosed above, is a porous flexible substrate which includes a reducing agent, a binder, and a promoter. Heater 6 is also activated with an electrolyte solution. Furthermore, heater 6 has a wet porosity of between approximately 15-35%.

[042] Such a heater will provide a sufficient amount of heat and reach the desired temperature within an acceptable amount of time, based in part, upon the porosity of the heater itself.

[043] It is to be understood that additional embodiments of the present invention described herein may be contemplated by one of ordinary skill in the art and that the scope of the present invention is not limited to the embodiments disclosed. While specific embodiments

of the present invention have been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention, and the scope of protection is only limited by the scope of the accompanying claims.

CLAIMS

What is claimed is:

1. A heater comprising:

a composite heater substrate that exothermically reacts with oxygen, wherein the composite heater substrate has a wet porosity of between 15-35%.

2. The heater of claim 1 wherein the composite heater substrate has a dry porosity of approximately 60%.

3. The heater of claim 1 wherein the composite heater substrate has a dry porosity of approximately between 60-65%.

4. The heater of any one of claims 1 through 3 wherein the heater comprises: a reducing agent, a binder, a promoter and an electrolyte.

5. A heater comprising:

a porous flexible substrate including a reducing agent, a binder, and a promoter, the porous flexible substrate being activated with an electrolyte solution; and,

a package surrounding the porous flexible substrate to selectively prevent oxygen access to the porous flexible substrate to control an exothermic reaction between the porous flexible substrate and atmospheric oxygen,

wherein the porous flexible substrate has a wet porosity of between approximately 15-35%.

6. The heater of claim 5 wherein the porous flexible substrate has a dry porosity of approximately 60%.

7. The heater of claim 5 wherein the porous flexible substrate has a dry porosity of approximately between 60-65%.

8. The heater of any one of claims 5 through 7, wherein the heater includes approximately 82% by weight of the reducing agent, approximately 6.5%> by weight of promoter, and approximately 12% of binder.

9. The heater of claim 8, wherein the heater has a dry porosity of approximately 60%.

10. The heater of any one of claims 5 through 9, wherein the heater includes between approximately 5-8 g of electrolyte solution.

11. The heater of claim 10, wherein the electrolyte solution is a 20% by weight solution of potassium chloride.

12. A heater comprising:

a flexible substrate that includes a binder and a reducing agent that will produce heat in the present of oxygen;

the flexible substrate being porous;

the flexible substrate being activated by an electrolyte solution such that the flexible substrate includes a wet porosity sufficient to achieve a desired temperature in an acceptable amount of time.

13. The heater of claim 12, wherein the desired temperature is 140 °F.

14. The heater of claim 12 or 13, wherein the acceptable amount of time is less than 15 minutes.

15. The heater of any one of claims 12 through 14, wherein the wet porosity is between approximately 15-35%.

16. The heater of any one of claims 12 through 15, wherein the desired temperature is approximately 100°F than an initial temperature of the heater.

17. A heater as described herein.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/20353

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C06B 45/00 (2013.01)
USPC - 149/2
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) .
IPC (8) - C06B 45/00 (2013.01)
USPC : 149/2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 149/40; 126/263.01

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase - heater heating heated microheater porosity pores porous voids wet wetting wetted binder electrolyte potassium magnesium reducing air oxygen
Google - (personal OR portable) oxygen-activated heater wet-porosity reducing-agent binder electrolyte

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2010/016301 1 A1 (TINKER, ET AL.) 01 July 2010 (01.07.2010), paras [0012], [0023], [0045], [0054]	12-14 ----- 4-9
X --- Y	US 3,301,250 A (GLASSER) 31 January 1967 (31.01.1967), col 1, ln 12-21; col 3, ln 44-54; col 4, ln 1-25	1-3 ----- 4-9
A	US 2009/0293859 A1 (COFFEY, ET AL.) 03 December 2009 (03.12.2009), entire document	1-9, 12-14
A	US 2,533,958 A (ROOT, ET AL.) 12 December 1950 (12.12.1950), entire document	1-9, 12-14
A	US 4,522,190 A (KUHN, ET AL.) 11 June 1985 (11.06.1985), entire document	1-9, 12-14

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 February 2013 (17.02.2017)	19 MAR 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/20353

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 17
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
omnibus claim

3. ¾ Claims Nos.: 10-1 1,15-16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. Ill Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.