A self-healing system for an insulation material initiates a self-repair process by rupturing a plurality of microcapsules disposed on the insulation material. When the plurality of microcapsules are ruptured, reactants within the plurality of microcapsules react to form a replacement polymer in a break of the insulation material. This self-healing system has the ability to repair multiple breaks in a length of insulation material without exhausting the repair properties of the material.
Outer Insulation
Chemical Heater
Fusible Polymer
Insulation material

Damaged Insulation
Repaired Insulation

FIG. 1

Protective adhesive coating
Kapton
Chemical Heater

Microencapsulated reactants to produce a polyimide

FIG. 2
SELF-HEALING WIRE INSULATION

CROSS-REFERENCE TO RELATED APPLICATION


ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

1. Field of the Invention
The present invention relates to a self-healing system, primarily for repairing a break in an insulation material, including a plurality of microcapsules containing at least two reactants that form a polymer upon the rupturing of the microcapsules.

2. Description of Related Art
An electrical conductor generally contains electrical wires that are protected by surrounding the electrical conductor with an insulation material. Due to various stresses applied to the electrical wires and insulation material, a break may occur in a portion of the insulation material. Often, this break is not observed or even monitored. Additionally, any such break in the insulation material may, because of inaccessibility, be difficult to repair. Insulation breaks can cause the electrical wires to short, thus acting as a source of ignition if combustibles are present. Additionally, the breaks may lead to the prevention of power transmission, the monitoring of a transducer or the control of a relay valve. This, in turn, may lead directly to a catastrophic breakdown of an electrical system. Typically, a break in the insulation material may go undetected for an extended period of time before an electrical problem occurs, which may endanger the entire electrical system. For example, catastrophic failures could occur if the electrical system is present in aircraft and spacecraft, such as the NASA space shuttle.

Conventional methods of repairing the insulation material result in a repair that has a much larger diameter than the original insulation material and the thermal properties of the repaired insulation material are diminished. For example, Boeing procedure OEL (orbiter electrical)-4000-Wire/Cable: Mystik Tape Repair for 0-10 AWG Single Application requires that twelve layers of Mystik 7503 (Teflon tape, ½ inch wide, pressure sensitive adhesive) are wrapped over the break in the insulation material. Then the end of the Mystik 7503 tape wrap is secured with a spot tie. The type of insulation material repaired by this procedure is not specified, but requires that twelve layers of Mystik 7503 tape wrap is secured with a spot tie. The type of insulation material repaired by this procedure is not specified, but requires that twelve layers of Mystik 7503 tape wrap is secured with a spot tie. The type of insulation material repaired by this procedure is not specified, but requires that twelve layers of Mystik 7503 tape wrap is secured with a spot tie.

25 Polyimides can be prepared by reacting dihydrides with diamines to yield poly(anic acids). Once the poly(anic acids) are heated, a rearrangement occurs followed by a loss of water to produce the polyimidies. This chemistry was successfully commercialized by DuPont under the trade name of KAPTON. There are a number of KAPTON polyimide polymers that have the general chemical structure that is given below in Formula 1:

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{N} & \quad \text{O} \\
\text{O} & \quad \text{H}
\end{align*}
\]

A large number of polyfluorocarbons, such as TEFLOW, are known and the methods of synthesis have been well documented in the literature. Most of the preparation procedures for fluorocarbon polymers start with gas-phase reactions at high pressures. Preparation of these materials would not be practical on a small-scale, which means that it is unlikely that a direct synthesis method could be found for the polyfluoro- carbons. However, heat-sealable materials are commercially available, as indicated in the discussion above under the clamshell repair method.

Many chemical reactions are exothermic, i.e., combustion processes, which rely on oxygen in the air to react with a fuel. Other materials release heat when two reagents are combined, as illustrated by the hypergolic reactions that occur when hydrazine is reacted with nitrogen tetroxide. These reactions can occur in the gas, liquid, or solid phases and their rates cover a wide range. Some compounds react under very controlled conditions to produce products that are non-hazardous and/or non-toxic. For example, development of the chemical heater for the United States Army meals-ready-to-eat (MRE) led to a number of controlled reactions that may only require water to initiate the exothermic reaction. For repair systems
that require local heating to melt a specific material or to stimulate a polymerization or rearrangement reaction, chemical heaters could be the solution. This approach would apply the heat energy to the specific location and minimize the impact to other components.

While there is no known self-healing electrical insulation material, there has been some recent investigation with composite materials. In particular, it is known to encapsulate a reactive monomer and disperse a polymerization catalyst in the structural composite. The arrangement of dispersing the catalyst in the structural composite requires that the reactive monomer diffuse through the structural composite before a repair can be initiated. Therefore, it would be advantageous to devise a self-healing system for insulation material that works immediately after the break in the insulation material occurs.

**BRIEF SUMMARY OF THE INVENTION**

The present invention is directed toward a self-healing system whereby a force, or a stress, that causes a break in an insulation material serves to initiate a self-repair process. It is recognized that the force from an impact is not the only source of insulation break, e.g., the break could result from stress-cracking due to aging or heating. As a result of the stress caused by the break or other forces, insulation fluids containing a replacement polymer flow into the break in the insulation material and begin the self-repair process. The self-healing system is similar in size to an initial insulation material and preferably should have similar insulating and strength characteristics. The self-healing system has the ability to repair multiple breaks in a length of insulation material without exhausting the repair properties of the material.

The self-healing system includes a plurality of microcapsules containing reactant that may be applied to the insulation material in a number of ways. For example, a wire conductor may be used to disperse the microcapsules into layers of the insulation material during its manufacture. Alternatively, a repair kit may be provided including a material containing the microcapsules. The preferred repair kit provides for the manual application of the self-healing system to a break in the insulation material. Once the material containing the microcapsules is applied, a sufficient stress is produced to cause the microcapsules to rupture, initiating the self-repair process. If a repair kit is utilized, the microcapsules are preferably coated on a plastic strip to form a repair tape that would be wrapped around a break in the insulation material.

The ability to self-repair a break in insulation material is a unique attribute of the present invention. Likewise, the present invention provides the added safety advantage of eliminating a single point failure that often occurs with electrical wiring.

Although the present invention may be used in a variety of electric systems, the present invention has clear application to the spacecraft and aircraft industries where severe, if not fatal, consequences may occur due to compromise of electrical insulation material at a critical stage of operation of the aircraft or spacecraft.

**BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)**

The features and advantages of the present invention will become apparent from the following detailed description of a preferred embodiment thereof, taken in conjunction with the accompanying drawings, in which:

FIG. 1 is an illustration of a damaged insulation material with a repair tape over the break;

FIG. 2 is an illustration of a section of KAPTON repair tape showing the micro-encapsulated reactants that will produce the polyimide replacement polymer that bonds to the KAPTON insulation material; and

FIG. 3 is an illustration of a preferred microcapsule containing a first reactant and a second reactant.

**DETAILED DESCRIPTION OF THE INVENTION**

A self-healing system for self-repairing a break in an insulation material is formed using a plurality of microcapsules containing reactants that form a replacement polymer upon rupturing of the microcapsules. Preferably, at least two reactants, known herein as a first reactant and a second reactant, are contained within the self-healing system. The preferred microcapsules include the following reactants: 1) a monomer and a catalyst; 2) two reactants of a condensation polymer; or 3) a fusible polymer and a chemical heater. In a preferred embodiment, the reactants are contained in a single microcapsule having a reactant shell around a reactant core. In an alternate preferred embodiment, the reactants are contained in separate microcapsules that are mixed together. Once the microcapsules are prepared, they are preferably dispersed into one layer of insulation material on a wire conductor. When the wire conductor is subjected to a stress and a break occurs in the insulation material, the microcapsules rupture and the reactants react forming an insulation fluid containing the replacement polymer, which initiates a self-repair process. The microcapsules may be combined with a foaming agent to increase the volume of the insulation fluid used to self-repair the insulation material. The insulation fluids flow into a break in the insulation material and when the reaction is complete, the break is filled with the replacement polymer, thus maintaining the integrity of the insulation material. If a number of breaks occur at different locations along the insulation material, each break would initiate the rupture of adjacent disposed microcapsules and the self-repair process would begin.

The self-healing system containing the microcapsules may be applied to the insulation material in a number of ways. For example, the plurality of microcapsules can be dispersed into a repair material. In a preferred embodiment, the repair material is itself the insulation material that surrounds the wire conductor. When the repair material is itself the insulation material, the microcapsules are dispersed in a layer of the insulation material during its manufacture. This assures that the length of insulation material includes sufficient microcapsules to self-repair any break that may occur whether or not it is accessible to monitoring. Alternatively, a repair kit may be provided including the repair material which is manually applied to a break in the insulation material at an area that does not already contain the microcapsules. After the repair material is applied to the area of the insulation material, the area is subjected to a sufficient stress to cause the microcapsules to rupture and initiate the self-repair process. If a repair kit is utilized, the microcapsules are preferably coated onto a repair material, such as a strip of material preferably a plastic strip, to form a repair tape that is wrapped around the area where the original insulation material has broken. FIG. 1 shows the preferred embodiment whereby the self-healing system is in the form of a repair tape that is wrapped around the break in a damaged insulation. In this preferred embodiment, the self-healing system contains a fusible polymer to fill the break and a chemical heater to bond the fusible polymer to the insulation material. Provisions to stabilize the replacement polymer and to retard heat loss during the self-repair process would also be included. By way of example, a
reactants. Some classes of polymers which can be prepared
in continuous phases where polycondensation occurs virtually instanta-
neously may be used in the fabrication of a polyimide that bonds
particles imbedded into their surface and a very small amount
resulting in the generation of heat. A variety of known chemi-
tical healar are used in the United States Army’s Meals-Ready-to-Eat (MRE). These preferred chemical heat-
ters are activated by water, oxygen in the air, or corona dis-
charge that results when the wire conductor is exposed. For
example, micrometer-sized magnesium particles that contain iron
particles imbedded into their surface and a very small amount
of sodium chloride could be used in this chemical heater
system.

A preferred self-healing system that can self-repair a break
in insulation material containing a polyimide, such as KAP-
TON, would require either the use of a polyimide copolymer
that has a softening point that is lower than the insulation
material or the fabrication of a polyimide that is similar to the
insulation process is disclosed in “Microencapsulation Process
for Producing Microcapsules” by George Baxter, whereby microencap-
sulation processes can be found in the literature. A preferred microencap-
sulation process is disclosed in “Microencapsulation Process in Business Form” by George Baxter, whereby microencap-
sulation by interfacial polycondensation is used to produce a thin,
high molecular weight polymer film as the polymer
shell. Essentially, the process comprises bringing two reac-
tants together at a reaction interface between the emulsion
phases where polycondensation occurs virtually instanta-
neously to form a thin film insoluble in the parent media of the
reactants. Some classes of polymers which can be prepared
by this technique and which have been used to microencap-
sulate a variety of materials include polyamides, polyure-
thanes, polysulfonamides, polyesters, polycarbonates, and
polysulfonates. Virtually any material can be microencapa-
sulated by the process provided reasonable precautions are
exercised to avoid selecting materials which tend to interfere
with the interfacial polycondensation reaction. The materials
to be microencapsulated can be gases, liquids or solids which
are water insoluble or water soluble. To control the formation
of the microcapsules, one reactant for the condensation poly-
mer, together with the material to be encapsulated, is first
emulsified in a continuous phase and thereafter additional
continuous phases containing the second reactant is added to
the emulsion. The polymer shell will then form at the inter-
face of the dispersed substance and encapsulate the material.

In a preferred embodiment, further described in the Experimental
Data section below, two difunctional reactants are microencapsulated such that they will undergo condensation
polymerization to produce a polydiamide. Each microcapsule
is produced by interfacial polymerization. The reactant core
preferably contains a first monomer, or first reactant, of seba-
coyl chloride and the reactant shell preferably contains a
second monomer, or second reactant, of hexamethylenedi-
amine. Each of these monomers is microencapsulated so that
the first monomer forms the reactant core of the encapsulated
second monomer. When the microcapsule ruptures, the
microcapsules produce a replacement polymer comprising
the two monomers, in this case, Nylon 6, 10.

A foaming agent may be applied to the self-healing system
to increase the volume of the final, insulation fluid used in the
self-repair process. The foaming agent may be contained in
the same microcapsule that contains a reactant and disposed
as a foaming shell around the reactant core. Alternatively, the
foaming agent may be contained in separate microcapsules
that are mixed with the microcapsules containing the reac-
tants. In either case, when the microcapsules are stressed, as
may occur during breakage of the insulation material, they
rupture and automatically self-repair the break.

Experimental Data

Sebacoyl Chloride/Hexamethylenediamine Microcapsules

All chemicals used herein were received from Aldrich
Chemical. Multiple surfactants may be used in the microen-
capsulation process. First, a solvent system consisting of an
oil-in-water (o/w) system, wherein the oil phase was hexane,
was used. The first surfactant used was Igepal CO-520, with
a hydrophilic-lipophilic balance (HLB) number of 10.0. The
amount of surfactant used was 4.6% (w/w) relative to water.

Addition of hexane to a cloudy water/surfactant mixture,
followed by agitation at 1500 RPM for 30 seconds, did not
produce a stable emulsion. Therefore, other surfactants were
investigated. Igepal CA-520 (HLB=10.0) was used and again
the emulsion was not stable. Igepal CO-720 (HLB=14.2) was
used and formed a more stable emulsion (stable for 2-3 min-
es). Igepal CA-720 (HLB=14.6) formed an emulsion that
was stable for 1-2 minutes. Gelatin formed a stable emulsion.
Therefore, food grade gelatin was used for a series of experi-
ments.

Dissolved in 12.0 ml of water were 0.075 g (0.65 mmol)
hexamethylenediamine, 0.0050 g (1.25 mmol) sodium
hydroxide and 0.600 g (5% w/w) gelatin. To this clear,
yellowish mixture was added a solution consisting of 0.275 ml
(1.29 mmol) of sebacoyl chloride dissolved in 0.500 ml of
hexane. This new mixture was agitated for 30 seconds at
1500 RPM. Nylon 6, 10 was formed, but mostly on the homogeniz-
ing head. It was determined that it was necessary to make a
stable emulsion first and then form the polymer.

The experiment was repeated as described above with the
exception that the hexa-methylenediamine was added after
the emulsion was formed. The mixture formed polymer, but
had a foamy consistency, i.e large amounts of foam floating
on top of the solution. Examination of the mixture under a
microscope showed that there were no microcapsules present.
This experiment was attempted again, with the amine and
base being added after the emulsion was formed. Again,
polymer was formed as well as a large amount of foam.
However, the presence of microcapsules, as well as gelatin,
was observed. The microcapsules exploded under the intense
heat of the microscope lamp. It was also apparent that the
gelatin was not going to be a good surfactant to use because of
the foaming problem that was occurring.
The next surfactant used was methyl cellulose. Into 10.0 ml of water was placed 0.050 g methyl cellulose. This heterogeneous mixture was placed in an 80° C oven for 1 hour after which time it became transparent. To this clear, slightly colored mixture was added 0.500 ml of hexane and the resulting mixture was agitated at 1500 RPM for 30 seconds. A large amount of foaming was observed.

Carboxymethyl cellulose sodium salt (CMC) was used next. Into 10.0 ml of water was placed 0.056 g CMC. This mixture was placed in an 80° C oven for 1 hour, after which time it became transparent. To this mixture was added 0.500 ml of hexane and the resulting mixture was agitated for 30 seconds at 1500 RPM. A large amount of solids fell out of solution. It appears that the CMC is not soluble in the water/hexane mixture. Therefore, a different solvent, dichloromethane, was used for the next series of experiments.

CMC, 0.070 g, was added to 10.0 ml of water and the mixture was placed in an 80° C oven for 1 hour. A solution consisting of 0.075 g (1.29 mmol) sebacoyl chloride dissolved in 0.500 ml of dichloromethane was then added. This new mixture was then agitated for 30 seconds at 1500 RPM. This cloudy mixture was then placed on a stir plate and stirred at 1200 RPM using a micro stir bar. A solution consisting of 0.077 g (0.66 mmol) hexamethylene-diamine and 0.053 g (1.25 mmol) sodium hydroxide dissolved in 2.0 ml of water was then added and the resulting mixture was stirred for 15 minutes. A white suspension formed. Analysis of the white suspension under a microscope showed the presence of many microcapsules, mostly between 90-200 μm in size. Surfactant, as well as a small amount of polymer, were also present.

The microcapsules still were not stable under the microscope light. It was determined that the walls of the microcapsules were too thin; therefore, a larger quantity, i.e., double, of diamine was used for the next experiment.

CMC, 0.058 g, was added to 10.0 ml of water and the mixture was placed in an 80° C oven for 1 hour. A solution consisting of 0.075 g (1.29 mmol) sebacoyl chloride dissolved in 0.500 ml of dichloromethane was then added. This new mixture was then agitated for 30 seconds at 1500 RPM. This cloudy mixture was then placed on a stir plate and stirred at 1200 RPM using a micro stir bar. A solution of 0.117 g (1.01 mmol) hexamethylene-diamine and 0.106 g (2.50 mmol) sodium hydroxide dissolved in 4.0 ml of water was then added. This mixture was placed in an 80° C oven for 1 hour. A solution consisting of 0.075 g (1.29 mmol) sebacoyl chloride was added and the new mixture was agitated for 30 seconds at 1500 RPM. A solution consisting of 0.154 g (1.32 mmol) hexamethylene-diamine and 0.106 g (2.50 mmol) sodium hydroxide dissolved in 2.0 ml of water was added in 1 ml portions with 1 minute between each addition. The resulting mixture was stirred at 1200 RPM on a stir plate for 30 minutes, after which time the mixture was analyzed under a microscope. The mixture contained a large number of microcapsules, mostly between 10-250 μm. The microcapsules were allowed to dry. Once dry, the particles collapsed.

The addition of a crosslinker was used to improve wall strength and minimize wall collapse. The crosslinker of choice is diethylenetriamine. The amount of crosslinker used was approximately 30% w/w. To 10.0 ml of water was added 0.062 g CMC. This mixture was placed in an 80° C oven for 1 hour. A solution consisting of 0.075 g (1.29 mmol) sebacoyl chloride dissolved in 0.500 ml of chlorobenzene was added and the new mixture was agitated for 30 seconds at 1500 RPM. A solution consisting of 0.154 g (1.32 mmol) hexamethylene-diamine and 0.106 g (2.50 mmol) sodium hydroxide dissolved in 4.0 ml of water was added in 1 ml portions, with 1 minute between each addition. The resulting mixture was stirred at 1200 RPM on a stir plate for 30 minutes, after which time it became transparent. To this clear, slightly cloudy mixture was added 0.500 ml of hexane at 1500 RPM. A large amount of solids fell out of solution. It appears that the CMC is not soluble in the water/hexane mixture. Therefore, a different solvent, dichloromethane, was used for the next series of experiments.

CMC, 0.069 g, was added to 14.0 ml of water. This mixture was placed in an 80° C oven for 1 hour. Chlorobenzene, 0.500 ml, was added and the new mixture was agitated for 30 seconds at 1500 RPM. The emulsion formed seemed fairly stable; very little coalescence was observed. Most of the particles in the emulsion were <200 μm. The emulsion was still stable after 30 minutes and was considered stable enough to work.

Into a vial was placed 0.053 g CMC and 10.0 ml of water was added. This mixture was placed in an 80° C oven for 1 hour. A 0.500 ml solution of chlorobenzene containing 0.075 g (1.29 mmol) sebacoyl chloride was added and the new mixture was agitated for 30 seconds at 1500 RPM. A solution consisting of 0.154 g (1.32 mmol) hexamethylene-diamine and 0.106 g (2.50 mmol) sodium hydroxide dissolved in 4.0 ml of water was added in 1 ml portions, with 1 minute between each addition. The resulting mixture was stirred at 1200 RPM on a stir plate for 30 minutes, after which time the mixture was analyzed under a microscope. The mixture contained a large number of microcapsules, mostly between 10-250 μm. The microcapsules were allowed to dry. Once dry, the particles collapsed.

Results

Microcapsules of Nylon 6, 10 were produced using interfacial polymerization in a o/w solvent system. A photograph of the microcapsules was taken and it was shown that microcapsules are being formed. However, the microcapsules are unstable when dry and collapse, giving an impression of a deflated soccer ball.

Discussion

Microcapsules were produced using the interfacial polymerization of sebacoyl chloride and hexamethylene-diamine in an oil-in-water system. However, the microcapsules formed were not stable when dried. A wide variety of surfactants were used, with the surfactant of choice being carboxymethyl cellulose, sodium salt. This surfactant gave minimum foaming and a stable emulsion in the presence of hexane, dichloromethane, and chlorobenzene. The changing of solvent did not produce more stable microcapsules. The use of a crosslinking monomer, diethylenetriamine, also did not improve stability.
A secondary polymer could be used to coat the Nylon 6, 10 coated microcapsule. This would improve the strength of the microcapsule and, if the correct polymer is chosen, could reduce the porosity of the microcapsule wall.

The examples provided herein are illustrations and are not expected to limit the methods of preparation or the materials used. Although the present invention has been disclosed in terms of a preferred embodiment, it will be understood that numerous additional modifications and variations could be made thereto without departing from the scope of the invention as defined by the following claims.

What is claimed is:

1. A self-healing system comprising, a repair material including a plurality of microcapsules, each having an outer polymer shell encapsulating a first reactant and a second reactant that react to form a replacement polymer upon rupturing of said outer polymer shell, wherein said first reactant and said second reactant are selected from the group comprising a monomer, a reactant of a condensation polymer, a fusible polymer, and a chemical heater, wherein said first reactant is a polyfluorocarbon and said second reactant is a chemical heater.

2. The self-healing system of claim 1, whereby said repair material is an insulation material.

3. The self-healing system of claim 1, whereby said repair material is a strip of material.

4. The self-healing system of claim 3, whereby said strip of material is a plastic strip.

5. The self-healing system of claim 1, whereby said first reactant and said second reactant are separated by an inner polymer shell.

6. The self-healing system of claim 5, whereby single microcapsule comprises a reactant core including said first reactant and a reactant shell including said second reactant, said reactant shell surrounding said reactant core, and said inner polymer shell separates said reactant core and said reactant shell and said outer polymer shell surrounds said reactant shell.