Corrosion Prevention by Detection of Aqueous Liquids Using Sensors with a Percolation Threshold Transition

Helge PFEIFFER*, Peter HEER**, Martine WEVERS*

* Katholieke Universiteit Leuven, Group Material Performance and Non-destructive Testing, Department of Metallurgy and Materials Engineering (MTM) Kasteelpark Arenberg 44, Bus 2450, B-3001 Leuven, +32/16/32 12 32 (Tel), E-mail: Helge.Pfeiffer@mtm.kuleuven.be
** Lufthansa Technik AG, Rhein Main Airport, 60546 Frankfurt/Main, Germany, +49-69-696-91078

Abstract. In airplanes aqueous liquids arising from spillage (especially in the galley and lavatory area) or from passengers boarding at rainy weather conditions can enter the space between the floor panels when sealings are damaged, and it is known that this penetration can cause heavy corrosion in the underlying floor beam structure. A reliable sensor for aqueous liquids which is interrogated at least on a monthly base, or even more frequently, could help to reduce the repair costs of floor beam structures considerably. An important challenge for the installation of sensors in the floor beam area is the limited space available. Furthermore, the sensor has to cover an extended area.

To obtain a sensor, an organo-ceramic composite was developed. This sensor is based on the collapse of percolation conductivity of the composite containing a conducting compound which is embedded in a hydrophilic matrix. When this composite is exposed to water, the system takes up liquid until the conductivity is essentially lost. The loss of the resistance due to the ingress of water can be monitored by a digital multi-channel multimeter that is equipped with appropriate data logging facilities. The applicability of the integral system could already be shown in a relevant lab-environment using different aqueous liquids. Furthermore, the implementation of a test-setup in an operational civil aircraft is foreseen for autumn 2010.

1. Introduction

Areas that are prone to corrosion are normally isolated from the wet environment. A typical example is the floor beam area in aircraft; the floor beams are covered by protective coatings, and the joints between floor panels are equipped using sophisticated sealing systems. However, coatings and sealings can be damaged due to the intensive use of the aircraft. Aqueous liquids arising from spillage (especially in the galley and lavatory area) or from passengers boarding at rainy weather conditions can enter the space between the floor panels, and it is known that this penetration can cause heavy corrosion in the underlying floor structure that is frequently made of aluminium alloys. As the regular maintenance of floor beams is scheduled with relatively long periods, a starting corrosion problem can remain undiscovered for a long time.
A reliable sensor for aqueous liquids which is interrogated at least on a monthly base, or even more frequently, could help reduce repair costs of floor beams considerably. An important challenge to tackle with the installation of sensors in the floor beam area is the limited space available. Furthermore, the sensor has to be extended to avoid the implementation of a network of point sensors.

In the present paper, a sensor is presented that is based on the collapse of the percolation conductivity of a composite containing a conducting compound which is embedded in a hydrophilic matrix. Percolation means in this context the theory of connectivity of conducting particles in randomised lattice structures. The most famous example of these composites are conductive polymers, i.e. materials that are used as electrical conducting glues or adhesives. To obtain a floor beam sensor, an organo-ceramic composite was developed. The components were mixed in an appropriate ratio, resulting in a composition so that the composite was just above the percolation threshold.

Fig. 1 shows how a conducting component, illustrated by spheres, is distributed in an insulating matrix, given by the space between the white walls. With an increasing volume fraction of the spheres, the probability that there will be conductivity between the white walls is increasing. This is normally not a continuous process, but there is a certain threshold when the material turns from an isolator into a conductor which is called the percolation threshold.

At the percolation threshold, the resistance can change with approximately 16 orders of magnitude [1]. As the percolation threshold is described as the conductivity as a function of the volume fraction, one can state that many physical quantities that are related to the volume fraction have an enormous influence on the conductivity. A material that exists in the range of the percolation threshold can thus be used as a very sensitive sensor for such quantities.

The electric conducting composites are usually made using graphite or metal powders as the conducting component. Especially silver powder is frequently applied. For polymer matrices, epoxy and other compounds are frequently used.

There is a widespread use of electrical conducting composites. Especially the possibility to have printed electronics has driven the development of this technology. Electric circuits can be produced by screen printing or even by inkjet printers and electronic devices can be made. Electric conducting glues establish wiring of electric components; a prominent example is also the rear-window heater of cars that is mostly an electric conducting polymer line with a higher resistance to enable heating.

The use of ceramic powder to produce electrical conducting polymers such as used for our sensor is relatively new, and we do not know any corresponding examples in the literature. The most important reason for the use of ceramic powders is the chemical stability of this
component with respect to flame safety or corrosion. Conducting polymers made with metal powder sometimes suffer from the decay of the metal component by e.g. corrosion. The application of gold powder is possible, but due to the high costs, the applications are limited.

2 Materials

An organo-ceramic composite consisting of Titantium carbonitride (TiCN) powder and Polyvinyl alcohol (PVA) was developed. The components were mixed in an appropriate ratio, i.e. the concentration was chosen that the system was relatively close to the percolation threshold. The composite is thus conducting at this volume fraction indicating that the amount and distribution of the TiCN powder particles allows conductivity.

The conducting compound is a ceramic powder (TiCN). Conducting ceramic powders are normally used for different purposes, e.g. to create electrical conducting ceramics, that can e.g. for the processing of ceramics allow spark erosion. The matrix material is polyvinyl alcohol (PVA), a polymer that is hygroscopic, i.e. it swells and finally dissolves when it can take up sufficient amount of water.

3. Results

3.1. Proof of concept

A stripe of the composite was exposed to water and as expected, the system takes up water until the conductivity was lost (follow the arrow in point P in Fig. 2). This occurs because the average distance between the conducting particles reaches a point when conductivity is not possible anymore. This process is completely reversible, thus when the composite is dried again, it reaches the previous conductivity. The absolute resistance as a function of the hydration time is given in Fig. 3.
Fig. 3 Conductivity of TiCN/PVA composite after exposing the sensor to “spilled liquids”

To get a deeper insight into the microstructure of our composite, advanced structural methods were applied. The following pictures were obtained by Scanning Electron Microscopy (Fig. 4). The size of the ceramic particles could be determined to be in the range of sub-micrometer until several micrometers. Due to the preparation of the samples (polishing), it might be that the distance between the particles are not completely the same as in the case of the conducting state.

Fig. 4 SEM picture of the interior of the sensor material
3.2 The sensor

An important problem that needs to be taken care of for the installation of sensors in the floor beam area, is the limited space available between the floor plates. Between the floor plates, the space is not much more than 1 mm. Furthermore, the sensor has to cover an extended length. On the other hand, it is not really important to determine the exact position of the spilled liquid because after the indication of the problem, bigger floor plate segments have to be removed anyway. The essential advantage is that in case of an early indication of water ingress, many resources can be saved when the floor beams replacement can be avoided.

![Diagram of connections](image)

Fig. 5 Extended sensor: left) A core consisting of an electric wire is surrounded by a nylon cord impregnated with the hygroscopic composite. The resistance of the wire is the parameter that determines the presence of the liquid. right) Diagram of connections, the core is actually inside the sensing coat.

An appropriate mixture was prepared according to the specifications determined in previous tests. The nylon cord was equipped with an isolated certified standard wire. The sensor obtained was situated in a flexible transparent tube to simulate conditions similar to the groove between the floor plates. The sensor (Fig. 5) itself was wired to a digital multimeter (Keithley 2000) and dedicated software was developed to analyse the recordings.

![Cut-out for ingress of liquids](image)

Fig. 6 Cut-out for ingress of liquids

After the deposition of 0.7 ml cola (Fig. 6 and Fig. 7), the response of the sensor was measured. There was a certain chance that the liquid being conductive (due to the ions present in the solution) would contribute to a diminishing of the sensitivity of the sensor.
But this effect was negligible. The liquid finally spread over a length of about 5 cm. After a while, the liquid was completely absorbed by the sensor leading to a remarkable increase of the resistance. Besides its sensing capabilities, the sensor itself works as a buffer when absorbing the liquid giving the airline maintenance more time to repair the sealings.

The measured resistance finally increased with a factor of about 5000. This is much more than the resistance variations that would occur at normal operational conditions. It is exactly the difference between the measures signal and the baseline variations that establishes a problem for various structural health monitoring systems, and the present sensor is able to circumvent this well-known drawback.

![Response of PCS after a "cola incident"](image)

**Fig. 7** Data obtained from the sensor. The diagram in the middle focuses on the percolation threshold region.

The next possible implementation steps contain activities for sensor miniaturisation and the preparation for the final implementation in the floor beam structure. In parallel, the hard and software will be extended to be able to measure up to 30 different sensors.

However, in order to help the certification effort, in principle, for our sensor system (Fig. 8) much less implementation steps are needed to bring it into an operational airplane. It is in practice sufficient just to measure the resistance of the sensing wire in a certain interval during line maintenance using a low-end multimeter. The non-conductive state is very stable because entered water will barely have the possibility to escape, thus, the sensor represents a kind of a fuse. So, it is not necessary to have data logging facilities in the airplane during operations.
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