

Full Length Research Paper

Image formation of the Turin Shroud: Hypothesis based on water vapor effects of light absorption

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The Shroud of Turin displays a weak front and back body image which *inter alia* is very superficial and possesses three-dimensional properties. Up to now it has been impossible to reproduce all its characteristics at the same time albeit several attempts were made in many laboratories. But lately, coloration similar to that of the Shroud has been imprinted on dry linen cloths with a powerful VUV radiation of an excimer laser, which however does not exclude the fact that a different laser source could do the same. In fact, a new hypothesis is advanced here which is based on the irradiation of wet linen cloths with a short and powerful pulse of a CO₂ laser. Besides the well known features of pulsed IR laser, the hypothesis is based solely on the peculiar optical and thermal properties of water and vapor, and therein an experimental investigation is proposed to prove its validity.

Key words: Body image, Shroud of Turin, light, lasers, heat, vapor.

INTRODUCTION

In 1960 the first laser emission was produced in the red region of the spectrum from a rod of crystalline ruby (Maiman, 1960). In 1964 the Nobel prize winner in Physics Alfred Kastler said "...a small cylinder of pink ruby, strongly illuminated produces a new light, coherent light, which is starting to revolutionize the optical science". Today, after 50 years from that discovery, lasers emits from x-rays to far infrared, and not only they have already revolutionized the optics and its applications, but they are still doing and will continue to do so in the foreseeable future, as witnessed by both scientists and ordinary people.

The reason for such fast success resides in their singular properties which can be summarized in five words: monochromaticity, power, directionality, coherence, and pulsed-regime. No other natural or artificial light source possesses such properties all together and at their extreme reaches (Hecht, 1992; Svelto, 1998). Such singular tool did not escape to a few researchers interested in the Shroud of Turin (Shroud from now on) and in particular in its front and back Body Image (BI)

which still intrigues them and escapes a rational explanation (Wilson, 2010). Indeed, one of the more frequently proposed scenario for the origin of the faint BI is the imprint left by a sudden burst of energy, likely in the form of electromagnetic (em) radiation, that is, light (www.acheiropoietos.info/proceedings/proceedings.php). Moreover, because the BI on the Shroud is rather resolved, lacks any substantial cylindrical distortion, and possesses three-dimensional (3-D) information, the powerful, directional, and pulsed light of a laser was a very welcome new entry in this controversial subject.

As a result, lasers started to be used on linens to check whether their radiation could reproduce some of the characteristics of the Shroud, but the first results were rather disappointing. For instance, it was proposed that vacuum UV radiation was very likely capable of reproducing many properties of the BI; among them the superficial coloration and 3-D information (Jackson, 1990). Soon, beams of pulsed UV lasers were directed towards linens, but they did not show any kind of coloration, but rather they were ablated and utterly destroyed, and often converted into a little amorphous powder and gas (Rogers, 1994). However, it was noted later on that such experiments could not disqualify vacuum UV radiation as a possible mechanism of BI formation (Jackson and Propp, 2004). Indeed, the

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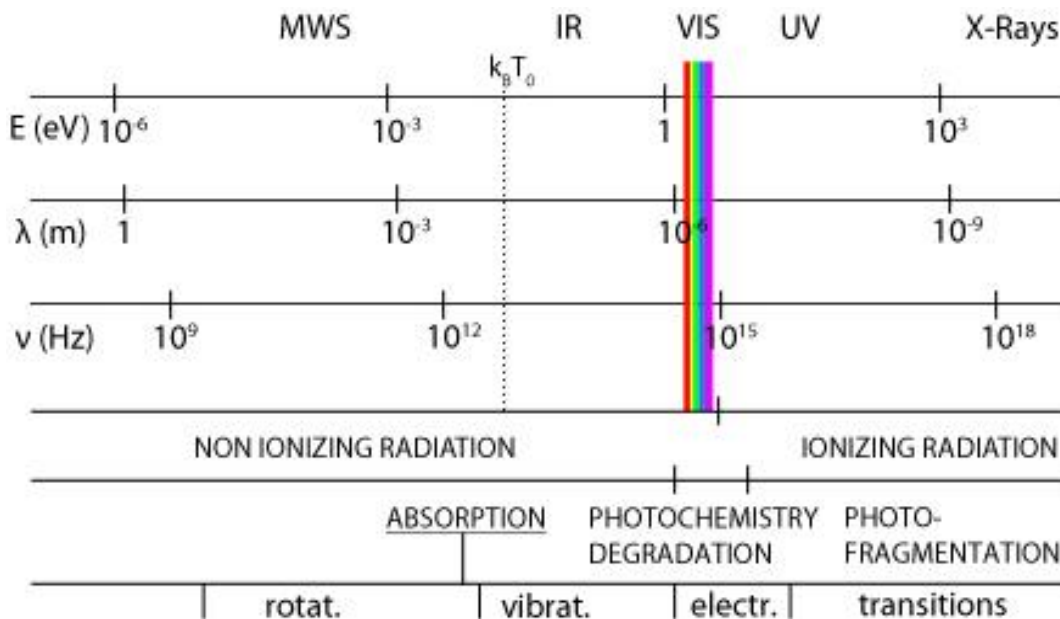


Figure 1. Effects of light-matter interaction sketched as a function of frequency, wavelength and energy of the EM radiation.

experimental parameters of the previous pulsed UV lasers were not specified at all (Rogers, 1994), so that the lack of useful results was not acceptable in view of all the possibilities provided by the many variables of the laser radiation. This last observation proved to be right when a vacuum UV laser was able to produce a coloration with many similarities with the BI of the Shroud (Di Lazzaro et al., 2010a).

However, light and laser sources have already provided many results with mixed successes. It is not the intention of the present work to go throughout all the previous investigations, but rather to study the main effects of laser beams on linens as a function of their peculiar characteristics and external experimental conditions.

To achieve these aims, this study will deal with the general effects of electromagnetic (EM) radiation, often referred as light in the text. On the matter, the effects of light and heat on cellulose, and a few relevant laser experiments will be discussed in detail. Finally, conclusions will be drawn, where also a new hypothesis of BI formation will be introduced, which is based on lasers and vapor, and on previous but incomplete experimental investigations.

INTERACTION BETWEEN LIGHT AND MATTER

As well known, light is composed of EM waves which in vacuum move at velocity c (≈ 300.000 km/s), and vibrate at frequency $\nu_i = c/\lambda_i$, where λ_i is the wavelength of one wave. Moreover, it is also characterized by the energy $E = \sum_i h \cdot \nu_i = \sum_i h \cdot c/\lambda_i$ which it carries, where h is Planck's constant and the sum is taken over all the waves

composing the light in question. Also, the matter, apart from the energy of the mass at rest, is organized in discrete energy levels, and so it is quite natural that light and matter interacts with each other. In this light-matter encountering, the main parameters which play a decisive role are for the light, wavelength and intensity (energy per surface and time), and for the matter, and its many properties, among them the evolution of the heat generated by the transformation/degradation of light.

Such parameters and other related ones have already been considered in various degrees in past scientific literature, especially in partial connection with the arguments in discussion in the present work (Feller, 1994), but here in the following they will be specified in some details for a better clarification of the subject under scrutiny.

Role of wavelength

Figure 1 shows part of the EM spectrum which is of some importance for the present work. As any material is made out of atoms and molecules, the light excites their electrons above the stationary states and, if the photon energy is bigger than the binding energy, the electrons are separated and set free from the material which remains charged positively. So, after the absorption of photons with energy bigger than 4.13 eV (300 nm, 10^{15} Hz), which is the approximate lower value for the electron binding, the matter is ionized, that is, it contains, apart from atoms and molecules, also electrons and ions. However, besides the above general subdivision in non-ionizing and ionizing radiation, many other phenomena

can happen in the two regimes which are worthwhile to be discussed in detail.

Indeed, non-ionizing radiation can be absorbed by the energy levels of matter, from the microwaves (MWS) to the VUV, which resonate with the rotational, vibrational, and electronic spectra of the matter in the order of increasing energy. After absorption, relaxation occurs with the emission of phonons, that is, heat, which may be followed by emission of light of longer wavelength, a phenomenon known as luminescence. Also, when a material is able to produce luminescence, there are many factors as interactions, impurities and temperature, which can decrease it up to the point of its total disappearance, which is commonly known as quenching effect. In this last case, all the light absorbed is transformed in heat. However, the previous optical cycle can happen only for $h\nu > k_B T_0$, while for $h\nu < k_B T_0$ the energy levels are quickly thermalized by the phonon bath, which results only in heat production. In the previous inequalities, k_B is the Boltzmann constant and T_0 the temperature of the material, mostly room temperature.

Going back to Figure 1, there is a range of energies, circa 1.24 – 8.3 eV (1000 – 150 nm, 3×10^{14} - 2×10^{15} Hz), across the boundary of non-ionizing and ionizing radiation, which can also stimulate photochemical reactions with the formation of new compounds. In this case, the energy of the photon is utilized to overcome the binding energy of the original compound or it furnishes the activation energy to initiate a chemical reaction with the production of new compounds which, in the case are simpler than the original ones, corresponds in practice to a degradation effect. So, in ultimate analysis, these photochemistry and/or degradation effects transform the energy of the photons in chemical energy rather than bare heat.

The story of the ionizing radiation is somewhat simpler. Indeed, the charged electrons and ions are rather disruptive, so that the original bindings of the atoms and molecules are further broken until the functionality of the matter itself is completely lost. This is especially true by increasing the energy of the light up to X-rays.

Thus, only the non-ionizing radiations and a small part of ionizing radiations are pertinent with the purposes of this work, and in general, the laser light absorbed by the matter is transformed as heat, luminescence and new chemical compounds in various proportions depending on the wavelength of the exciting light and the structure of the matter itself. This is particularly true for organic compounds, molecular and polymer alike, where light is absorbed between 150 and 400 nm and luminescence is emitted between 250 and 800 nm. However, triplets states mediate the emission up to retarding or/and quenching it, and intense light of appropriate wavelength can sever the molecular bindings with producing new organic compounds.

All that was said until now refers to what happens between light and matter when their interaction is treated

in the first-order approximation, that is, at low intensity laser light. When this is not true, the interaction with matter requires second-, third-, and superior-order approximations which give rise to non-linear effects, which produce among many other phenomena also multi-photon absorption.

Nonlinearity is typically observed at very high light intensities such as those provided by pulsed lasers. Indeed, the values of the electric fields should be comparable to interatomic electric fields, typically 10^8 V/m, which corresponds to an intensity of $1.3 \cdot 10^9$ W/cm² (Butcher and Cotter, 1990). However, when the intensity of light is high enough to initiate nonlinear optics, it also starts to be rather destructive especially for non transparent media, an argument which will be dealt with next.

Role of Intensity

The many and intriguing effects on the matter of a laser source, as far as its energy, that is, wavelength, is concerned, has been considered in detail previously, while the intensity has been introduced only in connection with non-linear optics in the extreme regime of intense laser beams. However, the light intensity is at work also in the linear optics, usually affecting the various phenomena in a proportional way. For instance, photochemistry products, heat of relaxation and intensity of luminescence are proportional to the laser intensity. Anyway, while the luminescence is quickly lost, new chemical compounds and heat remain, and the time of interaction between the laser beam and the material under irradiation plays also a role.

Figure 2 shows a general picture of the effects of laser sources which irradiates the surface of a generic material. These effects are described as a function of the power density, the interaction time, and the specific energy. The interaction time refers to the interval of time the laser beam interacts with the material, and it can be the result of a continuous wave (cw) laser switched on and off by a mechanical or electronic modulator, or of a pulsed laser. In the latter case, the interaction time is given by the pulse duration, or by a multiple of such duration if more than one pulse is utilized. However, because of limiting technical factors, cw lasers do not extend their effectiveness below 10^{-3} s, where pulsed lasers dominate the scene. For instance, pulsed excimer lasers work only in the range 10^{-8} - 10^{-7} s, while pulsed and cw CO₂ lasers work in the whole time regime longer than 10^{-8} and 10^{-3} s, respectively.

Whatever the laser utilized for irradiation, it is clear that its precise effects will depend also on the optical and thermal properties of the material under study, which will be considered in some detail later on. At the moment, let us focus attention on a large scale of the laser parameters, where the effects are independent from the

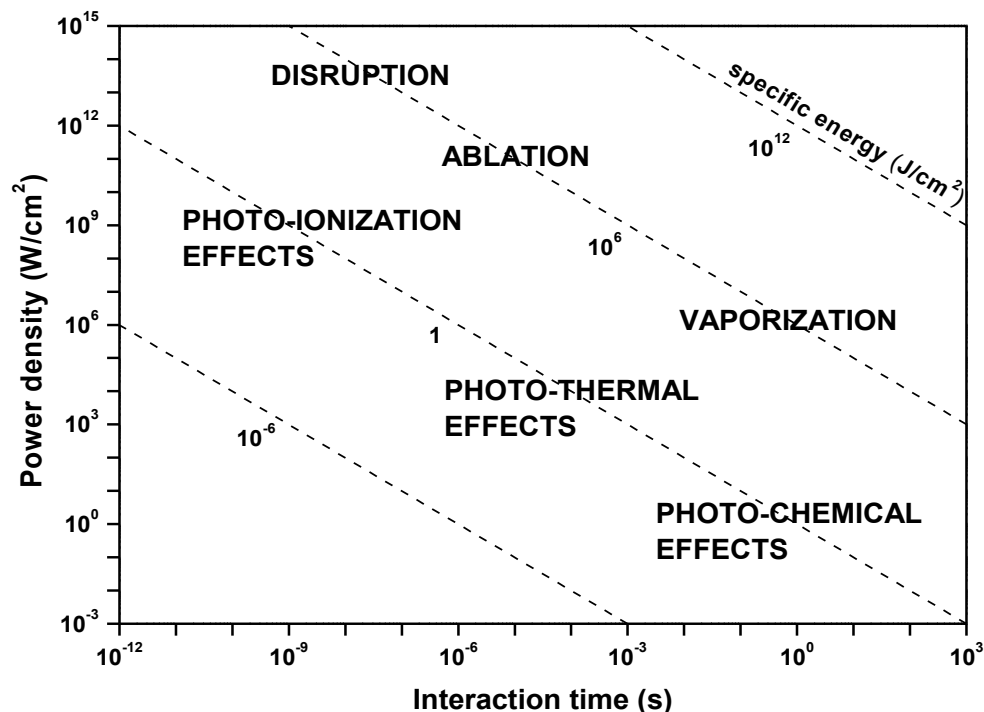


Figure 2. A comprehensive sketch of the effects of laser radiation on a generic material as a function of power density (ordinates), interaction time (abscises), and specific energy (oblique dotted lines).

material and can be displayed as in Figure 2. To understand better such trends, it is necessary to move along the oblique lines of the specific energies. For the intense value of 10^6 J/cm², moving from right to left, little or nothing of noticeable happens well above 1 s apart from heating, while below 1 s the material begins to vaporize first, to be ablated later on and finally completely destroyed. However, there are other effects which are not reported in the plot to avoid further congestion, such as the carbonization of organic materials before its vaporization. For the less intense value of 1 J/cm², at relatively long interaction times there are the already mentioned photo-chemical effects, followed with decreasing interaction time by photo-thermal effects first and later on by photo-ionization effect. Let us remind here that the previous general description does not exclude the possibility to have mixed effects. In particular, in the case of specific energy of 1 J/cm², photo-thermal effects continue to occur at times longer than 10^{-3} s, as photo-chemical effects at times shorter than 10^{-3} s.

Hence, there are not sudden variations of behaviors in Figure 2. For instance, at the top of the 10^6 J/cm² line, the same description is still valid but with much more extreme results, as there is the possibility of nuclear fusion still being pursued at the National Ignition Facility in Livermore, California, USA; where 192 UV laser beams, total energy ~ 1 MJ and pulse duration circa 1 ns, are directed on a tiny target to obtain nuclear ignition, and a flux of 10^{14} neutrons was produced during December

2010. The same holds at the bottom-left of the 1 J/cm² line where the laser effects are expected to decrease or disappear completely, while recently lithium fluoride has been ablated by using a soft x-rays laser with 10 mJ/cm² and pulse duration 7 ps (Faenov et al., 2009).

Heat evolution

It has just been shown that the absorption of laser light from a generic material results in a certain number of phenomena and, among them, the production of heat is probably the most conspicuous one. So it is imperative to study the dynamics of generation and propagation in space and time of the heat produced locally by the laser irradiation.

In general, when a laser beam hits the surface of a material, part of the light is reflected and part goes through the material itself, where it can be totally or partially absorbed. Clearly, the case of a transparent material is of no interest in this work; so it is further supposed that the non reflected part of the laser beam is completely absorbed in a finite depth d . So, the problem to be solved is what happens to the heat generated in a thickness d of the material. In the most general case, after a small volume of material at temperature T_0 has been heated at a temperature $T > T_0$, the theory for heat propagation shows that the evolution of temperature depends on the thermal diffusivity given by:

Table 1. Thermal conductivity (K), heat capacity ($C = \rho \cdot c_p$), thermal diffusivity (α), and thermal constant time (τ) for a few representative materials (Anderson, 1989). ρ and c_p represent density and specific heat.

Material	K (W/cm·K)	C (J/cm ³ ·K)	α (cm ² /s)	τ (s)
Diamond (type I)	9.1	1.8	5.1	0.080
Saturated vapor	$1.9 \cdot 10^{-4}$	$4.6 \cdot 10^{-5}$	4.1	0.10
Copper	4.1	3.4	1.2	0.35
Air	$2.6 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	0.2	2.0
Carbon steel	0.61	4.0	0.15	2.8
Sandstone (Bedford, Indiana)	$2.2 \cdot 10^{-2}$	2.2	$1.0 \cdot 10^{-2}$	41
Glass (pirex)	$1.1 \cdot 10^{-2}$	1.7	$6.4 \cdot 10^{-3}$	63
Mahogany (parallel to fibers)	$3.1 \cdot 10^{-3}$	0.7	$4.4 \cdot 10^{-3}$	92
Mahogany (normal to fibers)	$1.6 \cdot 10^{-3}$	0.7	$2.3 \cdot 10^{-3}$	176
Saturated water	$6.1 \cdot 10^{-3}$	4.4	$1.4 \cdot 10^{-3}$	287

$$\alpha = K/\rho \cdot c_p \quad (1)$$

With K the thermal conductivity, ρ the density, and c_p the specific heat of the material (Brown and Marco, 1958; Holman, 1992).

The exact solution of a specific problem can be found analytically or with numerical calculations, once the geometry of the experiment and the properties of the material are known. But here we are mainly interested to know an approximate evolution of the temperature. On this regard, it is well known that if a slab of dimensions large in comparison to its thickness d is heated at a temperature bigger than the rest of the same or different material, its temperature returns to the initial one with a quasi-exponential behavior which is described by a time constant τ . Values of such constant are reported in Table 1 for a few relevant materials (Anderson, 1989). Also, thermal conductivity, capacity and diffusivity are given, and it is immediately observed that, while thermal diffusivity and time constant are monotone for the various materials chosen, thermal conductivity and capacity are not, which is a further indication that the former parameters are the meaningful ones for the propagation of heat. Anyway, Table 1 tells us that a thermal disturbance moves, for instance, very slowly in water, 287 s, and very quickly in diamond, 80 ms. In particular, Table 1 indicates that a laser beam with interaction time or pulse width shorter than τ produces thermal effects practically isolated from the rest of the material, so that the heat released in the volume of the beam remains there with a consistent increase of the local temperature. On the contrary, any laser with interaction time or pulse width longer than τ cannot produce a consistent increase of temperature because the heat released is quickly carried away by the material.

DISCUSSION

The previous description of the properties of lasers and their effects on various materials has served useful the

purpose of understanding the mechanisms in general, but now it is time to specify the material so that also the effects can be better described. As stated in the introduction, our interest resides in the BI of the Shroud, which is well known to be imprinted on a big piece of linen (Wilson, 2010).

Thermal and physical properties of the linen of the Shroud are not easily accessible, so it is necessary to deduce them from what is known directly and indirectly, and Table 2 has been assembled accordingly. It contains different kind of linens, cellulose, which is the main component of linen, wood, which is made mainly of cellulose, and the linen of the Shroud. Finally, the properties of interest are projected arbitrarily in "standard" linen which should be similar to those of the Shroud. In particular, the density ρ has been taken from the Shroud itself, a value which is compatible with cellulose and other linen cloths. The reported specific heat c_p belongs to cellulose, smaller with respect to wood as expected. The thermal conductivity K refers to a woven linen, probably the nearest one to the Shroud.

Having made the previous apparently reasonable choices, the thermal diffusivity is $6.14 \cdot 10^{-4}$ cm²/s and the relaxation time 658 s. These values attribute to the linen of the Shroud the smallest thermal diffusivity and the longest relaxation time among the materials listed in Table 1, which is not a completely unexpected result. Indeed, vegetal fibers are good insulating materials, especially when properly and artfully woven, as testified by their common use since ancient times by mankind. Such small thermal diffusivity means that the heat generated in a linen cloth by a laser beam remains essentially in the volume of the laser spot for several minutes without spreading consistently to the rest of the cloth. Indeed, temperatures as high as 100°C can be reached with laser intensities as low as 1 mW/cm² in a depth of 0.1 cm during 100 s of continuous irradiation. However, this is true only if the laser light is completely absorbed by the cloth, which is not the case in general.

Typical absorption values can be retrieved from the reflection measurements which have been performed on

Table 2. Surface density (σ), thickness (t), density (ρ), specific heat (c_p), thermal conductivity (K), thermal diffusivity (α), and relaxation time (τ), for various cellulose materials and an arbitrarily chosen standard linen.

Material	σ (g/cm ²)	t (cm)	ρ (g/cm ³)	c_p (J/g·K)	K (W/cm·K)	α (cm ² /s)	τ (s)
Linen Mesh ¹	0.026	0.098	0.265		$7.7 \cdot 10^{-4}$		
Linen Woven ¹	0.0195	0.033	0.591		$7.0 \cdot 10^{-4}$		
Cellulose ²				1.423			
Cellulose ³			1.27-1.61				
Linen ³					$8.8 \cdot 10^{-4}$		
Wood ³				1.76			
Linen Shroud ⁴	0.0275	0.0345	0.80				
Linen standard			0.80	1.423	$7.0 \cdot 10^{-4}$	$6.14 \cdot 10^{-4}$	658

Sources: ¹ Rood (1921); ² The Shroud Image and Radiation: Compressible Flow Part1, in internet; ³ Handbook of Chemistry and Physics (1960); ⁴ Schwalbe and Rogers (1982).

the linen of the Shroud itself in several intervals of wavelengths from the UV and VIS (Gilbert and Gilbert, 1980) to the IR (Accetta and Baumgart, 1980). These intervals do not overlap each other but, because the reflection does not exceed 15% in the IR and 60% in the UV-VIS, it has been possible to join the existing gaps approximately with straight lines. By supposing that the transmission throughout the whole spectrum is about 10%, as estimated in the IR (Gilbert and Gilbert, 1980), the derived absorption is displayed in Figure 3 from 250 nm to 13.5 μ m, where only the intervals 0.25 to 0.75, 2.80 to 5.40 and 7.50 to 13.50 μ m have been really measured. It is noteworthy to observe that in the UV-VIS region, the absorption values coincide enough well with a recent measurement on a modern linen cloth manufactured following ancient technologies (Di Lazzaro et al., 2010a).

Anyway, the data show that, apart from the interval 0.4 to 2 μ m where there is a broad minimum as low as 30%, in the IR there is an almost constant absorption of about 80%.

This means that UV, violet-blue and IR lasers are better suited to heat up linens with respect to VIS and near IR lasers. But, while all kinds of lasers heat up linen, UV and VIS lasers can also stimulate photochemical reactions, and only UV lasers possess a photon energy high enough to break the chemical bonds of cellulose. So, at this point it is of paramount importance to describe the effects of heat and light (photolysis) on cellulose.

Effects of heat on cellulose

Heat can be generated in the cellulose of linens by a laser beam, by contact with a hot body, and by heating the air components surrounding the cloth, which all produce an increase of temperature more or less homogeneous depending on the space and time characteristics of the heating methods. Moreover, the thermal properties of linen keep the heat in loco for several minutes.

Cellulose, which constitutes about 90% of cotton, 80%

of linen and 50% of wood, is a linear polymer of about 3000 glucose units joined together by special chemical linkages, while glucose is a complex benzene-like molecule (C₆H₁₂O₆), with saturated structures, that is, without double bonds.

It is worthwhile to note that cellulose does not absorb selectively in the visible spectrum, and so it appears whitish to eyes, while double-bond formation leads to coloration at various degrees from pale yellow to dark brown according to the type of unsaturated structures and their density.

When cellulose in dry air is subjected to heating up to 150°C, thermal oxidation occurs with the onset of carbonyl groups (=C=O) with considerable conjugation, that is, cross-linking and double-bond formation from neighboring hydroxyl groups (–O–H) by elimination of water. The fact that this chemical reaction can easily be observed by the yellowing of cellulose, remains a phenomenon under close scrutiny both for its technical (Nakagoshi and Yoshizumi, 2011) and basic (Mosca Conte et al., 2012) aspects. In particular, the Yellowness Index (YI) increases by a factor 10, that is, the color moves in the sequence white→yellow→beige. The color is caused by the above-mentioned conjugated unsaturated structures which absorb heavily above 330 nm differently from the simple carbonyl groups (–(C)=O) which absorb weakly at 260 and 300 nm. Apart from the coloration, the strength of cellulose also decreases and the length of its molecular chain is slightly shortened (Bos, 1972; Yatagai and Zeronian, 1994). Moreover, if the temperature increases above 150°C, the chemical structure of wood (cellulose) is decomposed and the phenomenon of pyrolysis starts with several products volatilizing from the surface. These products react with oxygen and produce more heat, causing an increase of temperature and a strongly growing chain reaction, until at 233°C the classical combustion starts. Another pathway is also possible, when the higher temperature of circa (300°C) is reached with the production of tar before the final combustion. Anyway, once the pyrolysis starts, and well before the combustion,

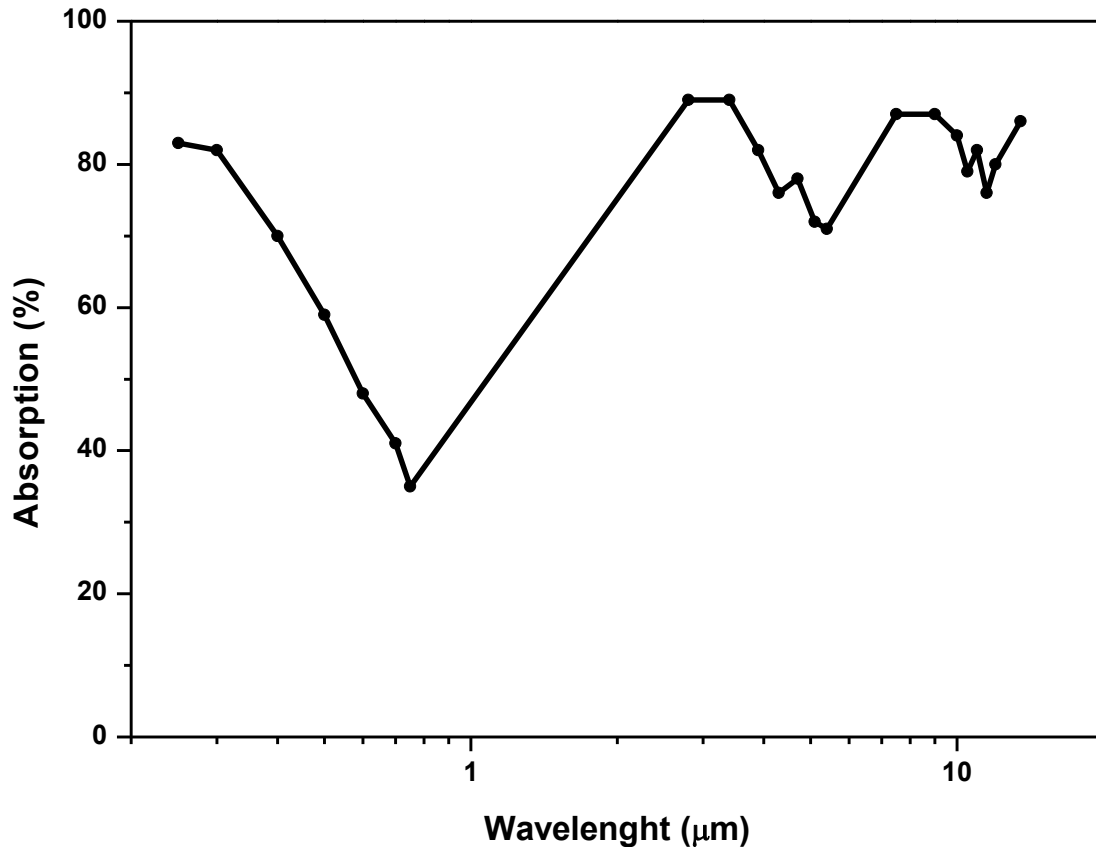


Figure 3. Optical absorption of the clear linen of the Shroud of Turin in the UV, VIS and IR range of the electromagnetic spectrum. The dots are experimental measurements, while the straight lines are simple adjoining traits.

the cellulose appears more and more blackish and carbon-like.

Effects of light on cellulose

When cellulose in dry air is subjected to light irradiation, several chemical changes, that is, photolysis, occur which depend on the wavelength of the radiation.

Light below 200 nm VUV, decreases the degree of polymerization (DP) and alpha cellulose (AC) without atmospheric oxygen, and produces a noticeable yellowing (Alpha cellulose is a highly refined, insoluble cellulose from which sugars, pectin, and other soluble materials have been removed, and it is also known as chemical cellulose). So, it is not a photo-oxidation process but double bonds are formed, very likely carbonyl groups (Launer and Wilson, 1949).

Light in the range 200 to 300 nm decreases DP and AC to a greater extent than below 200 nm, but now using the atmospheric oxygen, and a slight yellow coloration is observed. So, a photo-oxidation is at work and very likely carbonyl groups are oxidized to acids (Launer and Wilson, 1949; Bos, 1972).

Light in the range 300 to 1000 nm reduces the strength of cellulose, shortens the cellulose chain, and the YI decreases, that is, the cellulose bleaches (Yatagai and Zeronian, 1994).

Light above 1000 nm, besides a probable and negligible bleaching effect, essentially is absorbed by the cellulose and produces heat with the effects already described.

Thus, in dry atmosphere, light always degrades cellulose, by decreasing the strength and shortening the length, but produces a noticeable yellowing only in the VUV region, while the coloration decreases by moving towards the UV region up to a complete bleaching in the VIS.

Effects of heat and light on cellulose

Light and heat increase their action on cellulose in air more than if applied singularly. For instance, at 253.7 nm degradation increases markedly with temperature and, because there is no degradation in absence of oxygen, photo-oxidation is at work with production of carbonyl groups (Egerton et al., 1962).

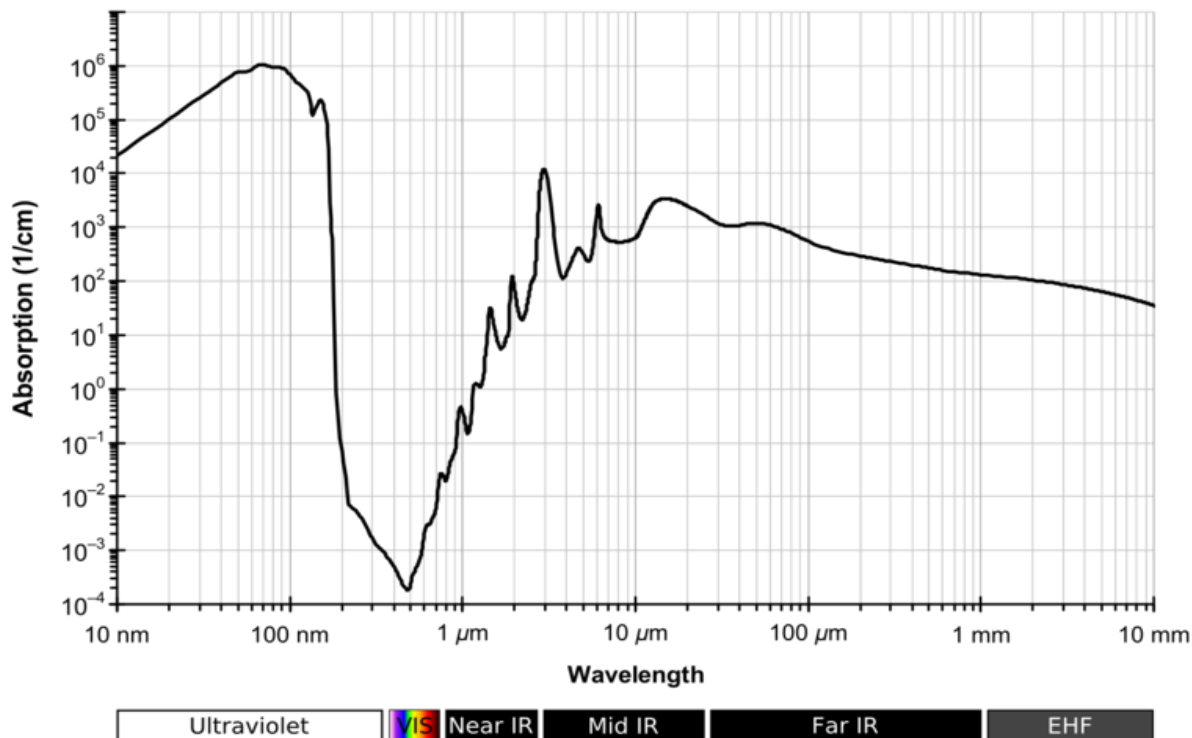


Figure 4. Liquid water absorption spectrum across a wide wavelength range. Vapor features are similar but shifted 60 nm to shorter wavelengths. Source: Toselli (1992).

Also, in the range 300 to 1000 nm, light and heat degrade cellulose more efficiently than if applied singularly, but have different effects on the coloration. Indeed, while light bleaches, heat colors cellulose with the final result that the yellowing or beige is even more consistent than with heat alone (Yatagai and Zeronian, 1994). Moreover, an initial light exposure accelerates heat degradation and produces what is already known as latent image process (Launer and Wilson, 1949).

The coloration is caused, as for heat alone, by the introduction of chromophore groups formed as the heat treatment induces oxidation of the cellulose, and so conjugated unsaturated structures, but the light introduces new efficient reaction pathways. However, it has not been established yet whether the mechanisms of the two treatments are the same, which is very unlikely.

Effects of light and vapor on cellulose

Water vapor decreases and/or retards the effects of degradation, DP and AC, of cellulose exposed to light at 184.9 nm, and also the yellowing is less intense than in light alone (Launer and Wilson, 1949). At 253.7 nm the effects of vapor seem to be contradictory because, while the tensile strength is restored, the fluidity is increased, which means that the role of vapor in the photochemical reactions is more complex (Egerton et al., 1962). In the

region 330 to 750 nm, vapor promotes DP while producing mixed effects on cellulose of different origin, a behavior opposite with respect to the VUV region (Launer and Wilson, 1949). It seems that the degradation of cellulose is not localized in the molecular chain in presence of moisture, while it is highly localized at the end of the chain in dry air, and probably there are fundamental chemical combinations between cellulose and water.

As far as vapor is concerned, it is also necessary to consider the extreme case when the cloth is heavily soaked with water, which absorbs as in Figure 4. Referring to thicknesses less than 1 mm, water is practically transparent from 180 nm to 2 μ m, where the light effects are the same ones as just described. Different is the case above 2 μ m when the light is essentially absorbed by the water which, in case of intense irradiation, is transformed to vapor at high temperatures. If the interaction time is less than 0.1 s, the hot vapor heats the linen cloth which so experiences the effects of heat and vapor in a different way than when the water is absent.

Comparison with known experiments

It has been shown that the effects of heat and light are essentially different because they act via different chemi-

cal and physical processes, with the notable exception when light degenerates in heat. Indeed, when a laser beam irradiates a linen cloth, its effects depend on the specific energy and wavelength. The role of specific energy and power density has already been discussed and it is well sketched in Figure 2, while the role of wavelength is briefly summarized in the following. At very short wavelengths, VUV and UV, there are only photo-chemical effects, which decrease with increasing wavelength in the VIS and disappear in the IR. Conversely, photo-thermal effects are dominant in the IR and decrease while moving back to VUV. Moreover, in the VIS photo-bleaching effects also appear in a consistent way.

The effect of vapor is different at different wavelengths, but it is evident that the water molecule enters actively in the photo-chemical reactions by reducing the oxidizing effects of light and heat. However, it is also necessary to consider the effects of laser beams on a moisturized cloth, which in the IR range produce thermal effects via the hot vapor, differently from the normal photo-thermal effects on the cloth itself. On this subject, we will return later on, while now it is time to consider a few experiments performed with mainly laser light.

The CO₂ laser at 10.6 μm has been very frequently utilized in both cw and pulsed regime, most probably because it is one of the most common type of laser present in laboratories and industries since its introduction in 1964.

A cw CO₂ laser, power density 160 W/cm² and interaction time 0.2 s, has been used on linen cloths dry and soaked with water, and blackish scorches have been produced only in the latter ones. The tonality of the scorches was strongly dependent on the degree of wetting, and luminescence was not detected from the scorched linens upon irradiation with UV light. A reproduction of the face of the Shroud has been realized which looks very similar to the original one by sight, but at a microscope observation the fibrils are ragged, burned and ablated (Cerri et al., 1986). The parameters of the irradiation place these experiments in the right-bottom region of Figure 2, and so the results were reasonable enough taking also in account the effects of the wavelength.

A cw CO₂ laser, power density 3 W/cm² and interaction time up to 300 s, has been used on linen cloths for studying thermally induced chemical transformation in cellulose. After the irradiation, the linens looked slight yellow to yellow-brown. Four thermally excited processes have been observed, corresponding to four chromophore states strongly dependent from oxygen, which implies an oxygen dependent thermal degradation with the onset of carbonyl groups. Following UV irradiation at 254 nm, which bleached the sample initially, subsequent heating resulted in a faster degradation (Jackson et al., 1988), that is, latent coloration process as has been discussed (Yatagai and Zeronian, 1994; Launer and Wilson, 1949).

The results described here are very similar to those obtained by heating cellulose at about 150°C by using an air oven (Bos, 1972; Yatagai and Zeronian, 1994). The parameters of the irradiation place these experiments in the right-bottom region of Figure 2, where photo-thermal and photo-chemical effects are described.

A pulsed CO₂ laser, average power 10 W/cm², pulse duration about 10 μs and repetition frequency 300 Hz, has been used on linen cloths with the aim to reproduce the image of the Shroud. The very purpose of the experiment was reached by obtaining a very good reproduction of the face of the Shroud, which possesses a continuous degree of darkening and 3-D features. However, accurate analyses did show cellulose degradation as swelling and explosion, yielding a sponge like structure. The dark shades could be ascribed to surface tar formation rather than conjugated carbonyl chromophores (Ferrero et al., 2002). The parameters of the irradiation are not described, but they can be inferred from the scarce data and from similar laser systems which can easily emit a power density up to GW/cm². So, this laser very likely was operating in the center-top region of Figure 2 and the obtained results are reasonable enough.

Excimer lasers, which emit VUV and UV light only in pulsed regime, were introduced in 1970 but only in 1975 became practical enough to be utilized currently in laboratories and industries.

As we have seen in the introduction, their use to simulate the BI of the Shroud has been proposed following detailed experiments with the line at 254 nm of a mercury lamp, which produced interesting results similar in many aspects to the BI of the Shroud (Jackson, 1990). However, subsequent experiments with excimer lasers were rather negative in dry linens (Rogers, 1994) and in linens treated with a mixture of aloe and myrrh (Rodante, 1993). However, in both experiments, laser sources and experiments were not described at all, so that the negative results could not be taken as a final answer.

Finally, an excimer laser, 0.4 J energy at 308 nm in 33 ns of pulse duration, was used on dry linen cloths, and permanent macroscopic colorations was obtained (Baldacchini et al., 2008). However, this rather superficial coloration appears only with a power density of about 20 MW/cm², and the color tonality is yellow-brown. More recently, the previous result was improved as far as color tonality and superficiality are concerned (Di Lazzaro et al., 2010a). Indeed, an excimer laser in the VUV, 0.08 J at 193 nm in 12 ns of pulse duration, yellowed linen cloths for a shorter depth than above at a power density 1 to 4 GW/cm².

This result approaches even more the characteristics of the BI of the Shroud, and so the hypothesis that vacuum or extreme UV radiation could be a good candidate for having imprinted the BI of the Shroud, is becoming more and more reasonable (Jackson, 1990).

CONCLUSIONS

Up to now, we have discussed in details the effects of heat and light applied on linen cloths, and several experimental situations have been taken into account together with many different results, having in mind their comparison with the BI of the Shroud. However, we have not given yet a full account of the properties of this singular BI, apart from some information here and there when needed for the matter in discussion. It seems now is the right time to do so. The Shroud is a linen cloth 4.3 m long, 1.1 m large and 0.34 mm thick. It has been fabricated in three-to-one herringbone weave with yarns about 300 μm in diameter, each yarn composed of about 200 fibrils "Z" twisted and about 20 μm in diameter. Among other remarkable marks, it shows on one side of the fabric surface a weak frontal and dorsal image. The Shroud has been studied scientifically since 1898, when the first photographs were taken, but the most detailed investigation was performed only during 5 days in October 1978 by the Shroud of Turin Research Project (STURP) (Schwalbe and Rogers, 1982).

The main conclusions of this famous project have been:

- i) The image is better perceived from a distance of 4 to 5 m.
- ii) The linen fibrils are both clear and colored yellow to faint yellow, and more yellow fibrils are present in image areas than in non-image areas.
- iii) The faint image does not reside in an applied pigment, but rather some cellulose oxidation/dehydration process is involved.
- iv) The image is rather superficial.
- v) Three dimensional profiles, generated from the frontal image densities, strongly resemble the human form, that is, the front image possesses 3-D properties, and the blood stains are indeed blood.

Since 1978, other important features have been discovered, and among them the following ones are more pertinent with the present work:

- i) The image appears on an already yellowed linen cloth as a faint but darker yellow-brown discoloration (Jackson et al., 1984),
- ii) There is no image under the blood stains (Heller, 1983),
- iii) The color resides in the most external (two or three) fibrils in the threads (yarns), depth 30 to 60 μm , and single colored fibrils are only altered for a thickness of 200 nm, that is, their internal part, the medulla, is not altered (Fanti et al., 2010),
- iv) A weak and hazy image has been found in the back surface of the Shroud in correspondence to the face image in the front surface, that is, double superficiality of the BI (Fanti and Maggiolo, 2004).

The previous features, and other ones reported else-

where (Fanti et al., 2005), can be explained in the frame of the hypothesis of a sudden burst of Vacuum or Extreme UV radiation (Jackson, 1990), and it has already been shown that a VUV excimer laser generates a coloration very similar to the BI of the Shroud (Di Lazzaro et al., 2010a). Indeed, depending on the conditions of irradiation, the coloration obtained is light yellow, yellow, and yellow sepia, and the color penetration depth is mostly 26 μm and even less (Di Lazzaro et al., 2010a, b).

However, recently it has been found that the image of the Shroud can also be explained by a corona effect, an electrical discharge in air at high voltage which produces electron beams and light (Fanti, 2010). It is worthwhile noting that the corona effect, which can explain also the double superficiality of the image, generates as one of its byproducts intense UV light which is the main imprinting factor in the hypothesis of the burst of light (Jackson, 1990).

At this point, it is interesting to ask ourselves whether other modalities connected with a burst of light could generate the same type of coloration or discoloration observed in the Shroud.

It has been already discussed that only VUV and UV radiation possesses the photonic energy necessary to initiate the chemical processes leading to the formation of chromophore groups or to break the long molecular chain of cellulose. Moreover, the right coloration, pale yellow or yellow-sepia, is obtained only by radiation well below 250 nm, which is also extinguished in a few tens of μm , another essential condition required by the BI of the Shroud. The heat in itself, generated by hot air, hot body and laser absorption in the VIS or IR spectral region, is excluded because both the irradiated linen appears yellow-brown or dark-brown, when not burned, and the penetration depth is much bigger than tens of μm . However, it has been shown that the degree of darkening can be finely tuned up to obtain a slight yellow coloration upon irradiation with a low power CO₂ laser (Jackson et al., 1988), and water strongly conditions the whole irradiation effects with a medium power CO₂ laser (Cerri et al., 1986). So, the presence of water seems to be important in the photo-thermal and photo-chemical processes of cellulose, as it was already observed (Egerton et al., 1962).

To understand deeper the effect of water in the present context, let us go back to its relevant properties. First of all, Figure 4 shows that only electromagnetic radiation below 180 nm and above 2 μm is completely absorbed for a depth less than 100 μm . Moreover, Table 1 shows that water is one of the most insulating materials as far as thermal diffusivity and thermal relaxation time are concerned, while vapor is one of the most conducting, immediately after diamond.

These peculiar properties means that when a linen cloth is heavily soaked with water, it is the water which is having the active role following irradiation with laser beam in the IR, for instance a CO₂ laser, while the linen cloth is relegated to have a mere passive role. Indeed, the laser

radiation is absorbed almost exclusively by water, which warms up to become vapor, and finally it is the vapor which heats the linen cloth, with all the consequences which have already been described. Really, the final results depend on the power density and the interaction time of the laser beam on/with the soaked cloth, as described in part in Figure 2; however, let us move with order.

In case of a cw CO₂ laser and very long interaction times, at power densities lower than a few Watts, nothing remarkable happens until the water remains in the cloth, and only when it is evaporated some photo-thermal effects appear, which is not at all interesting in this context. However, if the power density increases and the interaction time decreases, the produced vapor can induce photo-thermal effects which are water-dependent. Indeed, water molecules combine chemically with cellulose retarding the oxidation/dehydration phenomena, while chromophore groups are induced with the result of a yellowish coloration, which may not be yet identical with that of the Shroud but much nearer to it than the brown/dark coloration obtained in dry linens. It has already been noted that the presence of water influence greatly the degree of coloring (Cerri et al., 1986); however, until the interaction time is of the order of few seconds, the vapor has the time to heat in depth the cloth so that the coloration loses the superficiality of the BI of the Shroud.

Different is the case of a powerful pulsed CO₂ laser with the interaction time coinciding with the pulse duration, a few microseconds or even less. In such case, the water is vaporized instantaneously and only the surfaces of the fibrils have the time to heat up to begin photo-thermal effects leading to coloring of the cloth. It is clear that not all the experimental conditions are suitable to obtain the desired results, but it is possible that a range of parameters as power density, pulse duration and water content exists for obtaining a coloration similar to that of the Shroud. In this respect, it is worthwhile to remember that the first attempts to color linen cloths with excimer lasers failed, and only later on systematic experiments were successful, but only in a very narrow range of irradiation parameters (Baldacchini et al., 2008; Di Lazzaro et al., 2010a, b).

In conclusion, it is proposed that a pulsed laser emitter above 2 μ, for instance a CO₂ laser, may be suitable to obtain coloration on linen cloths soaked with water, similar to the BI of the Shroud. Accurate experimental investigations should be performed in order to test such hypothesis which at the moment is based only on theoretical guesses and some incomplete experimental evidences.

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