Towards the development of a novel CNTs-based flexible mild heater for art conservation

Nanomaterials and Nanotechnology

Towards the Development of a Novel CNTs-based Flexible Mild Heater for Art Conservation

Regular Paper

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Received 30 Dec 2013; Accepted 12 Mar 2014

DOI: 10.5772/58472

Abstract Mild heating devices currently available to conservators are still limited in terms of precision, versatility, mobility, accessibility and cost. Moreover, they lack a range of operational features, such as low power requirements, efficient power use, temperature stability and uniform heat distribution. Carbon nanotube-based technologies can provide a wide range of technical solutions for overcoming these limitations, thereby allowing the development of more precise, flexible and portable heating devices. This work describes the design of an innovative carbon nanotube-based intelligent mobile accurate thermo-electrical mild heating device, to be used in the art conservation field. The device consists of three different types of flexible heating mats with different designs (opaque and ultra-thin/woven and breathable/transparent) and different operational and physical properties. The entire heating system is completed by a control unit that controls, monitors and registers the heating and by a power supply unit. First tests performed on a series of prototypes of the designed heaters showed that the device was able to convey uniform heating on different working materials, thus proving to be effective for thermal consolidation.

Keywords Mild Heating Devices, Carbon Nanotubes, Cultural Heritage

1. Introduction

Thermal treatments and integration of accurate heating are commonly used in the conservation of paintings, works on paper and other cultural heritage objects. Heat transfer factors are amongst the most important phases for the majority of structural treatments, such as consolidation, treating planar deformations, reinforcing degraded support and others. Particularly in the conservation of paintings, a highly accurate and steady temperature, applicable either selectively in targeted areas or universally, is a crucial factor, as lack of control over temperature may lead to incomplete or failed treatment (if not damage to the artwork). Even in relatively small areas, uniform and accurate heat application is problematic and as the area of application increases, control of the temperature and uniformity of distribution of heat become progressively more difficult to achieve with the tools currently available.

The prevalent heating instrumentation currently available and in use that is capable of treating larger scale artworks is the heating table fitted with suction. This equipment was developed to serve the increasingly pervasive practice of complete impregnation of paintings with natural wax-resin, followed by the widespread use of synthetic thermoplastic resins from the 1970's onward. While the heating table has had some improvements in design and today comes in various models and sizes, it has not been essentially changed since the mid 1980's. Its ubiquitous presence as a laboratory device is long established, yet for most conservators, it constitutes a limited piece of machinery because of its large environmental footprint and fixed location, and its inaccessibility to many conservators due to its high market price.

The heating table also has many limiting inherent characteristics, such as high power requirements (10-15 kW, 380 V for larger applications) and high heat sink mass, which results in slow response, inefficient power use and high consumption costs. More importantly, even the best heating tables reveal significant temperature fluctuations and uneven heat distribution that render the all-in-one apparatus out of step with current conservation methodology and laboratory needs.

a) b)

Figure 1. a) The first experimental flexible mild heater prototype applied during the in situ treatment of a 1930's mural painting by H. Sewell in Oregon City (OR), USA in 2003; **b**) the second prototype used in the treatment of a 17th century painting by Willem van Aelst, Amsterdam, 2006.

Present-day conservation practices are moving towards minimal, targeted and less invasive treatments, and accordingly, the challenges and best practices faced by the conservation profession are becoming ever more global and mobile. It seems clear that the future of heating devices in art conservation will involve mobile, versatile, accurate and cost effective "smart" devices. In the search for mobile alternatives, flexible heaters offer the most attractive option: they are lightweight and portable, can be designed in a variety of shapes and sizes, applied selectively and combined with other treatment devices in a most versatile way.

For this reason, the first steps toward the implementation of flexible mild heating systems were taken in 2003 [1], whereby a prototype to be used in the treatment of mural paintings on canvas by H.S. Sewell (1899-1975) in Oregon City, Oregon, USA (see Figure 1a) was devised. The device was made of silicon rubber and wound wire heating elements connected to a custom designed control unit, with an external thermal sensor adapted from industrial use. Later, a second prototype was created in 2005 [1] with some improvements in its design (see Figure 1b). Both prototypes and other later designed heaters have been used since in the treatment of numerous artworks that differ in size, period and materials used, with results soliciting considerable interest from the conservation community.

The simple application, impressive precision, mobility and versatility showed by the silicone and wound-wire prototypes encouraged further development of the concept of a mobile mild heating system for art conservation, improved by novel technologies such as carbon nanotubes (CNTs) [2-4].

As is widely known [5], CNTs are molecular scale sheets of graphite (called graphene) rolled up to make a tube and can be described as a new member of the carbon allotrope family, falling between fullerenes and graphite. Single Wall Nanotubes (SWCNT) consist of single rolls [6,7], while Multi Wall Nanotubes (MWCNT) consist of two or more coaxial tubes-within-a-tube [8]. Properties of individual CNTs can be influenced significantly by their chirality (twist) and geometry. Held together by the Van der Waals force, CNTs tend to bundle in ropes, forming agglomerates, but depending on the production ("growth") method can also form highly aligned structures. CNTs are of interest to various applications in cutting edge electronics, optics and material engineering, since they are characterized by interesting physical and mechanical properties: thanks to sp_2 bonds, they are the strongest and the stiffest materials currently known, with an E-modulus 10 times greater than steel; they are lightweight and highly conductive, and have numerous other outstanding properties and applications that are still in the process of being discovered. They are the best field emitters of any known material and, in theory, metallic nanotubes can carry an electric current density of 4 × 109 A/cm^2. Moreover, CNT thermal conductivity has been measured as high as 3500 [W m^{-1} K^{-1}], although in theory [9], it could reach a value equal to 6600 [W m^{-1} K^{-1}].

Although metallic CNTs are excellent conductors, they do not have metal bonds and possess very unusual features: they are exempt of thermoelectric effect [10] and from a quantum mechanics point of view, SWCNT do not follow Joule's law (P=IV) as stated in [11].

While CNTs are revealing ever more remarkable features that will enable the creation of a broad range of "smart" materials and products with revolutionary characteristics, most researchers agree that perhaps the greatest technological potential at the present time lies in the electrical properties of CNTs to generate heat in a way unattainable with other technologies. The material is not only extremely light and robust, but can also efficiently heat up surfaces of any size, and feature a very rapid thermal response, which is an important factor in maintaining ultra-steady temperatures and in reducing heating and cooling times. For traditional materials, the change in temperature is usually slow and delayed, due to their large thermal mass. In contrast, the thermal response of CNTs can be very fast, even up to the incandescent state. Conductive films made with carbon nanotubes and metal nanowires, in addition to their low sheet resistance, possess an optical transmittance in the visible spectrum and can form quite electrically conductive, yet almost completely transparent films, measuring only about 50-100 nanometres thick. Other promising developments in this sector were introduced in 2010 by Bayer Material Science (Leverkusen, Germany), which produced at industrial scale the first highly purified MWCNT, called Baytubes®. Baytubes [12] in aqueous suspensions were applied to multifilament yarns, resulting in a new textile heater made by weaving CNTEC® conductive yarns from Kuraray Living Co., Ltd. in Japan in 2010. This fabric heater is lightweight, thin and compact, thus demonstrating sustained durability to bending. Highly conductive CNT coatings, which could be applied like a varnish, were developed by Future Carbon (FC, Bayreuth, Germany) in 2009 and transparent conductive coatings have been researched [13] with reported sheet resistance values as low as 1 ohm/square (henceforth indicated as Ω/sq) for the opaque FC Carbo-E-Therm coating, and 0.3 Ω/sq in a transparent coating. All of these products were developed for very different uses than art conservation and were applied exclusively to glass, polycarbonate, or PET substrate, rendering them impractical and difficult to use in art conservation, where the substrate must be soft and resistant to the impact of solvents, heat and to frequent rolling or bending.

Inspired by the above mentioned impressive research results, the present work describes the steps for creating innovative state-of-the-art precision instruments for mild heating and designed specifically for art conservation, in the form of lightweight, flexible, transparent and breathable CNT-based flexible mat heaters. The developed mats are controlled by a small, programmable touch screen console that provides the operator unprecedented command of the temperature and heating pattern, characteristics that are unmatched in class in the field of art conservation. The device's flexible design architecture is advantageous in structural treatments, empowering conservators to critically apply mild heat in a targeted manner, either locally or over very large areas. The portability and low energy consumption make the devised prototypes an ideal multi-use instrument for work in the field or in the laboratory, indispensable in the treatment of large scale works, but also in areas of limited access and are uniquely equipped for use in emergency response conditions. Henceforth, the devised mats are called "Intelligent Mobile Multipurpose Accurate Thermo-Electrical Device" (IMAT). The paper focusses mainly on the development of IMAT prototypes (including some details about the control console), a description of which is provided in Section 2. In Section 3, some experimental results obtained by testing the devised prototypes are described and a few final considerations are drawn.

2. Materials and Methods

2.1. Conceptual design and architecture of the new flexible mild heaters

The conceptual design and architecture of the proposed mild heating device (Figure 2) sees it composed of a conductive film heater, made with CNTs and an associated control unit (console) that also serves as a power outlet for the heater. The console includes an electrical "power box" that drives the heater, a digital touch screen console to control and programme the heating process, and a thermocouple (TC) that is connected to the console via a Bluetooth (wireless) connection. The architecture was designed to provide maximum versatility and mobility for the device in the most diverse treatment situations by separating the sensor, control pad and power source elements of the console. For example, the heavier "power box" can be conveniently placed under the working table and the touch screen console can be kept nearby the treatment area. The wireless TC may be positioned easily in any location and the flat flexible connecting cable makes placement of the heater uncomplicated. In all aspects, the mild heater's design aims for miniaturization and simplification in design solutions. The prototypes operate with a universal 110-230 V input and have two separate power boxes; 24 V (for smaller heaters) and 96 V (for larger heaters).

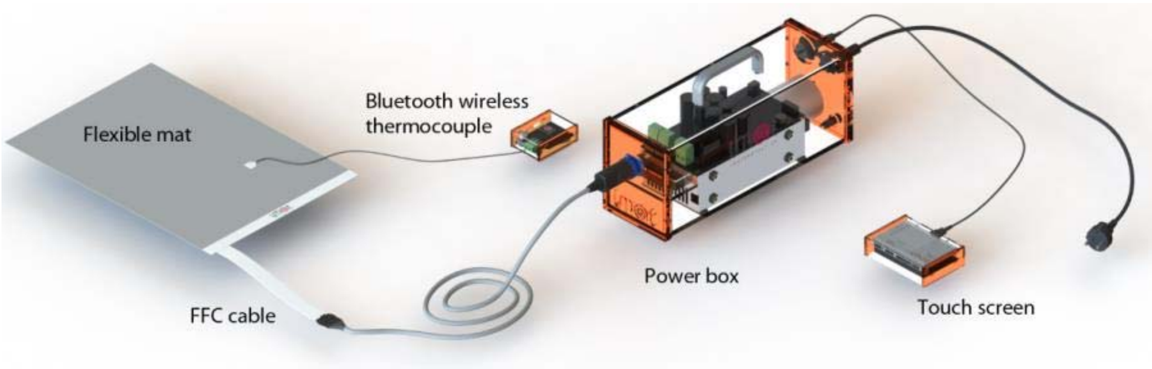


Figure 2. Conceptual design of overall IMAT architecture

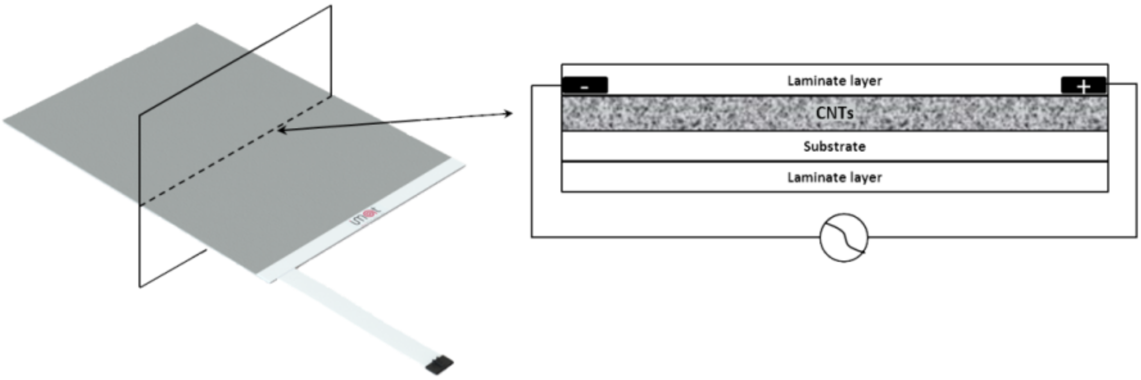


Figure 3. Basic composition of IMAT

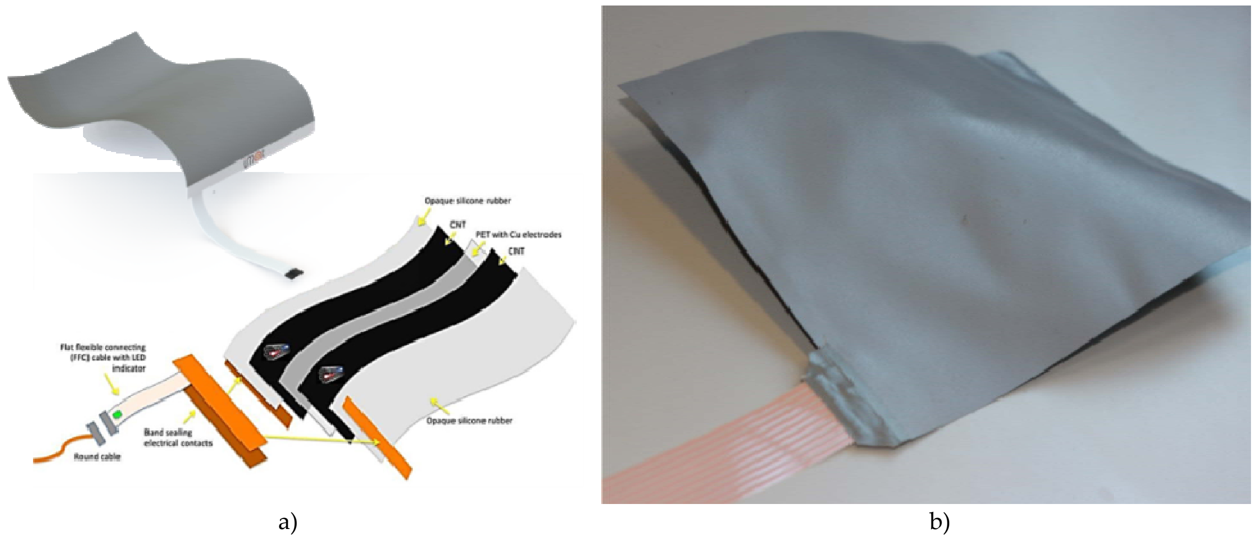


Figure 4. a) Conceptual design of IMAT standard heater IMAT-S; b) IMAT-S prototype

The flexible mat is composed of a substrate (see Figure 3), covered first with a conductive nanomaterial coating and then finished with an exterior protective coating, which also provides the non-tack surface and electrical insulation. Highly entangled CNTs in a flexible and chemically cross-linked binder matrix are the basis for the coating system to be developed for the IMAT heaters. When permeability to gases is desirable, the specially formulated CNT coating is deposited on an open weave textile substrate. The IMAT heater has integrated parallel electrodes and when voltage is applied, the current is uniformly distributed over the conductive layer of the nanomaterials, and heat is instantly generated evenly over the entire surface.

Three distinct types of IMAT-heaters are proposed: standard (named "IMAT-S"), breathable (named "IMAT-B") and transparent (named "IMAT-T"). The IMAT-T is still under investigation; as such, only its conceptual design is described in this paper.

2.1.1 Design of an opaque heater: IMAT-S

IMAT-S consists of a conductive low voltage heater with a soft and non-tack surface, which is opaque and non-breathable. The IMAT-S (see Figure 4) is intended for thermal treatments where visibility and breathability are not required. In terms of its use, it is similar to the pre-IMAT prototypes, but new added features have improved distribution of heat over the surface, instant thermal response, increased accuracy and notably, low voltage application, as well as its easy handling, which allows rolling it up and using it at any location "in the field".

The IMAT-S prototype substrate consists of transparent polyethylene terephthalate (PET) film, characterized by good adhesion to any kind of coating due to its chemical base units, which permits the formation of strong chemical bonds between coating [14,15] and substrate (see Figure 5). For the experiments, two copper electrodes were glued onto one side of the polyester film and the CNT coating was applied by roller and by doctor blade, respectively. Since temperature distribution of the finished film is slightly uneven, the coating was applied using a spray process. Qualitative adhesion of the coating material to the substrate and to the copper electrodes was greater than 95%.

Figure 5. Adhesion of Carbo e-Therm on PET film

The IMAT-S was coated using Carbo-e-Therm, a high-efficiency, electrically conducting coating developed for use in a non-hazardous low-voltage range [16]. Carbo e-Therm is suitable for temperatures up to 500°C. Its excellent applicability to very different geometries and surfaces, along with its high heating power has opened up a wide field of possible uses. Carbo e-Therm consists of a binder matrix and a specially matched carbon formulation. The excellent conductivity of the coating makes it possible to implement high heating power on non-hazardous low voltage (e.g. 12/24 V). Compared to conventional resistance heating, Carbo e-Therm distributes heat evenly without creating hot spots. Carbo e-Therm heating layers are highly rugged mechanically; depending on the product type, they exhibit very good permanent elasticity or high hardness. Additionally, they are characterized by excellent resistance to water and alkalis.

The coating is dimensioned starting from the relationship between power (P), voltage (E) and current (I) according to the following equation:

$$P = E \cdot I \tag{1}$$

Furthermore, it is possible to state how the applied voltage E, the length L (separation between the electrodes) and the sheet resistance R_s are connected in the conductive film heater, according to the following equation [3]:

$$P_D = \frac{E^2}{R_s L^2} \tag{2}$$

where:

E = Applied voltage [V];
L = Length (i.e., separation between the electrodes) of conductive coating [m]
R_s= Coating resistance [Ω/sq];
P_D = Power density [W/m²].

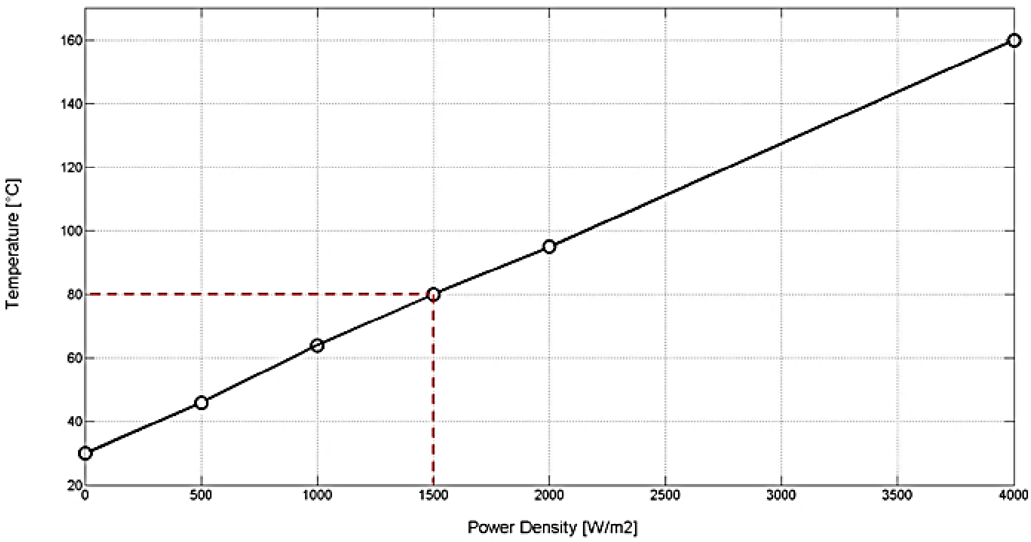
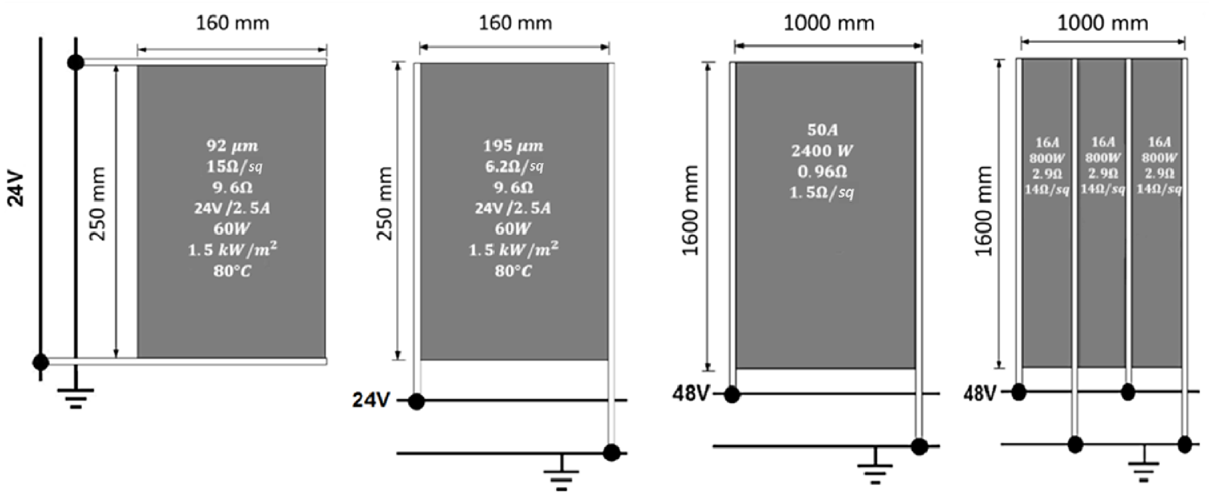


Figure 6. Power density vs. temperature; the curve, almost linear, is obtained experimentally



a) b) c) d)

Figure 7. a) Carbo e-Therm coating properties for the exemplificative case in which electrodes are placed along the long sides of the coated area; **b**) Carbo e-Therm coating properties for the exemplificative case in which electrodes are placed along the short sides of the coated area; **c**) Power needs for larger sizes; **d**) segmentation, allowing for a reduction in power needs, thereby increasing sheet resistance.

Moreover, coating resistance is related to the so called "resistance on the approximate line" R_L [Ω], i.e., the overall resistance of the heater, assuming negligible the resistance from electrodes, wire and connectors, or wire to wire:

$$R_s = R_L \frac{W}{L} \quad (3)$$

Finally, from equations (2) and (3) it can be demonstrated that:

$$WL = \frac{P_T}{P_D} \quad (4)$$

where:

W = length of conductive coating [m];
P_T = total power of the system [W].

The power density is determined on the basis of the heat requirements (desired temperature) according to the curve presented in Figure 6, stating an almost linear relationship between reachable temperature and power needs. If, for instance, a heater with a surface of 0.25m x 0.16m = 0,04m² is designed to reach a temperature equal to 80°C, the necessary power density results will be equal to 1500W/m². From Eq. (4), it is possible to derive a needed power P_T equal to 60 W. By considering Eq. (1), this means that if, for instance, a voltage of 24 V is used, the actual needed current is I=2.5 A and the resistance R_L results are equal to 9.6 Ω.

Once R_L is known, it is possible to evaluate the thickness of the heater. With this aim, it is first necessary to determine the coating resistance R_s using Eq. (3); depending on where the electrodes are placed (along the short or long sides of the coated area), a different coating resistance will be achieved. Referring to Figure 7a, since electrodes are placed along the long sides of the coated area, R_s results were equal to 15 Ω/sq. On the other hand, in the example of Figure 7b, where the electrodes are placed along the short sides of the coated area, the coating resistance results are equal to 6.2 Ω/sq.

Finally, from coating resistance, it is possible to evaluate the thickness of the coating layer according to the experimentally evaluated chart depicted in Figure 8, where the relationship between the layer thickness d and R_s is drafted. Referring to the example, when electrodes are placed along the long sides of the coated area, the thickness results equal 92 μm; when the electrodes are placed on the short sides, the coating results equal 195 μm.

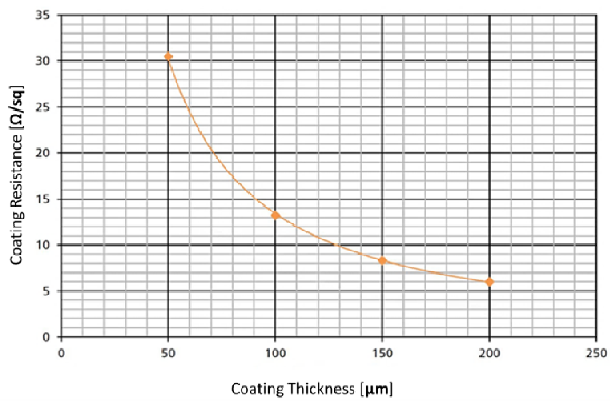


Figure 8. Coating resistance vs. coating thickness

On the basis of the above considerations, it has to be noted that for larger sizes (e.g., 1000 mm x 1600 mm in Figure 7c), high voltage and low sheet resistance are needed to reach the desired temperature (in this example, 48 V and 1.5 Ω/sq are required). In order to overcome this problem, segmentation is the best option. As illustrated in Figure 7d, by segmenting the substrate it is possible to reduce the power needs for each element (from 2400 W to 800 W per element), thereby increasing the sheet resistance up to 14 Ω/sq. Since the reduction of resistance using CNT-based materials is not a complicated task, segmentation may be considered a straightforward method for overcoming this relevant problem, i.e. for obtaining the same thermal behaviour with higher resistances. Using the above considerations, two prototypes were realized with sizes DIN A4 and DIN A3.

2.1.2 Design of a breathable heater: IMAT-B

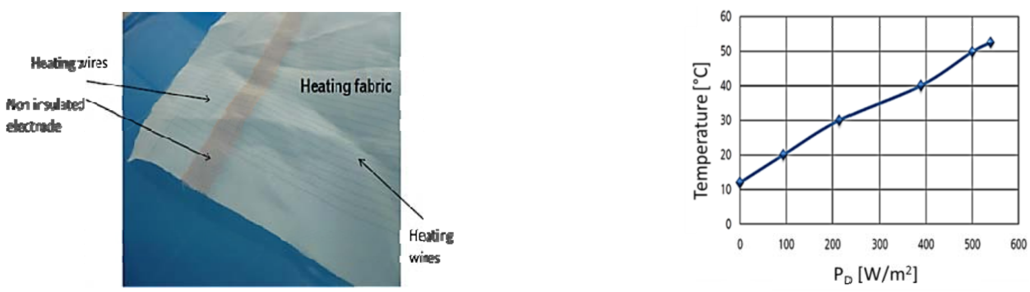
One of the most important issues for conservators working on painting consolidation is to have the possibility of allowing water vapour and airflow to pass through the painting. Consequently, the heating mat is required to not constitute a barrier for gases, i.e., to be permeable. For this reason, a further step in designing novel heating mats consists of developing breathable devices (see Figure 9). In particular, three different types of breathable heaters (named IMAT-B) have been devised. Two of them are made of a substrate consisting of a weave polyester textile and of a CNT sheet. The CNT-based coating was created using two types of nanomaterial: Carbo-e-Therm (also used, as already stated, for the IMAT-S) and CarboImpreg, an electrically conductive impregnation material for heating absorptive surfaces up to 100°C [3]. The third heater has a different structure: it is based on the modified textile based on the "heatable textile PowerHeat" proposed in [17].

The design of IMAT-B using Carbo-e-Therm was conducted using the same equations described in the previous paragraph. Adhesion of CNT coating to polyester proved to be excellent (more than 90%); in particular, by using diluted CNT coating mixtures and the air blasting technique, possible clogging of the weave has been widely avoided. The design of the heater using CarboImpreg is based on the creation of a binder matrix and a special, highly conductive, carbon preparation [3]. Excellent conductivity (R_s up to 1Ω) allows for high heating performance solutions on non-hazardous low voltages (e.g., 36 V). Furthermore, treated surfaces exhibit high ampacity, enabling very rapid heat build-up rates. The design of the heater using CarboImpreg takes into account the fact that CarboImpreg soaks into the surface of a material and fuses with it internally. In this way, full processing of the material without any restrictions is assured; additionally, it becomes highly wear-resistant.

The third option for designing a breathable, textile-based heater is a modified version of the "heatable textile PowerHeat". The devised mat consists of a Polyethylene terephthalate (PET)-based woven fabric (i.e., by a thermoplastic polymer resin with an intrinsic viscosity range equal to 0.40- 0.70) with electrically conductive filaments in a dense pitch (see Figure 10a). The first step for devising this type of heater consists of determining how much power is needed for obtaining the desired temperature. As depicted in Figure 10b, an experimental curve stating the obtainable temperature vs. the power density is available for this kind of heater.

a) b)

Figure 9. a) Conceptual design of IMAT breathable semi-transparent heater; **b**) standard textile-based heater coated with Carbo-e-Therm



a) b)

Figure 10. a*)* heatable textile PowerHeat; **b**) power input vs. average temperature output

Since the target temperature for this type of application is about 50°C, a power density equal to 500 W/m^2 is required.

Two different sizes of fabric have been developed: wide (named **V1a**) and DIN A4 (named **V1b**) sized. For the wide fabric (see Figure 11) sized 900 x 680, the warp is composed of 16 filaments/cm with a diameter equal to 200 µm. The weft can be adjusted in terms of density, varying in the range of 10-20 filaments/cm, with a diameter equal to 140-100 µm. The electrodes are made of stranded Ag coated copper wires with a cross section equal to 0.7 mm^2 and 20 mm in width. The overall power needed for heating the V1a sample resulted to being equal to 306 W.

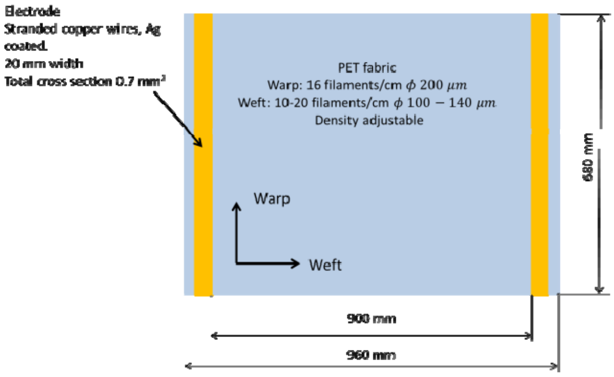


Figure 11. Fabric V1a *structure*

With regards to the DIN A4 size, the electrodes (again made of stranded Ag coated copper wires) have a total cross section equal to 0.19 mm^2 and 5 mm in width. As depicted in Figure 12, the warp has a density of 16 filaments/cm with a diameter of 200 µm and the weft is adjustable in the range of 10-20 filaments, with a variable diameter equal to 140-100 µm. The overall power needed for heating the V1b sample resulted to being equal to 31.2 W.

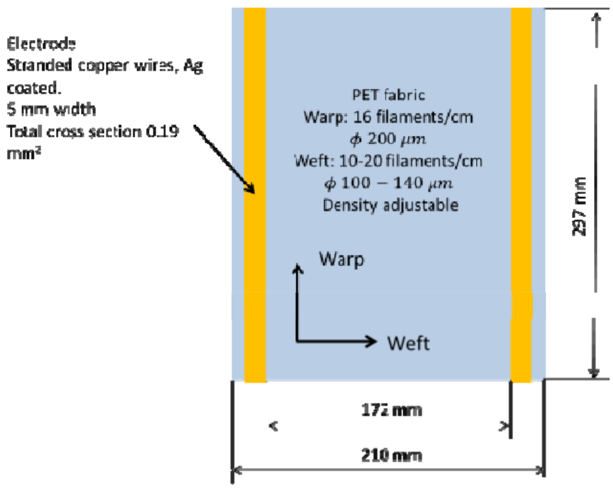


Figure 12. Fabric V1b structure

2.1.3 Conceptual design of a transparent heater: IMAT-T

The combination of low sheet resistance and excellent optical transmittance enables the design of efficient and nearly transparent film heaters, which allows the conservator to visually monitor the treatment process and accurately position the heater. The first experimental prototype of a transparent small scale (250 mm^2) film heater, where the heating element was constituted of a network of single wall carbon nanotubes (SWCNT), was created by the Korean Institute of Machinery and Materials (KIMM) in 2007 [18]. Efficient transparent heaters can also be designed with other prospective nanomaterials, such as silver nanowires (AgNW), which demonstrate low sheet resistance, falling below 1Ω/sq at 300 nm thicknesses and reaching as low as 13 Ω/sq in conductive films of 85% optical transmittance. AgNW conductive films on PET substrate are currently being manufactured by Cima Nano Inc. USA and are already being used by Dontech Inc., USA for small scale *Therma-Klear®* heaters [19].

On the basis of such considerations, a conceptual design of a transparent IMAT, named IMAT-T, is under investigation. Although the open-weave breathable heater also has a certain degree of transparency (around 65%), the authors are moving toward defining a flexible transparent heater [20] for art conservation (see Figure 13).

The IMAT-T design is largely based on SANTE™ EMI Shielding Film [19] with 7 Ω/sq sheet resistance and total transmittance greater than 80%. According to Eqs. 1-3, this low resistance value allows the heater to reach a temperature close to 80°C using a 36V voltage for mats sized 400mm x 300mm. Other promising technologies have recently been proposed by Kim et al. [21], where a high-performance transparent film heater based on a hybrid of carbon nanotubes and silver nanowires is presented.

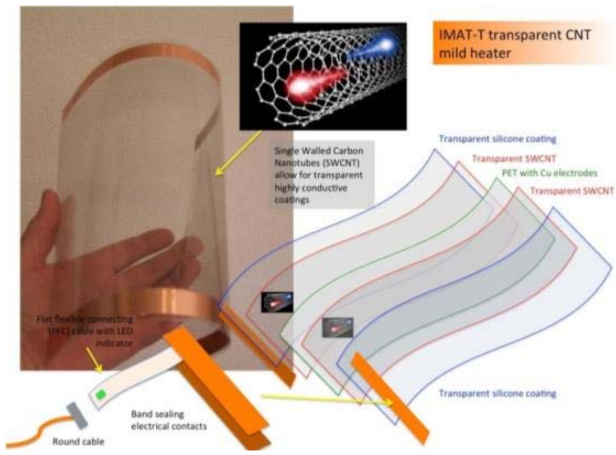


Figure 13. Conceptual design of transparent heater

2.2 IMAT Control Console

IMAT is powered and controlled using an associated control unit (console), which serves as a power outlet for the heater and controls and monitors and registers the heating process. The IMAT console (control unit) is responsible for controlling temperature, for the accuracy and steadiness of the heating cycle and for the heating and cooling times. Because of mat low thermal mass, the heating and cooling of the IMAT heater will be instantaneous and the heating software will allow the temperature to ascend and descend, either instantly or gradually, in the time set forth by the operator. The controls permit the desired temperature to be set with an accuracy of 0.5°C, which is sufficient for most thermal treatments and will also allow the desired heating and cooling time to be programmed. The IMAT consists of four distinct components: IMAT Power box, IMAT Control Unit and IMAT thermocouple (TC) Unit.

2.2.1 IMAT Power box

The IMAT Power Box (see Figure 14) is the unit dedicated to the regulation of the IMAT heater temperature. The Power Box is the central unit to which all the other devices are connected. The IMAT Power Box is composed of the voltage power supply and the IMAT Main Board. This device analyses the temperature data coming from the TC Board and then corrects and regulates the electric power using the classic approach of PID-PWM regulation (Proportional Integrate Derivative Pulse Width Modulation) of its AC/DC switching voltage supply source. Its configuration guarantees the galvanic insulation of the output voltage toward ground; thanks to an embedded microcontroller unit, it can emit and display acoustic and visual signals to alarm the user of errors and malfunctions that may occur.

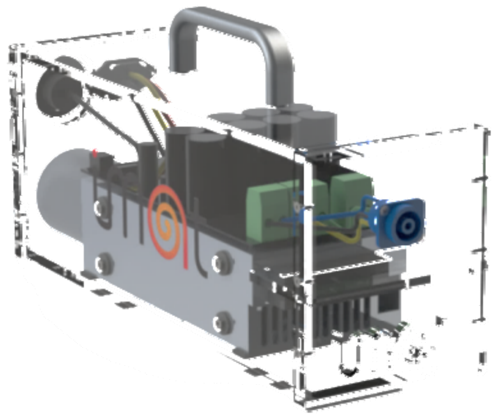


Figure 14. The IMAT Power Box, rendered here, is subdivided in its mains components: the IMAT Main Board and the AC/DC Switching Power Supply, which assures galvanic insulation of the output voltage

The IMAT Main Board is an electronic board that may be identified by its various sections. The electric power for both the IMAT control and the power box circuit is derived from a MeanWell AC/DC Power supply that supplies 36V or 48V to the IMAT Main Board, according to the output needs of the small and the large IMAT Consoles. The Main Board Core is the ATxmega16A4U Atmel Microcontroller, a small microprocessor with additional internal peripherals integrated into the same chip. This device has 16kB of flash memory, 2kB of SRAM and a 12MHz CPU master clock.

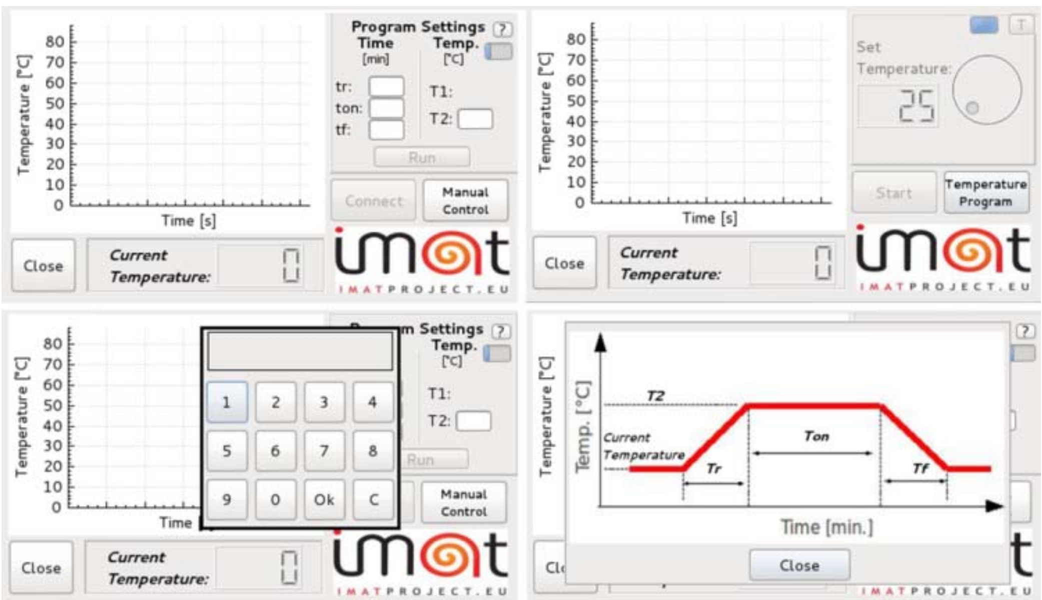


Figure 15. IMAT Program control GUI screenshots

2.2.2 IMAT Control and Thermocouple Units

The IMAT Control Unit is based on the Xflar Core produced by Qprel s.r.l. It is an extremely compact ARM9-based CPU module working at 240MHz with 64MB of RAM and 256MB NAND flash memory (memories are expandable) with integrated peripherals. A Linux operating system build around ARM architecture is installed into the Control Unit. A GUI (Graphic User Interface) has been developed in C++ programming language using the QT 4.8.3 Everywhere open source library. Two main windows have been created to allow the IMAT heater temperature to be set manually or programmed to rise and fall over time (see Figure 15).

The IMAT TC Unit (see Figure 16) is composed of the IMAT TC electronic board and a rechargeable lithium battery power source that renders it cordless and mobile. The TC Unit is equipped with a T-type thermocouple laminated with electrostatic film that serves as a detachable temperature sensor. This unit measures the IMAT heater temperature locally using a thermocouple and transmits data via Bluetooth to the IMAT Main Board.

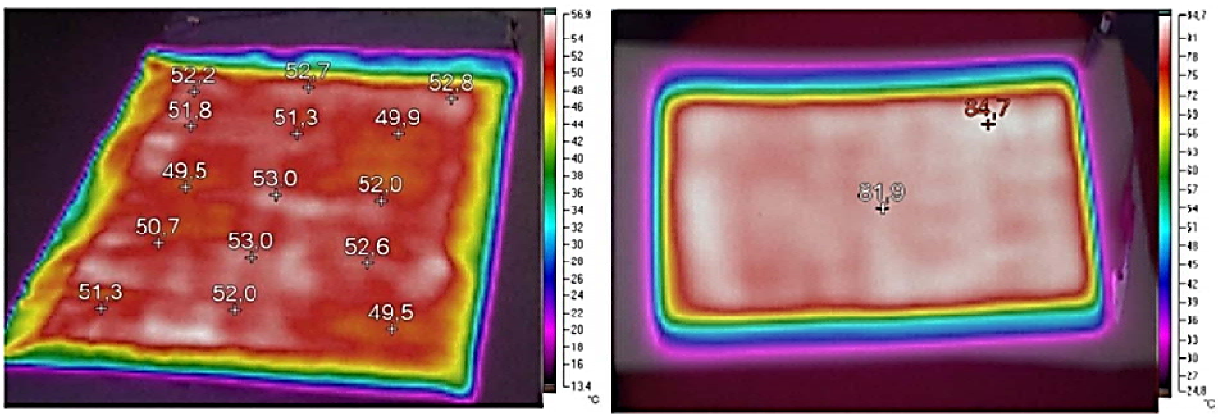
Figure 16. Rendering of the IMAT TC Unit

3. Results and Conclusions

The IMAT mild heater is an entirely new device with accuracy and other technical features that overcome several limitation of available heating tool in use in the field of conservation. Such advanced new technology, featuring custom-designed nanomaterials and the incorporation of other advanced materials, will open new vistas for the advancement of conservation methodology and techniques.

With the aim of assessing the actual performance of the devised prototypes, a series of experimental test have been performed using thermal imaging. For this purpose, a Flir® E60 thermal camera with a temperature range from -20°C to 120°C and resolution equal to 320x240 pixels[2] has been conveniently placed, so that the entire mat under inspection is framed (see Figure 17). The thermal camera had a declared thermal sensitivity of less than 0.05°C at 30°C and allowed for acquiring images with a 60Hz frequency and with a thermal accuracy of ±2°C. The acquisition device was calibrated in terms of Reflected Temperature [22]; moreover, the emissivity of the mat under inspection was evaluated so that acquired temperature was as accurate as possible.

Figure 17. Experimental setup



a) b)

Figure 18. a*)* thermal image obtained for IMAT-S prototype with a set temperature equal to 53°C; **b**) thermal image obtained for IMAT-B with a set temperature equal to 82°C.

Mild heaters to be tested were placed so as to adhere as much as possible to a wooden desk; however, adherence was not forced to be "perfect", since it was expected that in normal operational conditions, restorers will not pay particular attention to this aspect.

Tests were performed on the IMAT-S and IMAT-B prototypes. The thermal image of a DINA3 sized IMAT-S obtained by setting a target temperature equal to 53°C (to be reached after 400 s) is shown in Figure 18a. Figure 18b shows a thermal image of the IMAT-B obtained after 400 s with a desired temperature of 82°C.

Images show that, likely due to the presence of air pockets between the mat and the desk, some hot/cold spots occurred. This can be noticed, for instance, in Figure 18b, where the upper right inspected point reached a temperature of 2.7°C higher with respect to set temperatures. However, the obtainable thermal uniformity can nonetheless be considered quite good for typical applications in the art restoration field [1, 23, 24]. Obviously, it is expected that thermal response provided by the mats depends on the material to which the thermal gradient is applied. Consequently, in order to test the performance on different materials, the devised prototypes were coupled with three types of materials: wood, iron and textile. In Figure 19, the temperature trends in a selected point of the IMAT-S coupled with, respectively, a wooden desk, a metal table and a textile substrate are shown.

Results obtained by setting the console with a target temperature equal to 50°C, to be reached in 1200 s, clearly showed that the different heat capacities of the tested materials impacted on the thermal response of the mat; however, the desired temperature was eventually reached for all the couples (mat + substrate) after 1200 s. This suggests that, depending on the material to be treated, restorers should take into account possible delays or consider other factors when heating the mat.

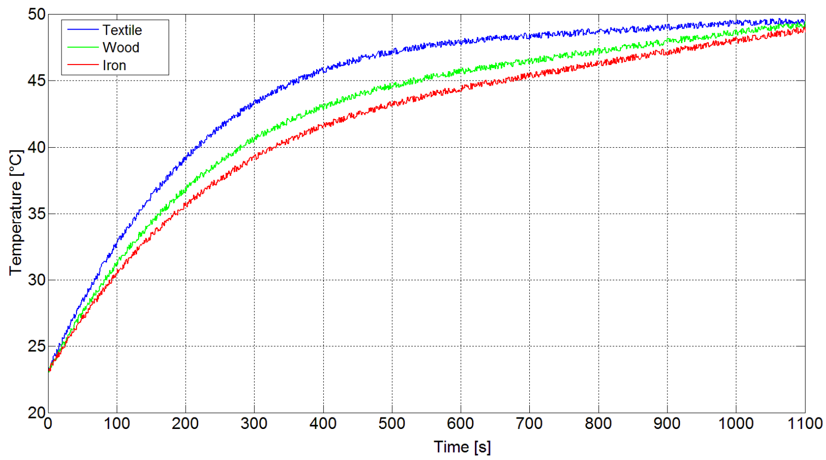


Figure 19. Temperature trends in a selected point of the IMAT-S coupled with respectively, a wooden desk, a metal table and a textile substrate

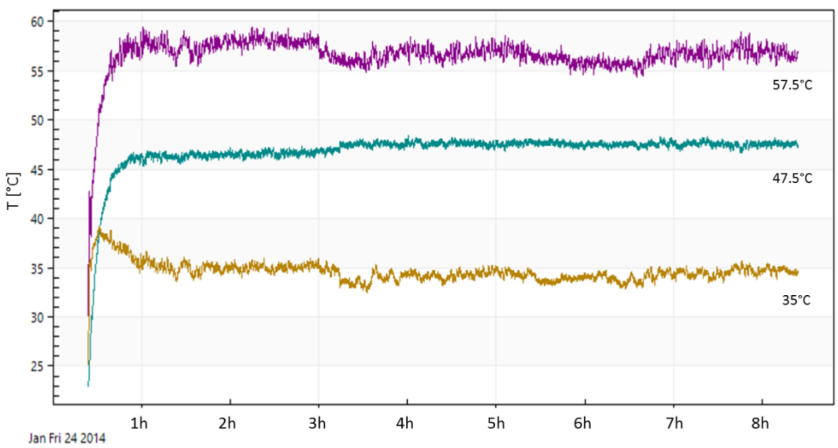


Figure 20. Temperature trends in a selected point of the IMAT-S tested for eight consecutive hours using three reference temperatures

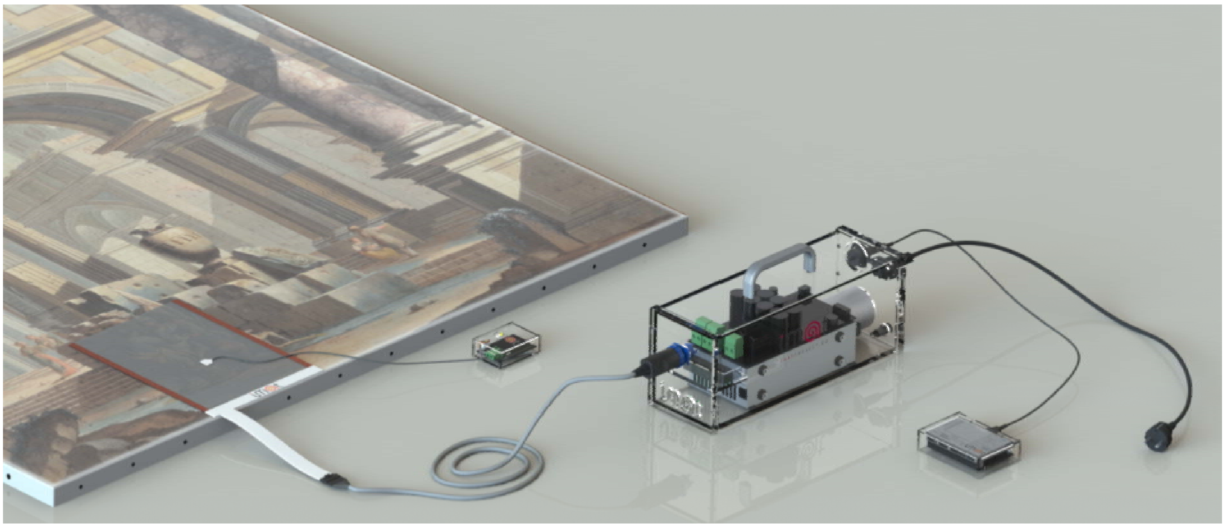


Figure 21. Rendering of the possible application of the IMAT-T prototype on an exemplificative field case

Since high temperature may slightly impact on the PET substrate structure, it is expected that heating efficiency will be related to aging effects on the mat. To partially test the possible damage on the IMAT-S due to long-term use, the heating device was run for eight consecutive hours with a target temperature of 35°C, 47.5°C and 57.5°C. The temperature trends for a given point on the mat at the three differently set temperatures (see Figure 20) showed that no significant temperature variation occurred. Moreover, visual analyses of the thermal mats, performed by technicians of the authors' laboratory, showed no visible changes in the overall structure of the IMAT.

Obviously, laboratory testing provides results that are not directly transferable to the Cultural Heritage field and further tests, performed by conservators, are required prior to declaring that the new device is confidently ready to replace traditional equipment. For this reason, future works will be addressed in testing the designed IMATs in the field. Testing will be performed first on mock-ups and will later be applied to real cases with varying technical aspects.

In Conclusion, the present paper described the fundamental steps carried out for creating new carbon nanotube-based Intelligent Mobile Accurate Thermo-Electrical mild heating devices for art conservation. The main aim of such a device is to resolve at its core the pressing need for accurate mild heating in conservation methodology by inventing a long awaited mobile and accessible nanotechnology that aspires to become an integral part of the conservators' tool box, and to expand the technical capacities of conservators worldwide. The device will create new, yet-to-be discovered possibilities in treatment methodology and enable local communities to safeguard their heritage and sustain their culture for future generations.

The device could, for instance, entirely replace the metal heating tables often found in laboratories, as well as the numerous other thermal devices such as handheld irons, home-made heating tables, heating plates, etc., which are often adopted but highly inaccurate for conservation standards. In Figure 21, a rendering of the possible application of the IMAT-T prototype on an exemplificative field case is presented.

The new device will have a particularly broad application in the conservation of artworks and of heritage objects in general, providing conservators with an essential treatment instrument for their everyday work. After prototyping, the new heater can be produced in a variety of configurations and sizes and fully integrated with all conservation treatments where accurate thermal application is required. First experimental results carried out by coupling the devised mats with three different materials and using several temperature settings showed that the newly created devices were promising for use in conservation practice.

4. Acknowledgements

The present work is a part of the Collaborative Project - Proposal No: 283110 – IMAT – CP, supported by the European Community in the context of the EC-FP7 Environment Theme (ENV-NMP.2011.2.2-5). The project, coordinated by the Dipartimento di Meccanica e Tecnologie Industriali dell'Università di Firenze, is carried out by a consortium of SMEs and research centres comprising the following institutions: Future Carbon, Germany, Laura Amorosi Restauro Italy, Stichting Restauratie Atelier Limburg, The Netherlands, Lorenzo Conti, Italy, Nardini Editore, Italy, C.T.S., Italy, Reuther Verpackungen GmbH & Co. KG, Germany, Istituto per l'Arte e il Restauro, Italy, Pranas Gudynas Restoration Centre, Lithuania, Tomas Markevicius, Lithuania.

5. References

[1] N. Olsson, T. Markevicius (2010) Flexible thermal blanket and low pressure envelope system in the structural treatment of large scale and traditional paintings on canvas. Proceeding of Annual Meeting of American Institute For Conservation of Artistic and Historic Works of Art (AIC) May 5-9, 2010, Milwaukee, USA.

[2] T. Markevicus, N. Olsson, M. Carfagni, R. Furferi, L. Governi, L. Puggelli (2012) IMAT project: From innovative nanotechnology to best practices in art conservation. Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics), 7616 LNCS, 784-792.

[3] T. Markevicius, N. Olsson, R. Furferi, H. Meyer (2012) Flexible mild heaters in structural conservation of paintings: State of the art and conceptual design of a new carbon nanotubes-based heater. Journal of Applied Sciences, 12(3), 211-220.

[4] F. Valentini, M. Carbone, G. Palleschi (2013) Carbon nanostructured materials for applications in nano-medicine, cultural heritage, and electrochemical biosensors. Analytical and bioanalytical chemistry, 405(2-3), 451-465.

[5] S. Iijima (1991) Helical Microtubules of Graphitic Carbon. Nature, 354: 56-58.

[6] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund (1995) Science of Fullerenes and Carbon Nanotubes. Academic Press. ISBN: 978-0-12-221820-0.

[7] Y. H. Yoon, J.W. Song, D. Kim, J. Kim, J.K. Park, S. K. Oh, C. S. Han (2007) Transparent Film Heater Using Single-Walled Carbon Nanotubes. Advanced Materials, 19(23), 4284-4287.

[8] R. Yudianti, L. Indrarti, H. Onggo (2010) Thermal Behavior of Purified Multi Walled Carbon Nanotube. Journal of Applied Sciences, 10, 1978-1982.

[9] E. Pop, D. Mann, Q. Wang, K. Goodson, H. Dai (2006) Thermal Conductance of an Individual Single-Wall Carbon Nanotube above Room Temperature, Nano Lett., 6(1), 96-100.

[10] M. A. Kuroda, J. P. Leburton (2009) High-field electrothermal transport in metallic carbon nanotubes, Physical Review Letters Phys. Rev. B 80.

[11] T. Ragab, C. Basaran (2009) Joule heating in single-walled carbon nanotubes, Journal of Applied Physics 106, 063705, American Institute of Physics.

[12] J. Pauluhn (2010) Multi-walled carbon nanotubes (Baytubes®): Approach for derivation of occupational exposure limit, Regulatory Toxicology and Pharmacology, 57(1), 78-89.

[13] D. Jung, D. Kim, K. H. Lee, L. J. Overzet, G.S. Lee (2013) Transparent film heaters using multi-walled carbon nanotube sheets. Sensors and Actuators A: Physical, 199, 176-180.

[14] R. Furferi, L. Governi, Y. Volpe (2012) Modelling and simulation of an innovative fabric coating process using artificial neural networks, Textile Research Journal, 82(12), 1282-1294.

[15] R. Furferi, L. Governi, Y. Volpe (2011) Neural network based classification of car seat fabrics. International Journal of Mathematical Models and Methods in Applied Sciences, 5(3), 696-703.

[16] S. Volkmar (2011) Funktionelle Lacke. JOT Journal für Oberflächentechnik, 51(12), 20-23.

[17] H. Meyer, K. Saborowsky, T. Markevicius, N. Olsson, R. Furferi, M. Carfagni (2013) Carbon Nanotubes in Art Conservation. International Journal of Conservation Science, 4(5), 633-646.

[18] Y. H. Yoon, J. W. Song, D. Kim, J. Kim, J. K. Park, S. K. Oh, C.S. Han (2007) Transparent Film Heater Using Single-Walled Carbon Nanotubes. Advanced Materials, 19(23), 4284-4287

[19] A. W. Funkenbusch, C. I. Bright, R. J. Fleming (2004) Durable transparent EMI shielding film. U.S. Patent No. 6,818,291. Washington, DC: U.S. Patent and Trademark Office.

[20] D. Langley, G. Giusti, C. Mayousse, C. Celle, D. Bellet, J.P. Simonato (2013) Flexible transparent conductive materials based on silver nanowire networks: a review. Nanotechnology, 24(45), 452001.

[21] D. Kim, L. Zhu, D. J. K. Chun, Y.Y. Bang, S. R. Kim, J. H. Kim, S. K. Oh (2013) Transparent flexible heater based on hybrid of carbon nanotubes and silver nanowires, Carbon, 63, 530-536.

[22] G. Machin, R. Simpson, M. Broussely (2009) Calibration and validation of thermal imagers. Quantitative InfraRed Thermography Journal, 6(2), 133-147.

[23] N. Ghedini, C. Sabbioni, M. Pantani (2003) Thermal analysis in cultural heritage safeguard: an application. Thermochimica acta, 406(1), 105-113.

[24] E. Meli, A. Ridolfi (2013) An innovative wheel–rail contact model for railway vehicles under degraded adhesion conditions. Multibody System Dynamics, in press.