

## Article

# Yellowing of Ancient Linen and Its Effects on the Colours of the Holy Face of Manoppello

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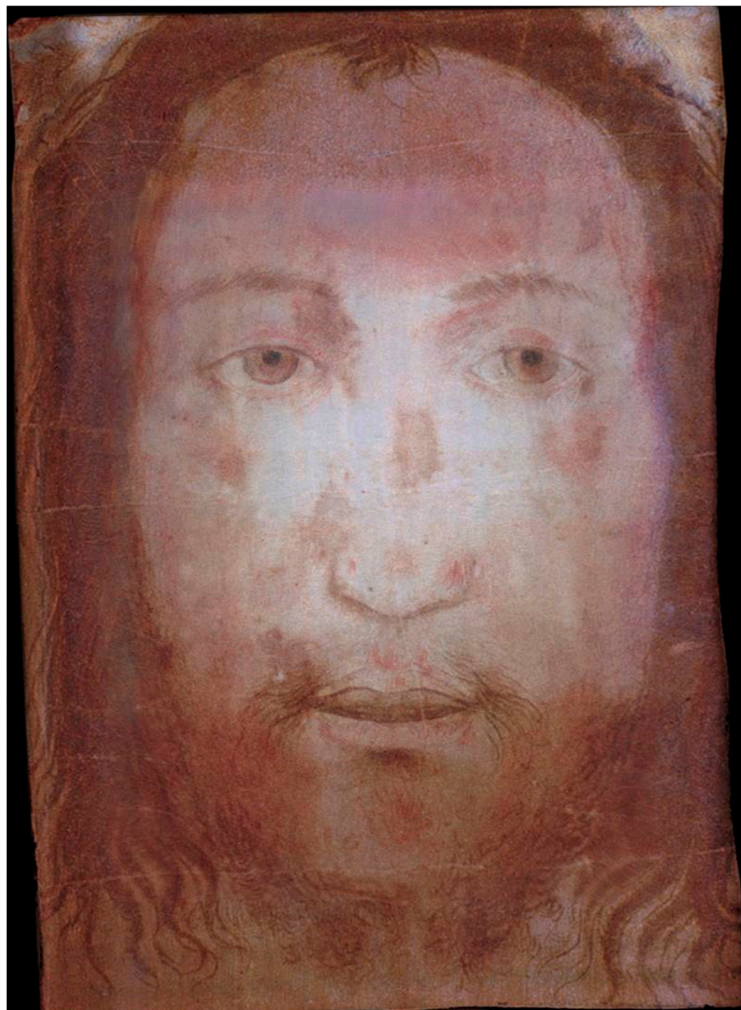
**Abstract:** On both sides of the Veil of Manoppello, made with very thin linen, translucent linen threads, probably starched, a Holy Face of Jesus Christ is visible. During the centuries, the yellowing of the linen threads has changed the aspect of the original face, in particular producing unnatural colours of the eyes. Indeed, as inferred by some experimental evidences, both on a microscopic and a macroscopic scale, the eyes were probably originally blue. Blue was the colour mainly affected by the yellowing of the linen threads, leading to greenish shades not compatible with human irises' colours. Thus, we think that this finding compelled an artist to retouch the eyes' irises with brown colour. The theoretical analysis of degradation times of the cellulose contained in starched linen indicates that, at ambient temperature, the yellowing takes about ten centuries to reach 95% of its maximum. Due to its peculiar optical characteristics and historical vicissitudes, the Veil of Manoppello likely coincides with the Veronica's Veil, the alleged relic of the face of Christ impressed during his Passion, just before his crucifixion. If the Manoppello and Veronica's Veils are the same object, any hypothesized colour retouch was done just before its first known public procession and exhibition in Rome, i.e., before the year 1200, after ten centuries of yellowing. Therefore, the Veil of Manoppello could be very ancient, even of the Roman epoch.

**Keywords:** Veil of Manoppello; Veronica's Veil; Jesus Christ iconography; linen yellowing; cellulose degradation

## 1. Introduction

The Veil of Manoppello, kept in a sanctuary of the Italian town of Manoppello in Central Italy, is a rectangular canvas of  $240 \times 175 \text{ mm}^2$ , representing the face of Christ (Holy Face). Recently, we have studied its unusual optical properties [1,2] and have compared it with the Turin Shroud Face [3], to figure out something more about the origin of the Veil. Its peculiar characteristic is being semitransparent. The face is visible on both sides (front-back) and, depending on lighting and observation conditions, it shows some differences in the anatomical details [1,2]. It is a linen fabric of very thin threads, with a thickness of about 0.1 mm, separated by distances even twice the thickness of the threads, so that about 42% of the Veil is empty space [1]. A substance, probably organic, has cemented the fibres of the linen threads, having chemical composition similar to cellulose, presumably starch. The cementing substance eliminated almost all the air between the fibres [1]. Such a structure causes the optical behaviour of the medium to be intermediate between that of a translucent medium (cemented linen threads) and that of a transparent one (empty space between the threads) [1].

As the Holy Face is deformed due to distortions of the meshes of the Veil of Manoppello, caused by the yielding of the very fine structure of the fabric, we first tackled the problem of digital image restoration to correct the Holy Face deformations [1]; secondly, we performed a spectral analysis of the transmitted image [2]. As evidenced in [1], the thin linen threads of the Veil of Manoppello are translucent, so that a nonnegligible percentage of incident light passes through them. As a result, both the yellowish colour of the ancient linen and starch contribute to the final hues of the Holy Face, especially when the Veil of Manoppello is lit from the backside with grazing light. Spectrophotometry measurements have allowed for calculating how the fabric absorbs the various chromatic components. Through these quantitative evaluations, it has been possible to compensate the colours of the transmitted Holy Face image, by subtracting the contribution due to the yellowish coloration of the thin linen threads [2]. The final result of the digital restoration and colour compensation is shown in Figure 1.



**Figure 1.** Digitally restored and colour-compensated Holy Face visible on the Veil of Manoppello in transmission, with back-grazing illumination.

Furthermore, the rotational spectrum of the image has been studied after digital restoration [2]. The linear fit of the power spectrum in bi-logarithmic scale with a power law  $f^P$  provided a surprising value for the slope parameter  $P = -3.49 \pm 0.03$ . This result was unexpected because it is typical of photographs of human faces, not of portraits of human faces painted by artists, which instead have statistical properties of fractal type, with slope  $P = -2.0$ .

In a third paper [3] we have compared the restored face of the Manoppello Veil with the face visible on the Turin Shroud, a linen cloth indelibly impressed by the front and back images of a complete

human body, which, according to the Catholic tradition, is the burial cloth of Jesus of Nazareth. We showed that the face of the Turin Shroud, after a logarithmic transformation of the intensity, and a background correction of the vertical stripes, which affect the image, shows different cheeks' profiles, which well overlap with those of the restored face of the Manoppello Veil [3]. In particular, the cheeks' profiles of the two faces are similar, although the profile on the Turin Shroud appears only after the digital processing [3].

The analysis performed in [1,2] leads one to think that some parts of the Holy Face might have been retouched. More precisely, in [1] we discussed that infrared characterization of the Veil of Manoppello indicates that the colour of the hair gradually changes from a lower intensity in the upper part of the head to a higher intensity in the lower area. These experimental data could be compatible with a hair colour that, from brown in the upper part of the head, becomes brown-red in the lower area. In addition, the colour of the iris is clearer than what can be observed in the visible light, although colours that tend to brown become darker under infrared. Moreover, the corneal limbus, which is the darker-colour circle that characterizes the outermost part of each iris immediately before the white sclera of the eye, is clearly visible with visible light, but disappears almost completely and shows noncircular contours under infrared radiation [1]. These results could suggest the possible presence of some touch-ups and the possible contribution of other underlying chromatic components, different from those directly seen with visible light, in particular for some important anatomical parts of the Veil of Manoppello Holy Face, such as hairs and eyes.

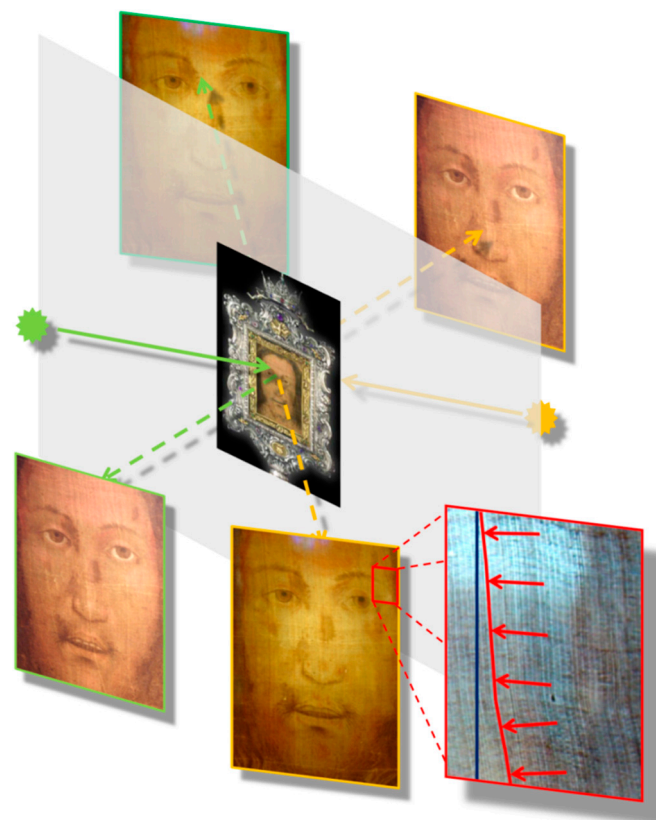
If this is the case, why and when has the colour of the irises and of other anatomical parts of the Veil of Manoppello Holy Face been retouched? Due to its peculiar optical characteristics and its historical vicissitudes, H. Pfeiffer has conjectured that the Veil of Manoppello very likely coincides with the Veronica's Veil, the alleged relic of the face of Christ impressed during his Passion, just before his crucifixion [4]. Indeed, we have no historic documentation of the Veil of Manoppello before the XVI–XVII century [4]. Moreover, we have no clear historic documentation of the Veronica's Veil after the XVI–XVII century, from which it derives the hypothesized coincidence between the Veil of Manoppello and Veronica's Veil, supported by some scholars [4]. Given these premises, in this paper we focus our attention on the possibility that the hypothesized coincidence of the two veils could explain why the colour of some parts of the Holy Face, in particular of the eyes, were retouched. Therefore, the aim of this paper is twofold: (i) to investigate the original colour of the eyes of the Holy Face of Manoppello; (ii) to search for further evidence in favour of the conjecture that the Veil of Manoppello and the Veronica's Veil are the same object.

Thus, in Section 2, we point out some correlations between the Veil of Manoppello and the Veronica's Veil, both in literary and artistic works, which can further support the above conjecture. In Section 3, we discuss some indirect proofs concerning the probable presence of starch on the Veil of Manoppello threads. In Section 4, we discuss the analyses of some photographs of the Veil of Manoppello taken with an optical microscope in the region of the right eye, and we show that the original colour of the eyes could have been blue. Indeed, if the Veil were made of starched linen, then both linen and starch would have become yellow due to the deterioration of these materials over the centuries [5]. Spectrophotometric measurements have shown that the maximum absorption of light in the Veil of Manoppello is in the range of wavelengths near blue [2]. Therefore, in the reflected Holy Face image, the colours with predominance of the blue component have been particularly altered due to the yellowing process, as we discuss in Section 5, the blue being the complementary colour of the yellow. Indeed, we will show that the blue colour, affected by the yellowing of the linen threads, would acquire greenish shades not compatible with human irises' colours. For these reasons, we conjecture that the Holy Face originally had blue eyes, and study how the yellowing of the linen, which affects mainly the blue components, could have changed the original colours, suggesting the possible retouches of some artists of the degraded colours of some parts of the Holy Face, in particular, of the eyes' irises. In Section 6, we estimate how long it takes to reach the maximum yellowing of the linen fibres, a time of the order of many centuries at room temperature, to obtain indirect information

about the historical period in which the retouch of the colours could have happened. In Section 7, to obtain some indirect information on how old the Manoppello Veil is, we correlate the estimates of this time, and the consequent change of colours, with some historical information on the exposure of the Veronica's Veil during processions. Finally, in Section 8 we discuss our findings and draw some conclusions.

## 2. The Correspondences between the Veil of Manoppello and the Veronica's Veil

In a document, written in the XIV century by Julian of Norwich, the Holy Face visible on Veronica's Veil is described with the following characteristics: "*diverse changing of colour and countenance*" [6,7]. As shown in Figure 2, the correspondence with the peculiar characteristics of the Veil of Manoppello, which changes colour and aspect of the face according to the illuminating conditions [1,2], is so straightforward to support the conclusion that this document attests its existence already in the XIV century. Indeed, these optical characteristics of the Veil of Manoppello are unique in the world, as it can be evinced by the most complete archive in the world dedicated to the Veronica's Veil and Veil of Manoppello, where several thousands of artworks and documents dedicated to the Veronica, that is all which are known and discovered, have been catalogued and described [8]. None of the catalogued artworks of the Veronica Route are described with the same optical characteristics of the Veil of Manoppello, showing a Holy Face which changes colour and aspect according to the illuminating conditions [8].



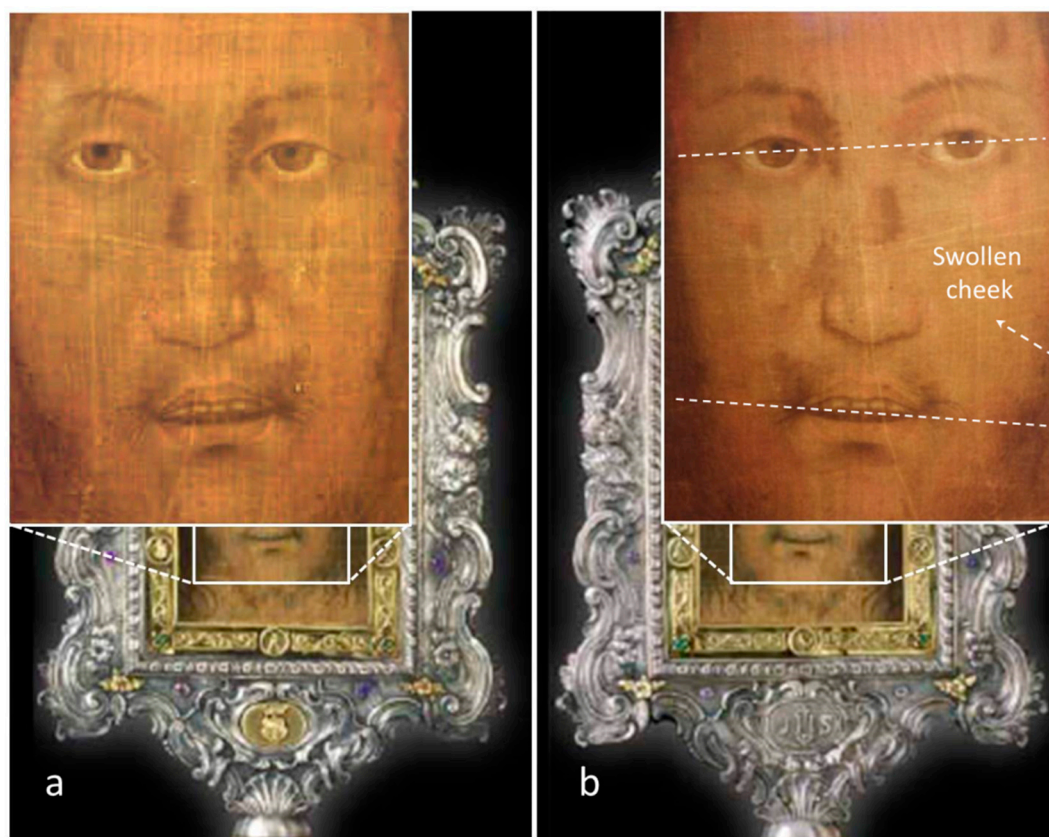
**Figure 2.** Source: Heritage, Volume 1, Issue 2 cover (December 2018). The Holy Face of Manoppello is visible on both sides (front–back) and, depending on the lighting and observation conditions, shows differences in colours and anatomical details. The Holy Face is deformed because of distortions of the meshes of the Veil, highlighted by the red arrows in the figure, due to the shear yielding of the very fine structure of the fabric.

Thus, the document written in the XIV century by Julian of Norwich is an important historical clue to support the conclusions that the Veil of Manoppello was already existing at that epoch and



that the Veil of Manoppello and the Veronica's Veil should be the same object, as conjectured by some scholars [4]. Indeed, the chance that Julian of Norwich, referring to the Roman Veronica, was describing by a mere coincidence the Holy Face as changing in colour and face's appearance, as it can be seen on the Veil of Manoppello, should be reasonably excluded because its optical characteristics, schematized in Figure 2, are unique in the world, as verifiable by the catalogued artworks dedicated to this topic [8].

Another indirect clue that the Veil of Manoppello and the Veronica's Veil are the same object can be found by an accurate inspection of some medieval representation of the Holy Face visible on Veronica's Veil. To verify this point, let us start to evidence the marked asymmetry observable on the Veil of Manoppello Holy Face. The two cheeks are markedly unequal because one appears swollen. The chin and the mouth are not in axis with the rest of the face, and are not parallel to the axis joining the eyes, as evidenced by the dashed white lines drawn in Figure 3. As shown in Figure 2, this marked deformation is due to the yielding of the very fine structure of the linen fabric [1,2].



**Figure 3.** Veil of Manoppello Holy Face in the reliquary, seen by the same side from which it is illuminated, frontside (a) and backside (b).

Now, it is interesting to point out that the Holy Face depicted on the Veronica's Veil in the *Liber Regulae Hospitalis Sancti Spiritus* (ca. 1350 AD) has colours and appearance very similar to the Veil of Manoppello, as Figure 4 shows. In this picture, Pope Innocent III holds in his right hand the Veronica's Veil and in the left hand holds the Rule that he is handing to Guy of Montpellier for the newly constituted confraternity [9]. The right insert of Figure 4, inside the white dashed box, shows an enlargement of the face, flipped left–right. The Holy Face has no mustache on the upper lip, the beard is thin on the cheeks and bipartite, a wisp of hair is at the center of the forehead. All these iconographic details are also visible in the face of the Veil of Manoppello.



**Figure 4.** Detail of the Holy Face visible on Veronica's Veil depicted in the *Liber Regulae Hospitalis Sancti Spiritus* (ca. 1350 AD) [10]. The right insert, inside the white dashed line box, shows an enlargement of the face, flipped left-right. Notice the asymmetry of the face, evidenced by the dashed white lines, and the unusual swollen cheek and the chin profile not parallel to the axis joining the eyes.

The asymmetry of the face of Figure 4, evidenced by the white dashed lines, is very similar to that of the face of the Veil of Manoppello (Figure 3). In other words, a cheek is swollen, the chin is twisted and not parallel to the axis joining the eyes, all features that recall the same distortions observable on the Veil of Manoppello (Figure 3). All these common elements between the Veronica's Veil depicted in the *Liber Regulae Hospitalis Sancti Spiritus* (ca. 1350 AD) and the Veil of Manoppello (attested to be in this town only in the XVI–XVII centuries) cannot be merely ascribed to chance. Therefore, also these evidences further support the hypothesis that the Veil of Manoppello and the Veronica's Veil are the same object.

For a further check, Figure 5 shows the superposition of the Veil of Manoppello Holy Face (seen with visible light in transmission) with the face of the *Liber Regulae Hospitalis Sancti Spiritus*. The result is surprising: The similarity between the Veronica's Face (left panel) and the Veil of Manoppello Holy Face superposed to the Veronica's Face (right panel), with a 50% transparency, is evident because various anatomical details are congruent. Again, we are led to suppose that the two Veils are the same object.

Thus, all of this seems to indicate what the artist who depicted the miniature in the *Liber Pontificalis* had in mind, as a reference model, the face visible on the Veil of Manoppello as it appears now to us.



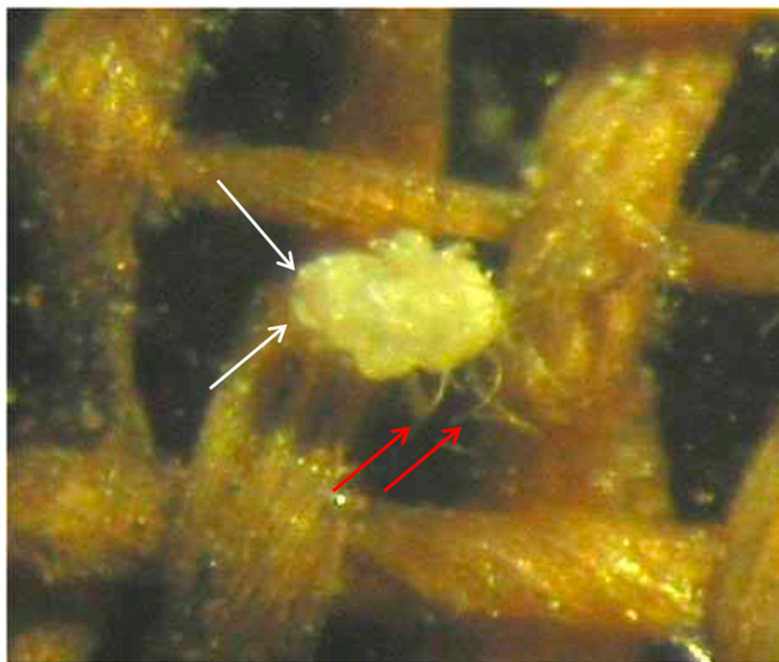


**Figure 5.** (Left panel): Detail of the Holy Face visible on the Veronica's Veil depicted in the *Liber Regulae Hospitalis Sancti Spiritus* (XIV century), flipped left-right. (Right panel): The Holy Face of the Veil of Manoppello, seen in transmission with visible light, superposed to the face visible on the left panel. The two faces are strikingly congruent.

### 3. The Veil Infested by Insects and Mites

This section could appear not directly centered with respect to the principal aim of the paper, but it is important in reference to a diffuse thinking relative to the fact that the Veil of Manoppello is not made of flax, but of marine byssus. If, in fact, it were of byssus, the main results discussed in the following would be not justified because the yellowing as a function of the aging time is a characteristic of linen fibres and not of those of marine byssus, which are brown regardless of aging. The presence of insects and mites on the Veil, as demonstrated by the following analysis, is an additional fact sustaining that the Veil of Manoppello is made of flax, whose fibres change colour over the centuries.

Indeed, according to the *Relatione Historica* written by the Capuchin preacher Father Donato da Bomba between the years 1642 and 1645, when the Veil arrived at the convent of Manoppello, it was infested by insects [11]. As we have already shown with polarized-light characterization of the Veil's fibres [1], this historical detail causes us to exclude, once more, that the Veil of Manoppello is made of sea byssus, because its fibers, soaked with salt, are indigestible to insects. On the contrary, insects are very greedy of starch, more digestible than cellulose. In addition, the analysis done with an optical microscope has confirmed the presence of mites among the fibres of the Veil, so small and invisible to the naked eye, as the acarus shown in Figure 6. The acarus shown in this photograph, taken by the third author [12], has dimensions comparable to the average distance between threads, equal to 0.34 mm [1,2]. Its size, the long bristle in the backside (red arrows in Figure 6), and the structure of its rostrum (white arrows in Figure 6) seem to be compatible with those of the acarus *Tyroborus lini*, an acarus that eats starch and linen seeds [13]. The presence of mites further confirms the conclusions that emerged from the analysis conducted with a microscope with polarized light [1]: The fabric of the Veil of Manoppello is made of linen, likely starched.

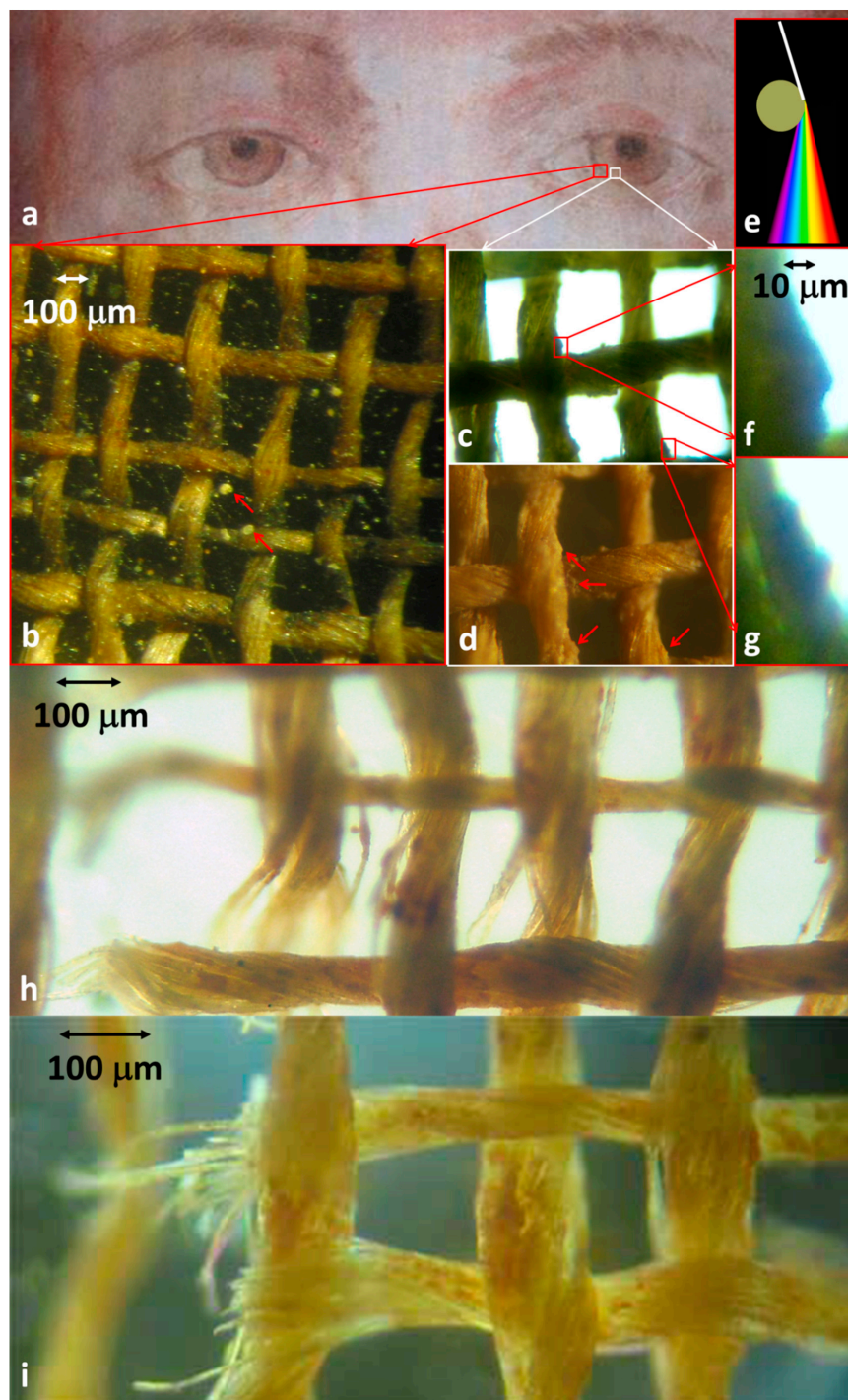


**Figure 6.** Enlargement of an optical microscopy photograph of the Veil of Manoppello, which shows the presence of an acarus. The long bristle in the backside (red arrows) and the structure of its rostrum (white arrows) seem to be those of the acarus *Tyroborus lini*.

#### 4. Optical Microscopy Characterization of the Right Iris of the Manoppello Holy Face

As shown in Figure 10 of [2], the corneal limbus of the left eye, which is the darker-colour circle that characterizes the outermost part of each iris immediately before the white sclera of the eye, is double. The colour of the two lines is different, with the innermost contour on the brown and the outermost one tending to purple-blue. This finding indicates the presence of a possible retouch in the irises' region of the Holy Face. To further clarify this point, Figure 7 shows some photographs, taken with an optical microscope by the third author, in a region of the right eye. Figure 7a shows the region of the eyes of the digitally restored Holy Face of Figure 1. Figure 7b shows the region corresponding to the red box of Figure 7a, in the area of the sclera close to the iris. The image is seen in reflection. The small grains visible in Figure 7b are either dust particles or insects/mites' eggs, having size up to 10  $\mu\text{m}$ , attached to the glass' reliquary containing the Veil, very likely due to electrostatic forces. The red arrows indicate some of them. In Figure 7c, we report a microscope photography corresponding to the white box of Figure 7a, in the region of the iris, when the Veil is seen in transmission. It is interesting to note that it is characterized by a greenish shade. This colour can be related to the yellowing of the linen. On the contrary, the threads are yellow-brown when the same region is observed in reflection mode, as shown in Figure 7d. Some regions of particular interest of this photograph have been indicated with red arrows. Indeed, the magnification of some regions on the lateral sides of the linen threads, seen in transmission, clearly shows that they are characterized by bluish rounded regions, about 10  $\mu\text{m}$  wide, compatible with dye particles, together with a very thin light-blue band, about 1  $\mu\text{m}$  wide, everywhere parallel to the threads' border and due to the chromatic aberration. Some of these blue rounded regions, on the lateral border of the threads, have been reported in Figure 7f,g. This finding can be considered as an indirect experimental confirmation that the original colour of the iris was blue and, consequently, an artist could have retouched the eyes with the brown colour. In fact, some small blue regions on the lateral sides of the linen threads could not be covered by the brown colour of the conjectured retouch. Now, we have discussed in [1,2] that thin linen threads, if they were cemented by starch, can act as translucent and even semitransparent optical medium, thus allowing light refraction inside the thin threads.





**Figure 7.** (a) Region of the eyes of the digitally restored Holy Face. (b) Optical microscope photography corresponding to the red box of Figure 7a (sclera-iris region). (c) Optical microscope photography of the Veil of Manoppello seen in transmission, corresponding to the white box of Figure 7a (iris region). (d) Optical microscope photography of the Veil of Manoppello seen in reflection corresponding to the white box of Figure 7a (iris region). (e) Scheme of light refraction by a cylindrical fibre border. (f) Magnification of the upper red rectangle of Figure 7c. (g) Magnification of the lower red rectangle of Figure 7c. (h,i) For comparison: Optical microscope photographs of other regions of the Veil, seen in transmission, in the middle of the forehead, in correspondence of a tear in the fabric.

Moreover, in optical microscopy, there can be refraction and chromatic aberration effects that cause dispersion of different wavelengths of visible light. Therefore, in principle, the bluish small areas

on the lateral sides of the linen threads could also be the consequence of a dispersion of the light's spectral components. However, Figure 7e shows a schematic diagram of wavelength dispersion due to the refraction of light caused by the border of a fibre of cylindrical section. As sketched in Figure 7e, the angle of refraction is proportional to the inverse of wavelength; therefore, with refraction effects, the lateral areas on the right side of the linen threads, seen in transmission, should appear reddish not bluish. Furthermore, in the presence of chromatic aberration, a blue contour should be visible everywhere along the threads' borders. However, the blue colour is present in correspondence of the small rounded regions at the lateral sides of the threads too, highlighted in Figure 7f,g, which have a shape and size typical of small dye particles. Finally, small irregularities in the ancient glass thickness of the theca, in which the veil is kept, should be in a spatial scale much larger than the thickness of the threads and, consequently, they could mainly cause the presence of slight geometrical distortions of the images seen through the glass. In short, everything suggests, and nothing is contrary to this supposition, that there could be traces of blue colour on the right iris region of the Holy Face. Indeed, for comparison, Figure 7h,i show the optical microscope photographs of other regions of the Veil, seen in transmission, in the middle of the forehead, in correspondence of a tear in the fabric. Similar results have been obtained in other regions of the face. In Figure 7h,i, it is possible to detect the presence of many dye particles, of several colours, prevalently red. It is also possible to check the absence of a concentration of bluish particles just on the threads' border. Also, these findings are compatible with the above interpretation of the bluish particles in the region of the irises as possible blue coloration of the lateral threads' sides. In synthesis, these experimental evidences on a microscopic scale, together with the macroscopic evidence of having the colour of more external corneal limbus characterized by an excess of the blue component [2], led to suppose that, on the irises, there could be two different overlapped colours, with the more superficial brown superimposed over the blue, whose presence is evident only at the lateral border of the thin threads where, evidently, the superimposed brown has not fully covered and hidden the preexisting coloration. In turn, this evidence leads to support the conclusion that some artist could have retouched at least the irises' colour of the eyes of the Veil of Manoppello Holy Face. In fact, infrared light characterization of the Veil of Manoppello [1] has shown that also other parts of the Veil of Manoppello Holy Face, e.g., the hairs, could have been retouched by some artist in the past.

## 5. The Colour of the Eyes of the Manoppello Holy Face Altered by the Yellowing of Ancient Linen

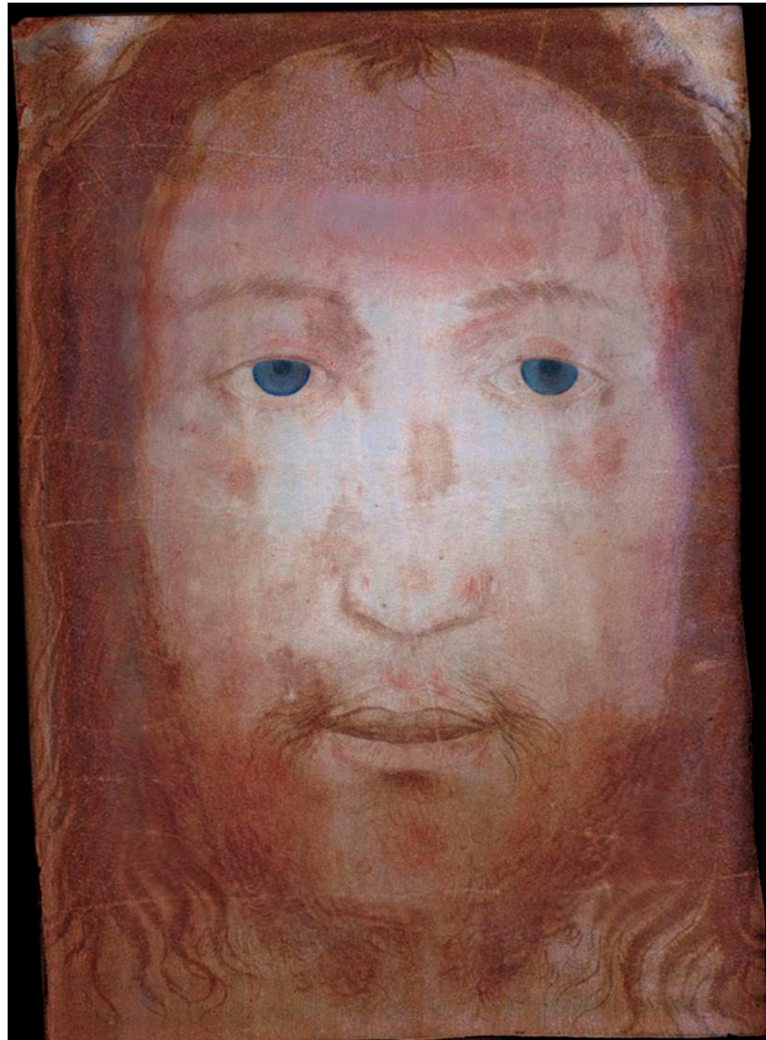
To give an idea of the resulting face with blue eyes, we can refer to Figure 8, obtained from Figure 1 by changing only the irises' colour, according to the bluish shade indications obtained by the optical microscopy results discussed in the previous Section 4. Let us note that the Holy Face shown in Figure 1 has been already digitally restored and colour compensated according to the procedure described in [2]. Here, we have further changed only the blue colour of the irises, according to what is evidenced by the optical microscopy characterization described in the previous section.

The questions we try to answer now are when the retouch of the irises' colour was done and why the irises' colour was probably changed from blue to brown.

We have shown that the Veil is very likely made of linen fibres, mainly composed of cellulose and hemicellulose. It is well known that natural aging degrades the cellulose, through the scission of the polymeric chains, by breaking the  $\beta$ -glucosidic bonds [5]. Carbonyl content and chain breaks are related. In the degrading process of cellulose and hemicellulose, the formation of carbonyl and carboxylic acid groups leads to yellowing of the fibres as a function of the aging time elapsed. With the aging of the fabric and its yellowing in the centuries, the blue colour could have been particularly altered because yellow fibres absorb preferentially the blue colour wavelengths, as shown in [2]. Therefore, the yellowing of the linen fibers has changed the colour of the eyes over time, as shown schematically in Figure 9.

The top panel of Figure 9 shows the image visible today on the Veil, when observed in transmission (detail of the eyes) and illuminating it with a back-grazing incident light. In this case, the Holy Face is

especially yellowed in its shades because of the particular coloration of its fibers. The effect is less evident if the Holy Face is seen in a reflection mode [1,2], because the reflected component of light is less influenced by the absorption in the Veil threads. The second panel, from the top, shows the image obtained after the digital restoration of the transmitted Holy Face [2], with brown eyes as it appears today.



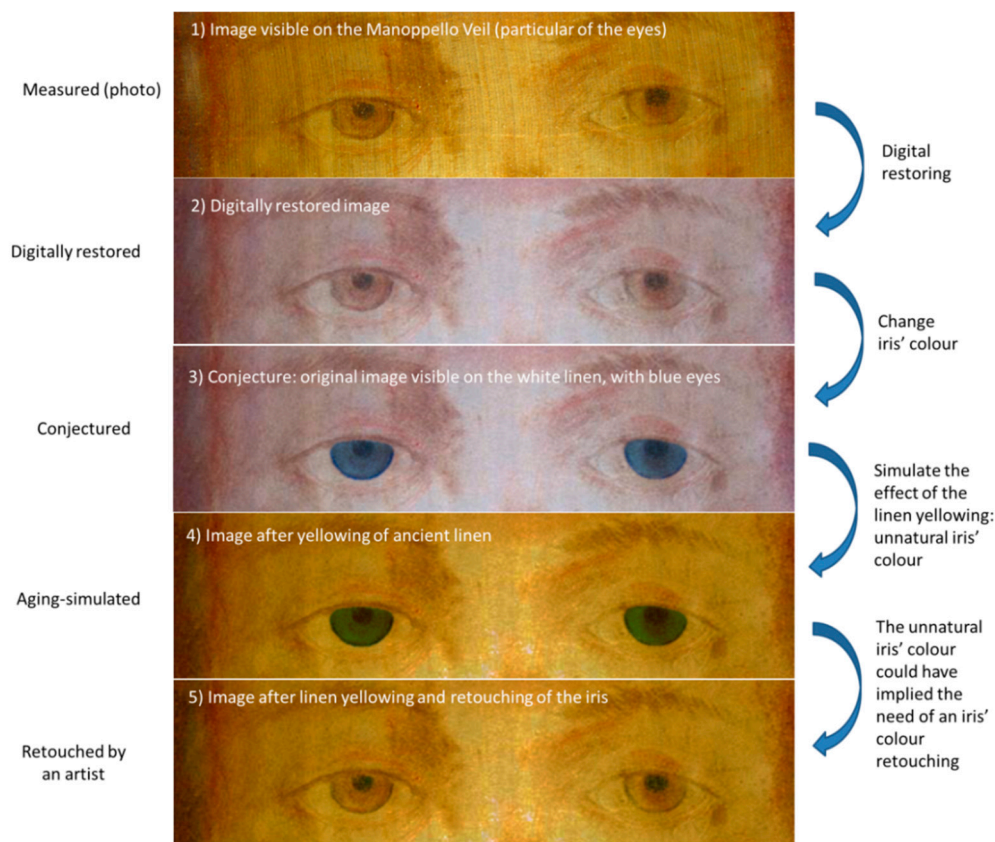
**Figure 8.** Digitally restored Holy Face visible on the Veil of Manoppello in transmission, with back-grazing illumination, with the iris' colour changed to a blue shade.

In agreement with the results previously discussed, the third panel shows the same digitally restored image, but with the supposed original blue eyes. If the original image was the one shown in the third panel, then, after the yellowing of the linen, and the consequent preferential absorption of the blue component, it would have appeared as that shown in the fourth panel. This latter image was obtained from the third by matching the histogram of the image's colours to that now measurable on the Veil, i.e., the one corresponding to the top panel. The histogram matching was done by using the Histogram Transform function of the Wolfram software Mathematica. Therefore, the linen fibres of the iris with aging should have gradually become greener, by adding yellow to blue.

In conclusion, we can conjecture that the unnatural greenish colour compelled someone to retouch the eyes of the Holy Face to brown, a colour more common in the Mediterranean world. To estimate the time when the retouch might have occurred, we have to assess how long of a time the linen fibres



need to turn to yellow, and to make the colour of the eyes so unnatural, to be no longer acceptable for a human face.



**Figure 9.** Explanatory diagram of the effect of yellowing on eye colour and the consequent need to retouch them (see main text for details).

## 6. Veil of Manoppello Yellowing Time Scales Due to Natural Aging

In Appendix A, we defined a Normalized Yellowing Index (*NYI*) to evaluate the time it takes for textile fibres to reach the maximum degree of yellowing due to natural aging [5].

$$NYI(t) = \frac{(1 - \omega_{DP}^*) \times (1 - e^{-k_{DP}t})}{1 - \omega_{DP}^* \times (1 - e^{-k_{DP}t})} \quad (1)$$

Equation (1) depends on the reaction rate  $k_{DP}$  of the degradation of the Degree of Polymerization (*DP*) of cellulose. In turn, the reaction rate  $k_{DP}$  depends on the *DP* activation energy  $E_{DPa}$  (see Appendix A). Moreover, the *NYI* depends on the maximum *DP* fractional loss  $\omega_{DP}^*$  (see Appendix A).  $t$  is the aging time. Starch is also subject to similar yellowing processes, but with different aging times from cellulose, essentially due to a different *DP* activation energy  $E_{DPa}$ , since at the atomic level its structure is different, even though it is made up of very similar monomers. It is important to consider this if we wish to calculate how long of a time the Veil of Manoppello could have taken to reach the maximum degree of yellowing because, as discussed, its linen threads appear starched.

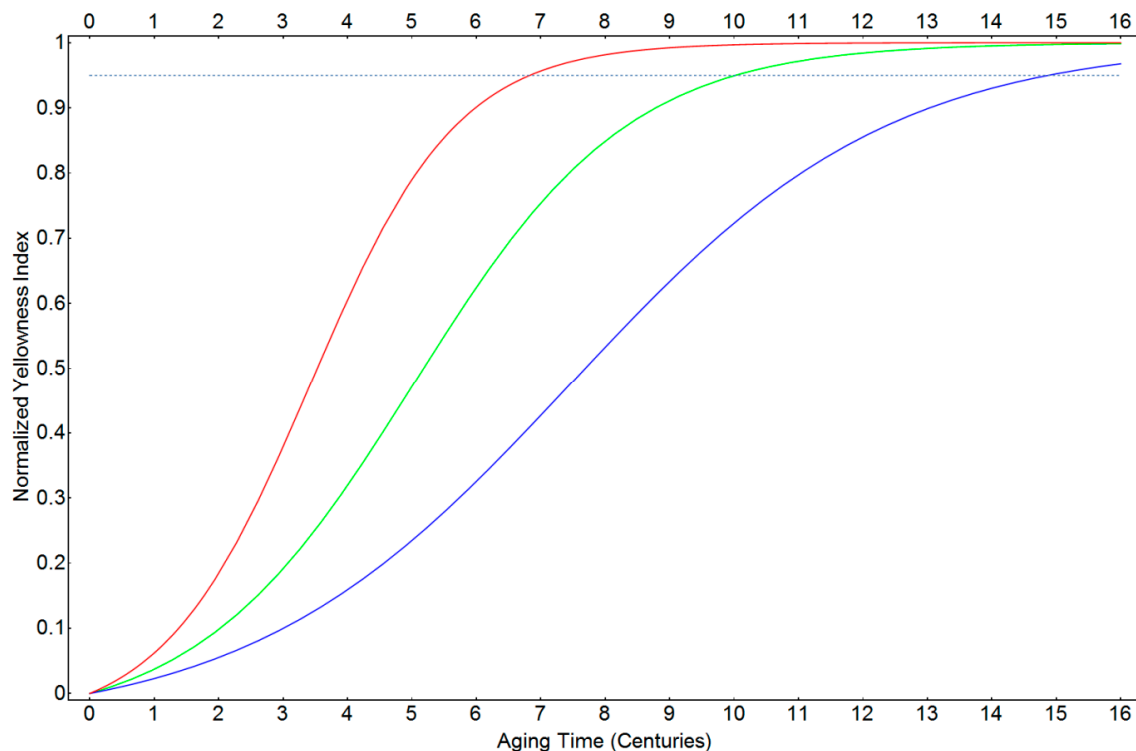
Thus, to calculate the time required to reach the maximum degree of yellowing in the case of the Veil of Manoppello, it is essential to estimate how much starch its threads can contain. The relative packing density of the microfibrils in the threads depends on the sections of the threads. For very thin threads, such as those of the Veil of Manoppello with an average diameter of approximately 0.12 mm, the thread fineness could be of about 10 Tex, i.e., a weight of 10 g if the thread were 1 km long [14]. For the starched linen threads, however, to the same diameter, it will correspond a higher fineness (i.e.,



a weight), since the empty spaces between the fibres are at least partially filled with starch. Starch and cellulose have about the same density of  $1.5 \text{ g/cm}^3$  [15]. For this reason, the Veil of Manoppello behaves like a translucent medium when it is illuminated [1]. In other words, its threads are very compact and homogeneous from an optical point of view, with very low residual spaces between starched threads, which are still filled by air. As the Veil of Manoppello is translucent, we will assume negligible these spaces with respect to the whole volume of its threads. This feature is also evident from the optical microscopies, as shown, for example, by the compactness of the microfibrils in Figure 7i. Therefore, one can reasonably assume that very compact textile starched threads, like those of the Veil of Manoppello, are characterized by the maximum packing density [16]. Maximum packing densities of microfibrils in very thin threads are of the order of 70% [16]. Thus, we can reasonably assume that the linen microfibrils occupy about 70% of the thread volume, whereas almost all the residual 30% of space is filled by starch. As the activation energy of the degradation process of wheat starch is about  $50 \text{ kJ/mole}$  [17], and that for natural aging of linen is about  $119 \pm 1 \text{ kJ/mole}$  [5], the activation energy of the *DP* degradation process for the Veil of Manoppello threads can be put equal to  $119 \times 0.7 + 50 \times 0.3$ , i.e., to  $98 \pm 2 \text{ kJ/mole}$ , an energy value smaller than that corresponding to linen. The threads of starched linen, therefore, turn yellow faster than those not starched.

To calculate how quickly starched linen threads reach maximum yellowing, it is necessary to know the average secular temperature at which the *DP* degradation process due to natural aging has occurred. In international databases, it is possible to find the average annual temperatures from 1901 to 2016 for most places [18]. The analysis of the annual growth of tree rings in the latest two thousand years [19] allows for verifying that the average temperatures of the last century, reported in [18], can be considered representative of the entire period of Christian history [5]. If the Veil of Manoppello coincides with the Veronica's Veil, then it was for a certain period in Rome, whose average secular temperature is  $15.9^\circ\text{C}$  [18]. Before Rome, in the hypothesis that it is very ancient, it is very probable that it was kept where Acheiropoietos images of the Holy Face have been reported to be in the history of the icons of Christ, such as Constantinople and/or Edessa [20]. In any case, we can assume that the Veil of Manoppello was always in the Mediterranean area, between Italy, Spain, Middle East, North Africa (Egypt), etc. In this geographical area, the long-term mean room temperature ranges from  $15^\circ\text{C}$  to  $20^\circ\text{C}$  [21]. The mean temperature between the extreme values is  $17.5^\circ\text{C}$ . If we assume a normal distribution of probability with mean value  $17.5^\circ\text{C}$  and a three standard deviation interval in correspondence of the bound values of about  $15^\circ\text{C}$  and  $20^\circ\text{C}$ , we obtain a standard deviation of about  $0.8^\circ\text{C}$  on the uncertainty of the temperature value, for the alleged period of time before 1200 in which the Veil could have already been existing. We are interested to estimate the yellowing rate of the Veil of Manoppello just in this period. Thus, we can adopt for the Veil of Manoppello a secular room temperature of  $17.5^\circ\text{C} \pm 1.6^\circ\text{C}$  to cover a temperature range corresponding to a 95% level of confidence (two standard deviations). By considering the temperature shift factor estimated from Equation (A3) in Appendix A for  $E_{DPa} = 98 \text{ kJ/mole}$ , in correspondence of a secular mean room temperature of  $17.5^\circ\text{C}$ , we finally obtain the *NYI* shown in Figure 10.

The results shown in Figure 10 can be used to verify the conjecture proposed in Section 3, namely that the Veil of Manoppello and the Veronica's Veil are the same object. Indeed, Figure 10 shows that after about 10 centuries (green line), the *NYI* of the starched linen threads reaches 95% of its maximum value. The minimum (red curve) and maximum (blue curve) times to reach the 95% of *NYI* are 7 and 15 centuries, respectively, corresponding to an interval of two standard deviation width (95% level of confidence). Therefore, as conjectured after the experimental evidence discussed in Section 2, if the original colour of the eyes was blue, after about 10 centuries it would have become so altered to become unnatural, as schematically shown in Figure 9. The minimum estimated time interval to reach 95% of the *NYI* is 7 centuries. The maximum is 15 centuries. These results can be related to historical documents about the Veronica's Veil to obtain some indications about the period in which the Veil of Manoppello should date back.



**Figure 10.** Normalized Yellowness Index for the Veil of Manoppello as a function of the aging time expressed in centuries. The red and blue curves correspond to the bounds due on the  $DP$  activation energy and the secular mean room temperature values (95% level of confidence interval). The green curve corresponds to the mean value. The dashed line indicates the 95% level of the maximum yellowing.

## 7. How Old is the Manoppello Veil?

It is interesting to mention that, at least since the beginning of the year 1200, the Veronica's Veil can be located in Rome, because it was shown there publicly. In fact, in the year 1208, Pope Innocent III, with the bull *Ad commemorandas nuptias salutare*, established that, on the second Sunday after Epiphany, the effigy of Jesus Christ, preserved in St. Peter (the Constantinian basilica at that time), was to be carried in solemn procession from the cathedral to the Church of the Hospital of St. Spirit, to be exposed to the faithful, who would receive an indulgence by attending procession and ostension [22,23]. Moreover, the Veronica's Veil was surely shown publicly in Rome in the Jubilee of the year 1300 by Pope Boniface VIII. For the next two hundred years, the Veronica's Veil was considered one of the most precious Christian relics.

After this brief historical sketch, let us return to the starting conjecture that the Veronica's Veil and the Veil of Manoppello are the same object. The coincidence between the two Veils, discussed in Section 2, is further supported by the fact that, before the sack of the Lansquenets in Rome, in 1527, the reliquary that contained the Veil of Veronica was a transparent glass. This finding could be related to a Holy Face visible on both sides. The Veil of Manoppello is characterized by this peculiar characteristic and it is unique in the world [8]. Therefore, our conjecture that the chromatic retouch of the eyes was done before the time the Veil started to be shown to the public is supported by various clues. If the above conjecture were fully established, then, at the beginning of the year 1200, the Veil of Manoppello had reached 95% of the maximum  $NYI$ . As 10 centuries are needed to reach 95% of the maximum  $NYI$ , this would imply that the Veil of Manoppello would be a fabric of the Roman epoch. The minimum time interval to reach 95% of the maximum  $NYI$  is 7 centuries (red curve of Figure 10). This implies that the Veil of Manoppello cannot be posterior to the 500.

## 8. Conclusions

The clues, discussed in this work, that the Veil of Manoppello and the Veronica's Veil are likely the same object, the digital analysis of the transmission image of the Holy Face, the optical microscope photographs of the Holy Face's eyes, associated with the calculations on the aging times of starched linen, and the history concerning the expositions of the Veronica's Veil in Rome, are in favour of the following conclusions:

- (i) The original colour of the eyes of the Holy Face could have been blue;
- (ii) If the irises' colour was blue, over the centuries, it has become altered because of the yellowing of the linen;
- (iii) After about 10 centuries, the colour of the eyes must have been so unnatural to compel an artist to retouch the iris, by covering the unnatural greenish color, with brown, more acceptable for public exhibitions.

Based on this technical analysis, our hypothesis is that the Veil of Manoppello is likely of the Roman period. In any case, the time needed for starched linen to reach the maximum yellowness excludes its realization by any artist in the XV century, e.g., Albrecht Dürer, as suggested in [24].

In conclusion, if the Veil of Manoppello is related to the tradition of the Veronica's Veil, the alleged relic showing the face of Christ just before his crucifixion, during the way to the Calvary, then it could be very ancient, of the Roman period. Consequently, the tradition of the Veronica's Veil should be much older than scholars have hypothesized so far [25]. A more accurate historical study on the origin of the Veronica's Veil tradition could open new perspectives about the Christ iconography. At the same time, a new and more accurate experimental analysis of the irises of the Holy Face of Manoppello could further support the findings presented and discussed. In particular, taking a small piece of thread, 1–2 mm long, making a small hole in glue between the glasses of the Veil of Manoppello reliquary, would allow an X-Ray dating of its fabric [5], to confirm how ancient it is.

In principle, further non-invasive analyses could be done to further confirm the presence of the blue colour in the irises of the Holy Face of Manoppello.

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## Appendix A. Yellowing of Linen Due to Natural Aging

Cellulose consists of linear, polymeric chains of cyclic units whose number per chain is called the degree of polymerization ( $DP$ ) [5]. The chains of cellulose first associate, in both crystalline and amorphous regions, to form microfibrils and, finally, to fibres. The increase in the number of chain scissions is the main mechanism of cellulose degradation. In a recent work [5], by means of Wide Angle X-rays Scattering (WAXS) measurements, we experimentally determined the  $DP$  activation energy ( $E_{DPa}$ ) and the maximum  $DP$  fractional loss ( $\omega_{DP}^*$ ) of ancient linen fabrics subjected to natural aging processes, i.e., to thermal, hydrolytic, photolytic, photochemical, and oxidative processes at room temperature and humidity conditions. The complete degradation of linen fibres requires very long times of many centuries.

The  $DP$  fractional loss can be defined as:

$$\omega_{DP} \equiv 1 - \frac{DP(t)}{DP(0)} \quad (A1)$$

where  $\omega_{DP}$  is the accumulate  $DP$  loss at time  $t$ , compared to the initial value  $DP(0)$ . The above quantity can be expressed also by means of the following Equation:

$$1 - \frac{DP(t)}{DP(0)} = \omega_{DP}^* \times (1 - e^{-k_{DP}t}) \quad (A2)$$

where  $\omega_{DP}^*$  is the maximum  $DP$  fractional loss, and  $k_{DP}$  is the reaction rate of the  $DP$  degradation.  $k_{DP}(T_o)$  can be measured in accelerated degradation processes in an oven at high temperatures  $T_o$  and then converted to the room values [26,27]. The accelerated oven  $DP$  reaction rate can be converted to the room temperature  $T_r$  at which the linen fabrics have been aged during the centuries by means of an Arrhenius shift factor  $a_{TDP}(T_o, T_r)$  [5,26].

$$k_{DP}(T_r) = a_{TDP}(T_o, T_r) \times k_{DP}(T_o) = \exp\left[\frac{E_{DPA}}{R} \times \left(\frac{1}{T_o} - \frac{1}{T_r}\right)\right] \times k_{DP}(T_o) \quad (A3)$$

which depends on the  $DP$  activation energy  $E_{DPA}$ .  $R$  is the gas constant (8.314 J/mole/K).

Chain Breaks ( $CB$ ), in mmol/100 g of cellulose, can be estimated by the following equation [27].

$$CB(t) = 1235 \times \left( \frac{1}{DP(t)} - \frac{1}{DP(0)} \right) \quad (A4)$$

From Equations (A2) and (A4), it follows:

$$CB(t) = \frac{1235}{DP(0)} \times \frac{\omega_{DP}^* \times (1 - e^{-k_{DP}t})}{1 - \omega_{DP}^* \times (1 - e^{-k_{DP}t})} \quad (A5)$$

The Yellowness Index ( $YI$ ) values in [27] have been evaluated according to the ASTM standard test method E313-00, assuming a CIE standard illuminant D65 and the 2° standard observer. Absolute  $YI$  value is a measure of the “distance” from the CIE white point. A positive  $YI$  means that the sample appears yellowish, a negative value means that the sample appears bluish. Changes of the  $YI$  due to aging are proportional to the  $CB$  values. For linen, as can be estimated from Figure 3 of [27], it increases by about 14.8% for  $CB = 1$  mmol/100 g of cellulose. We refer to this quantity as  $\Delta YI_{CB}$ . The  $YI$  being due to natural aging proportional to the  $CB$  values, we can estimate how  $YI$  changes as a function of the aging time  $t$  by the following formula:

$$\Delta YI(t) \cong \frac{1235 \times \Delta YI_{CB}}{DP(0)} \times \frac{\omega_{DP}^* \times (1 - e^{-k_{DP}t})}{1 - \omega_{DP}^* \times (1 - e^{-k_{DP}t})} \equiv C \times \frac{\omega_{DP}^* \times (1 - e^{-k_{DP}t})}{1 - \omega_{DP}^* \times (1 - e^{-k_{DP}t})} \quad (A6)$$

where  $C$  is a constant. We are interested only in relative  $\Delta YI$  variations from the maximum values  $\Delta YI_{max} = \Delta YI(\infty)$ , i.e., from the horizontal asymptotic value for very long aging times. Therefore, the value of the constant  $C$  in Equation (A6) is not needed. For  $t \rightarrow \infty$  from Equation (A6) we get:

$$\Delta YI(\infty) \cong C \times \frac{\omega_{DP}^*}{1 - \omega_{DP}^*} \quad (A7)$$

Therefore, the Normalized Yellowness Index variation ( $NYI$ ) is given by:

$$NYI(t) \equiv \Delta YI(t) / \Delta YI(\infty) \cong \frac{(1 - \omega_{DP}^*) \times (1 - e^{-k_{DP}t})}{1 - \omega_{DP}^* \times (1 - e^{-k_{DP}t})} \quad (A8)$$

The above equations are quite general and valid for any textile fiber, under the assumption that the changes of  $YI$  are linearly proportional to the  $CB$  values, even for very long aging times. For linen, at a mean relative humidity of about 55% and at  $T_o = 273.15 + 90$  K, i.e., at 90 °C, the following value can



be estimated:  $k_{DP}(T_o) = 0.0023 \pm 0.0001 \text{ h}^{-1}$  [5]. The values obtained by WAXS characterization for the other factors on which linen cellulose degradation and yellowing depend are  $\omega_{DP}^* = 0.953 \pm 0.001$  and  $E_{DPa} = 118.9 \pm 0.8 \text{ kJ/mole}$  [5]. For linen, the linear dependence of  $YI$  on  $CB$  has been verified in [27] for 4000 aging hours in an oven at a temperature of  $90^\circ\text{C}$  and a relative humidity of 50%. Let us note the exponential dependence of the Arrhenius shift factor  $a_{TDP}(T_o, T_r)$  on the temperature. By inserting into Equation (A3) the value of  $E_{DPa}$  determined in [5], it leads to the equivalence of one aging hour in an oven at  $90^\circ\text{C}$  to about 18,500 h of natural aging at a room temperature of  $17.5^\circ\text{C}$ , i.e., to more than two years. Thus, 1000 aging hours in an oven at a temperature of  $90^\circ\text{C}$  should correspond to about two millennia of natural aging. Therefore, the linear dependence of  $YI$  on  $CB$ , even for very long natural aging times, can be reasonably assumed. As a final remark, the relation between  $NYI$  and the age of the linen textile, through Equation (A8), actually holds only when the fabric, during the centuries, has suffered only natural aging, i.e., aging due to thermal, hydrolytic, photolytic, photochemical, and oxidative room processes [5]. The assumption of natural aging has to be explicitly stated because other physical/chemical processes than those involved in natural aging of textiles could accelerate yellowing processes [28].

## References

- De Caro, L.; Matricciani, E.; Fanti, G. Imaging analysis and digital restoration of the Holy Face of Manoppello—Part I. *Heritage* **2018**, *1*, 289–305. [CrossRef]
- De Caro, L.; Matricciani, E.; Fanti, G. Imaging analysis and digital restoration of the Holy Face of Manoppello—Part II. *Heritage* **2018**, *1*, 349–364. [CrossRef]
- De Caro, L.; Matricciani, E.; Fanti, G. A comparison between the Face of the Veil of Manoppello and the Face of the Shroud of Turin. *Heritage* **2019**, *2*, 339–355. [CrossRef]
- Bulst, W.; Pfeiffer, H. *Das Turiner Grabtuch und das Christusbild—Das Echte Christusbild*; Verlag Josef Knecht: Frankfurt, Germany, 1991; ISBN 378200633X.
- De Caro, L.; Giannini, C.; Lassandro, R.; Scattarella, F.; Sibillano, T.; Matricciani, E.; Fanti, G. X-ray dating of ancient linen fabrics. *Heritage* **2019**, *2*, 2763–2783. [CrossRef]
- Julian of Norwich. *Revelations of Divine Love*; Christian Classics Ethereal Library: Grand Rapids, MI, USA, 2002; Available online: <https://www.ccel.org/ccel/julian/revelations.toc.html> (accessed on 13 November 2019).
- Hilles, C. The Sacred Image and the Healing Touch: The Veronica in Julian of Norwich's Revelation of Love. *J. Mediev. Early Mod. Stud.* **1998**, *28*, 553–580.
- Veronica Route. Available online: <https://veronicaroute.com/> (accessed on 20 November 2019).
- Drossbach, G. The Roman Hospital of Santo Spirito in Sassia and the Cult of the Vera Icon. In *The European Fortune of the Roman Veronica in the Middle Ages, Cambridge, England, 4–5 April 2016*; Foletti, I., Ed.; Convivium Supplementum, Seminarium Kondakovianum, Series Nova; Masarykova Univerzita: Brno, Czech Republic, 2017; pp. 158–167. ISBN 978-80-210-8779-8.
- Wolf, G.; Drossbach, G. (Eds.) *Caritas im Schatten von Sankt Peter—Der Liber Regulae des Hospitals von Santo Spirito in Sassia: Eine Prachthandschrift des 14. Jahrhunderts*; III Incipit regula domus sanctis Spiritus in Saxia de Urbe: Capitulum I, fol. 15v; Verlag Friedrich Pustet: Regensburg, Germany, 2015; p. 181. ISBN 978-3-7917-2684-7.
- da Bomba, D. *Relazione Historica d'una Miracolosa Imagine del Volto di Christo*; Colombo, E., Colombo, M., Eds.; Marietti Editore: Milano, Italy, 2016; ISBN 9788821194160.
- Fanti, G. *Relazione Tecnica Sulle Indagini Eseguite sul Volto Santo di Manoppello*; Technical Report; Archive of the Sanctuary of Manoppello: Manoppello, Italy, 2010.
- Robertson, P.L. Tyroglyphid Mites in Store Products in New Zeland, *Trans. R. Soc. N. Z.* **1946**, *76*, 185–207.
- Křemenáková, D.; Mishra, R.; Militký, J.; Šesták, J. (Eds.) *Selected Topics of Textile and Material Science*; Publishing House of WBU: Pilsen, Czech Republic, 2011; ISBN 978-80-261-0062-1.
- Amiri, A.; Triplett, Z.; Moreira, A.; Brezinka, N.; Alcock, M.; Ulven, C.A. Standard density measurement method development for flax fiber. *Ind. Crops Prod.* **2017**, *96*, 196–202. [CrossRef]
- Thibodeaux, D.P.; Hebert, J.J.; Abd El-Gawad, N.S.; Moraitis, J.S. Relating Bundle Strength to Mantis Single Fiber Strength Measurement. *J. Cotton Sci.* **1998**, *2*, 62–67.

17. Dumitriu, S. (Ed.) *Polysaccharides: Structural Diversity and Functional Versatility*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2004; p. 405. [CrossRef]
18. World Bank Climate Change Knowledge Portal. Available online: <https://climateknowledgeportal.worldbank.org/> (accessed on 18 November 2019).
19. Esper, J.; Frank, D.C.; Timonen, M.; Zorita, E.; Wilson, R.J.; Luterbacher, J.; Holzkämper, S.; Fischer, N.; Wagner, S.; Nievergelt, D.; et al. Orbital forcing of tree-ring data. *Nat. Clim. Chang.* **2012**, *2*, 862–866. [CrossRef]
20. Pfeiffer, H. The concept of “acheiropoietos”, the iconography of the face of Christ and the Veil of Manoppello. In Proceedings of the International Workshop on the Scientific approach to the Acheiropoietos Images, Frascati, Italy, 4–6 May 2010; Di Lazzaro, P.D., Ed.; ENEA: Frascati, Italy, 2010. ISBN 978-88-8286-232-9.
21. Taricco, C.; Ghil, M.; Alessio, S.; Vivaldo, G. Two millennia of climate variability in the Central Mediterranean, *Clim. Past* **2009**, *5*, 171–181. [CrossRef]
22. Gaeta, S. *L'enigma del Volto di Gesù*; Rizzoli: Milano, Italy, 2010; ISBN 9788817039949.
23. Von Dobschütz, E. *Christusbilder: Untersuchungen zur christlichen Legende*; Hinrichs, J.C., Ed.; Hinrichs'sche Buchhandlung: Leipzig, Germany, 1899; Available online: <https://digi.ub.uni-heidelberg.de/diglit/dobschuetz1899/0001> (accessed on 21 November 2019).
24. Falcinelli, R. The face of Manoppello and the veil of Veronica: New studies. In Proceedings of the International Workshop on the Scientific approach to the Acheiropoietos Images, Frascati, Italy, 4–6 May 2010; Lazzaro, P.D., Ed.; ENEA: Frascati, Italy, 2010. ISBN 978-88-8286-232-9.
25. Wolf, G. *Schleier und Spiegel: Traditionen des Christusbildes und die Bildkonzepte der Renaissance*; Wilhelm Fink: Munchen, Germany, 2002; ISBN 978-3770536320.
26. Ding, H.Z.; Wang, Z.D. On the degradation evolution equation of cellulose. *Cellulose* **2008**, *15*, 205–224. [CrossRef]
27. Stephens, C.H.; Whitmore, P.M. Comparison of the degradation behaviour of cotton, linen, and kozo papers. *Cellulose* **2013**, *20*, 1099–1108. [CrossRef]
28. Rogers, R.N. Studies on the radiocarbon sample from the shroud of turin. *Thermochim. Acta* **2005**, *425*, 189–194. [CrossRef]



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