The Conservation of the Shroud of Turin: Optical Studies

The ancient linen cloth of the Shroud of Turin is one of the archaeological objects most studied in history, mainly because of the unexplained nature of its image. We have recently irradiated linen fabrics by excimer laser pulses obtaining a Shroud-like coloration, and have recognized photo-chemical processes that may have played a role in the formation of the image embedded into the Shroud. Our results suggest some actions aimed at a long-term conservation of the Shroud and its image

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Introduction

The detailed studies of the front and back images of a scourged man embedded onto the Shroud of Turin (see Fig. 1) show such a microscopic complexity that nobody has been able to reproduce an image identical in all its details [1–9].

The most important in-depth experimental analysis of the Shroud was carried out in 1978 by the multidisciplinary team of the Shroud of Turin Research Project, Inc. (STURP). They used the most advanced instruments available at the time. The Shroud was examined by ultraviolet, visible and infrared spectrometry, X-ray fluorescence spectrometry, microscopy, thermography, pyrolysis-mass-spectrometry, laser-microprobe Raman analyses, microchemical testing [1-2]. After years of study and data evaluation, the STURP team achieved the following results:

a) X-ray, fluorescence and microchemistry tests on the fibers preclude the possibility of paint being used as a method for creating the image. Ultraviolet and infrared evaluations confirm these studies. The Shroud image was not painted, nor printed.

b) Both kinetics studies and fluorescence measurements support the hypothesis that the image was formed by a low-temperature process. The temperature was not high enough to change cellulose, and no char was produced. Thus, the Shroud image was not made by pressing the cloth on a heated bas-relief.

c) The Shroud's image is superficial as the color resides on the outer surface of the fibers that make up the threads of the cloth. Recent measurements on image-fibers of the Shroud [3] confirmed that the coloration depth is extremely thin, about 200 nm.

d) The shallow coloration of the Shroud image is due to an unknown process that caused oxidation, dehydration and conjugation of polysaccharide structure of fibers, to produce a conjugated carbonyl group as the chromophore.

e) The image seen at the macroscopic level is an areal density image. This means that shading is not due to a change of color, but to a change in the number of colored fibers per unit area at the microscopic level.

f) The image fading has three-dimensional information of the body encoded in it.

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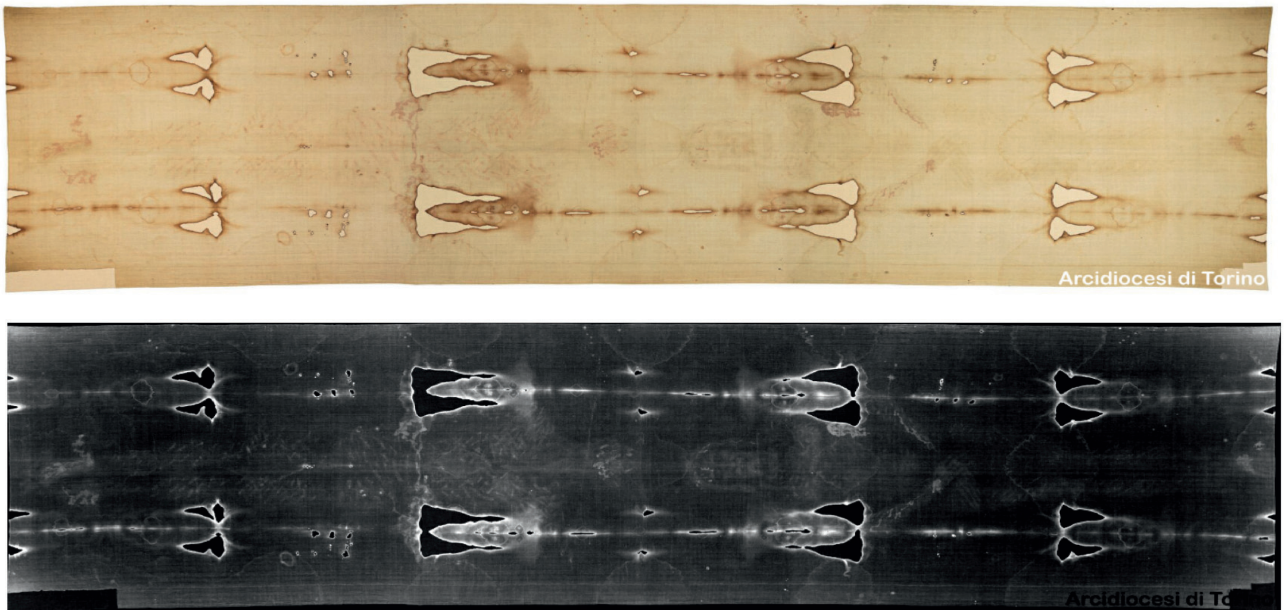

FIGURE 1 Photograph of the Shroud of Turin (top) and its negative (bottom). The image is clearly a negative, not a positive. The Shroud is a linen cloth of about 441 cm in length and 113 cm in width
Source: www.sindone.org

g) The blood stains tested positive for human blood, and there is no image beneath the blood. This means the image must have occurred after the blood flowed onto the cloth. As a consequence, the image was formed after the deposition of the corpse.
h) On the Shroud there are no signs of putrefactions, which occur at the orifices about 40 hours after death. This means that the image does not depend on the gases of putrefaction and the corpse was wrapped in the Shroud no longer than two days.
i) There is a perfect anatomical consistency of blood and serum versus wounds, including the presence of birilubin, which is invisible at the naked eye. These subliminal features require knowledge of anatomy and of forensic medicine not available before the XIX century.

According to the above results, the Shroud poses a scientific puzzle, independently of the middle age dating [5,6]. In this paper we summarize the main results of experiments carried out at the ENEA Frascati Centre, aimed at identifying the physical and chemical processes able to generate a Shroud-like coloration. The identification of these processes suggests actions aimed at a long-term conservation of this ancient relic.

Experimental Results by UV and VUV Laser Irradiations

In principle, ultraviolet (UV) or vacuum ultraviolet (VUV) electromagnetic energy incident on a linen could reproduce the main characteristics of the Shroud image, such as the absence of pigments, the shallowness of the coloration, the image in areas not in contact with the body, the gradient of the color, and the absence of image under the blood stains. To have an experimental check, we used two excimer lasers, emitting ns-pulsewidth radiation pulses at $\lambda = 308$ nm (XeCl) and $\lambda = 193$ nm (ArF), that were focused by a lens onto a linen fabric fixed on a frame.
In summary [7–9] we obtained a superficial and

Shroud-like linen coloration in a very narrow range of laser parameters. The hue of the color was brown and yellow after XeCl and ArF laser irradiations, respectively, see Fig. 2.

Aging can be a concause of linen coloration, after laser irradiations that at first do not generate any visible effect. We cut half of the laser spot on linen irradiated below the intensity threshold for coloration. As a consequence, the irradiated linen did not appear colored. We then heated one of the two parts with an iron at a temperature of 190±10 °C for 10 seconds, and coloration appeared immediately after heating. Figure 3 shows that the heating process, which simulates aging, colors only the surface irradiated below threshold, and does not color the non-irradiated area.

We also obtained a latent coloration similar to that of Fig. 3, which appeared after a natural aging of more than one year, maintaining the linen at room temperature in a dark environment [7].

We made additional experiments which gave the following results:

- When illuminated with a UV lamp, irradiated linen fabrics show a partial inhibition of fluorescence, exactly like the Shroud image [8].
- The measured absolute spectral reflectance of our linen shows a perfect overlap with the Shroud in the UV and VUV spectral region. Thus, when irradiated by UV and VUV light our linen behaves like the linen of the Shroud [8, 9].
- Using a petrographic microscope, we have observed some defects induced by UV radiation in the structure of irradiated linen fibers, see Fig. 4, similarly to very old linen fabrics. We can infer that short and high-intensity UV pulses change the crystalline structure of cellulose in a similar manner as aging and low-intensity radiation (Radon, natural radioactivity, secondary particles from cosmic rays) accumulated in a long term period do [7].
- Using an infrared camera we measured the surface temperature of our linen during irradiation with uncertainty of ±0.2 °C. The thermal heating associated with UV and VUV radiation is within a few degrees centigrade and therefore irrelevant for the purpose of coloring linens by scorching. As a consequence, excimer laser coloration is due to a photochemical process that does not involve significant thermal effects [9].

Chemistry of the Photochemical Coloration

We obtained a linen coloration (see Fig. 2) that approaches many of the characteristics of the image on the Shroud.

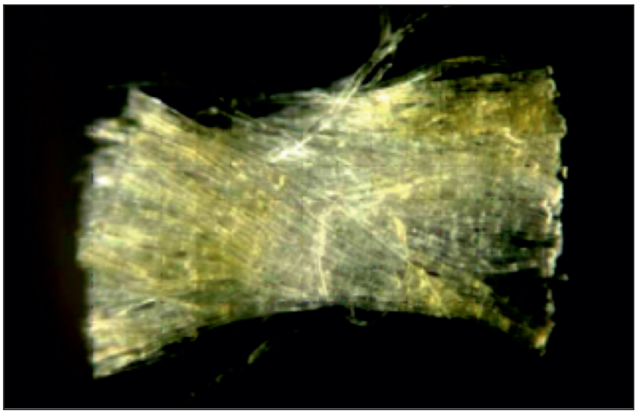

FIGURE 2 Photomicrograph of a warp thread of flax irradiated with ArF laser pulses. The thread was crushed with forceps to separate the fibers and highlight their yellow color. At the center of the thread there is an uncolored zone due to a weft thread that shadowed the laser radiation
Source: [9]

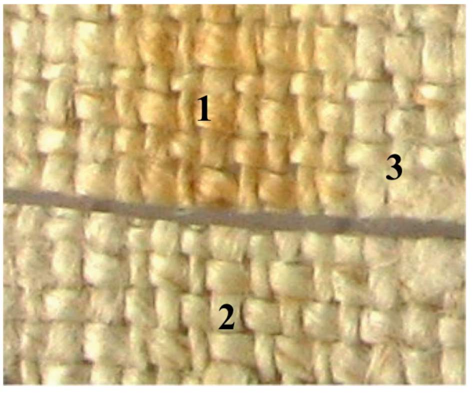

FIGURE 3 Linen fabric cut after irradiation below-threshold for coloration. 1) Irradiated area after heating. 2) Irradiated area not heated. 3) Non-irradiated area. Latent coloration of the linen area irradiated below threshold appears only after artificial aging of the upper part of irradiated linen
Source: [8]

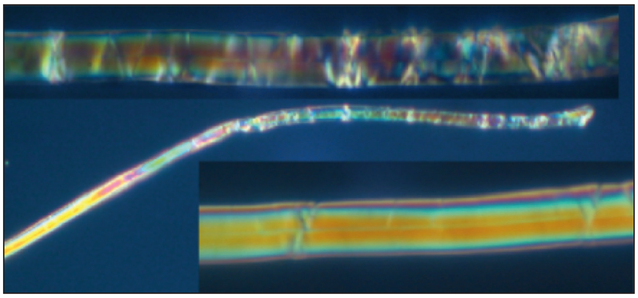

FIGURE 4 Microscope observation of a linen fiber. In the middle there is a fiber of linen between crossed polarizers to detect stress characteristics. The left part of the fiber is the non-irradiated region, which is enlarged in the inset below. On the right is the region irradiated by XeCl laser, enlarged in the inset above

Source: [7]

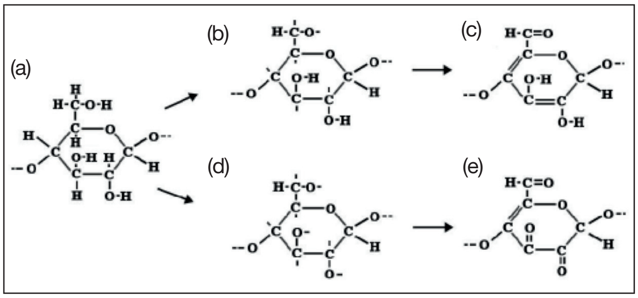

FIGURE 5 a) Main molecular structure of both cellulose and hemicellulose. There are two possible transitions (a) → (b) → (c) and (a) → (d) → (e) that generate chromophores after oxidation and dehydration. The C=C and C=O double bonds in (c) and (e) act as the chromophore and are responsible for the yellow color of the fibers of the image on the Shroud of Turin

Source: [9]

We also achieved a latent coloration that appears after a relatively long period (one year) or at once by an accelerated aging, following a laser irradiation that at first does not generate any visible image (see Fig. 3). We showed that the UV laser light produces fragility and stress of the irradiated fibers equivalent to an accelerated aging of the fabric (see Fig. 4). Finally, we have shown that the coloration is not due to a thermal effect, in analogy with the features of the Shroud image. So, the intimate chemical processes triggered by our laser irradiation may have something in common with the processes that generated the body image on the Shroud. Let us look at the details of these processes.

The STURP studies suggest the image chromophore is a conjugated carbonyl produced in the polysaccharide structure of fibers by a dehydrative oxidation process [1-2]. The color of the Shroud image is the result of an accelerated aging process of the linen, similar to the paper yellowing of ancient books [10]. Figure 5 shows two different chemical paths possibly involved in the formation of the image on the Shroud.

In our irradiations, a key-role is played by the VUV absorption band below 200 nm of alkene groups (-C=C-) [11] typically present in degraded cellulose and in organic impurities of the primary cell wall of linen fibers. The VUV absorption of these groups may trigger a reaction chain which leads to photo-oxidation (ageing) and to new alkenes and carbonyl groups. After a proper irradiation dose, new conjugated C=C and C=O groups are formed, increasing delocalization and thus shifting the absorption band to longer wavelengths, in the blue-green spectral region, to finally produce the yellowish Shroud-like coloration shown in Fig. 2.

In this frame, the formation of latent images (Fig. 3) can be explained by the oxidation and dehydration of cellulose (caused by heat or by natural aging), amending the new chemical bonds induced by laser irradiation, thus facilitating the formation of conjugated unsaturated structures that are essential part of the chemical transitions in Fig. 5. The synergy between heat and UV light is detailed in [12], showing how the process initiated by exposure to UV radiation is accelerated and reinforced by heat.

Conservation Issue: Physical, Chemical and Biological Parameters

Our experimental results show the photochemical reactions able to replicate many of the Shroud image characteristics. This can shed light on the chemical nature of the image, whose knowledge is essential to plan the long-term conservation of both the relic and the image.

Conservation of the Linen Cloth

The main component of linen is cellulose (see Fig. 5). The most important decomposition process of cellulose is dehydration. Linen adsorbs and absorbs water from air depending on both relative humidity RH and temperature T. For the sake of conservation, everything must be kept in equilibrium, as cellulose fibers will stretch and shrink when their degree of hydration changes. Thus, cellulose is well conserved if kept out of direct light, in a moderately dry atmosphere and at a constant T. These actions are necessary but not sufficient: kink bands and defects, shown in Fig. 4, can be limited only by shielding the Shroud from natural radiation such as Radon, natural radioactivity, secondary particles from cosmic rays. At sea level, secondary particles from cosmic rays can be neglected, and the main source of natural radiation is Radon, an invisible, odorless, radioactive gas formed by the disintegration of Thorium and Radium, the latter being a decay product of Uranium. Radon emits alpha particles and produces several solid radioactive products called radon-daughters. In this framework, the Shroud should be conserved in a building made by Radon-free materials (tuffaceous rocks, porphyry, basalt, syenite and granite must be strictly avoided) and built on a low Radon-emission soil. Putting the Shroud in a metal box guarantees a dark environment (absence of visible and UV-VUV light) and in addition, a few millimeters thick Aluminum (Al) stops the low-intensity beta particles emitted by radon-daughters, which are usually attached to airborne particles waving in the building atmosphere that may settle on the box.

Conservation of the Image Contrast and Visibility

Our experiments show that VUV light promotes photochemical processes leading to dehydrative oxidation of linen and formation of chromophores (Fig. 4). Smaller doses of VUV light, when coupled with heating (which simulates aging) produce latent coloration (Fig. 3). However, all these reactions require the presence of molecular oxygen O_2 to form chromophores. As a consequence, the gas in contact with the Shroud should be O_2-free in order to slow down the yellowing of non-image linen fibers that reduces the contrast of the image. An inert gas is recommended. Among inert gases, Helium is difficult to be sealed, while Krypton and Xenon are very expensive. Commercially available Argon (Ar) or Neon (Ne) with purity greater than 99,8% could be a good solution. However, a pure gas is too dry and may shrink linen, as mentioned previously. It is necessary to add some humidity, that is, water vapor. In addition, a 100% O_2-free environment favors the increment of anaerobic organisms on the Shroud. One must find a compromise between the requirements of a moderately dry environment to avoid shrinking of fibers, a low content of O_2 in contact with the Shroud to limit oxidation and the growth of anaerobic organisms. When seeking the compromise, one should consider that both dehydration and oxidation are responsible of the formation of chromophores, that is, of the linen yellowing. A compromise is RH ≈ 40%, like that of the most dry month in Jerusalem region, which corresponds to 9 mbar water vapor at T = 20°C added to the inert gas [13], and of a 0,4% O_2, which is enough to limit the growth of most anaerobic bacteria. A thorough microbiological study to assess the presence and nature of microorganisms on the Shroud should be undertaken, in order to assess the optimum value of O_2.

	Gases and pressure	Relative humidity, temperature	Box: material and thickness	Radon issue
Our suggestions	99.6% Ne or Ar, 0.4% O_2, 9 mbar water vapor P = 1,05 bar	RH ≈ 40% T = 20 °C	Al or Al-based alloy t ≥ 5 mm	Building materials and objects around must be Radon-free
Present reliquary [15]	99.5% Ar, 0.5% O_2 P equalized to the atmospheric pressure	RH = 50% T = 19-20 °C	Aeronautical alloy, t not available	Information not available

TABLE 1 Our suggestions of the optimum physical and chemical parameters and conservation measures of the Shroud, compared with the available characteristics of the reliquary made by Thales Alenia Space, where the Shroud is presently conserved
Source: Authors elaboration

Summary

In this paper we have briefly summarized the current state of knowledge on the Shroud image, and explained the reasons of the difficulty to create an image that matches its peculiar superficiality and chemistry at the microscopic level. We have demonstrated that short VUV light pulses generate a Shroud-like coloration on linen that matches many characteristics of the Shroud image. We have also identified the photochemical reactions triggered by VUV radiation that generate the Shroud-like coloration.

These results are interesting for the search of image formation mechanisms, and they also offer hints for long-term conservation measures. According to the arguments discussed above, the Shroud should be conserved in a few millimeter-thick Al (or Al-based alloy) box, filled with a proper mixture of high-purity Ne or Ar gas, O_2 and water vapor, in order to set an equilibrium between the dehydration and oxidation of linen fibers able to maintain the image contrast and visibility, while avoiding the growth of anaerobic organisms. The total pressure P should be just above the atmospheric pressure to prevent air and dust from entering inside the box. A constant T = 20°C eliminates any risk of autocatalysis-like processes from the acidic structures produced by previous oxidative activity [14]. The Al box containing the Shroud should be put in a building made of Radon-free materials, possibly in a room not on the ground floor, and every object, treasure, furnishing, floor, wall made of tuffaceous rocks, porphyry, basalt, gneiss, syenite or granite must be removed from around the box. The amount of Radon in the room should be monitored routinely.

Table 1 compares our proposals with the available characteristics of the reliquary made by Thales Alenia Space [15], where the Shroud is presently conserved.

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