THE SHROUD OF TURIN: AN AMINO-CARBONYL REACTION (MAILLARD REACTION) MAY EXPLAIN THE IMAGE FORMATION

Raymond N. Rogers* & Anna Arnoldi†

This article originally appeared in Melanoidins vol. 4, Ames J.M. ed., Office for Official Publications of the European Communities, Luxembourg, 2003, pp.106-113.

*University of California, Los Alamos National Laboratory, 1961 Cumbres Patio, Los Alamos, NM 87544, USA

†University of Milan, Department of Molecular Agrifood Sciences, via Celoria 2, 20133 Milano, Italy.

Summary. The Shroud of Turin is a large piece of linen that shows the faint image of a man on its surface: it has been claimed to be the shroud of Jesus. Here we report evidences that colour can be produced by reactions between reducing sugars, left on the cloth by the manufacturing procedure, and amines deriving from the decomposition of a corpse. Treatment of a cloth prepared according to the ancient technology gave a distribution of colour on the thread fibres in good agreement with the Shroud features. Such a natural image-production process would support the hypothesis that the Shroud of Turin had been a real shroud. However, these observations do not *prove* how the image was formed or the "authenticity" of the Shroud.

INTRODUCTION.

The Shroud of Turin is a large piece of linen that shows the faint image of a man on its surface (Jumper et al., 1984). It has been claimed to be the shroud of Jesus, making it very controversial.

In 1978, its custodians allowed the Shroud of Turin Research Project (STURP) to test the different image-formation hypotheses. The outstanding characteristic of the image on the Shroud of Turin is the discontinuous distribution of the colour on the surface. STURP members took many photomicrographs of the surface of the Shroud in 1978 (Pellicori & Evans, 1981). They reported that the image "consists of a light sepia colour with the darkest coloration on the thread tops." All image areas are very faint, and most image fibres are gold (Schwalbe & Rogers, 1982). The colour density seen in any area of the image appeared primarily to be a function of the number of coloured fibres per unit area rather than a significant difference in colour density, which was called the "half-tone" effect. A very specific feature is that the colour appeared only on the surface of individual fibres (Heller and Adler, 1981).

No image fibres were cemented together by any foreign material, which seemed to eliminate any image-formation hypothesis that was based on the flow of a liquid into the cloth. The hypothesis of a gaseous diffusion into the cloth would have produced a colour gradient through its thickness (Schwalbe & Rogers, 1982).

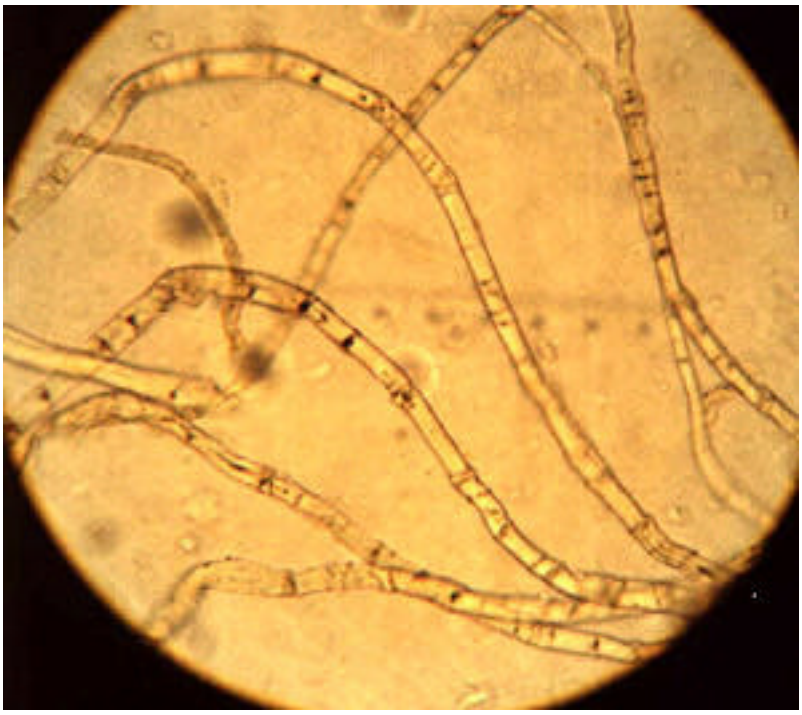
Visible and ultraviolet spectrometry, infrared spectrometry, x-ray fluorescence spectrometry, and direct microscopic viewing did not detect any known Medieval painting materials. Later microscopy, microchemistry, pyrolysis-mass-spectrometry, and laser-microprobe

Raman analyses failed to detect foreign materials. Pyrolysis-mass-spectrometry analysis was sufficiently sensitive to detect ppb levels of polyethylene oligomers that came from sample bags. Reflectance spectra of image areas, scorched areas, and aged linen were identical (Gilbert and Gilbert, 1982). In conclusion, all the observational methods applied by STURP failed to detect any of the historically known painting vehicles, media, or pigments, suggesting that the image was not a painting in any normal sense (Schwalbe & Rogers, 1982).

Taking into account all these results, it was decided to check the hypothesis that the image could derive from an amino-carbonyl reaction between sugar residues on the cloth and amino derivatives produced by the corpse post-mortem reactions. In order to get historically reliable results, experiments were performed on a linen cloth prepared following exactly the procedure described by Pliny the Elder (77).

RESULTS

Observations on the cloth.



Every scientific hypothesis for image formation has to take into account and explain a very important experimental fact: although the surfaces of Shroud image fibres show a characteristic golden colour, their medullas are clear (Figure 1 above), which supports the Heller and Adler observation that all image colour resides on fibre surfaces (Heller and Adler, 1984). They reported that: "The absence of products expected from a high-temperature cellulose degradation […] suggests that the process that formed the final chemistry took place at lower temperatures (less than 200ºC), because no pyrolytic compounds were found. The fluorescence of the scorch areas, however, demonstrates the presence of high-temperature pyrolytic products in these areas"(Heller and Adler, 1984).

Several holes were burned in the cloth when the shroud was badly damaged in a fire in 1532. Scorch colours between light lemon yellow and black appear around these holes and the fibres involved are coloured all of the way through their diameter. Fluorescent products are observed around the burned areas, confirming high temperature pyrolysis conditions.

Observations of weave density and lignin content of the shroud fibres (Rogers, 2001) indicate a very mild bleaching technique in agreement with the methods described by Pliny the Elder (77). The same technology was in use, with some minor differences, until after the last crusade in 1291 (Hochberg, 1980). Linen was spun by hand on a spindle whorl. When the spindle was full, the spinner made a hank of thread. Each hank of thread was bleached separately, and each was a little different. Different parts of the same thread in the shroud's weave show slightly different colours, like a variegated yarn. The warp thread was protected with starch during the weaving process, making the cloth stiff. The final cloth was washed in a solution made from *Saponaria officinalis. Saponaria* produces four glycosidic saponins, and all hydrolyse to produce sugar chains. (Ya Chirva et al., 1969) The following carbohydrates were identified in those chains: galactose, glucose, arabinose, xylose, fucose, rhamnose, and glucuronic acid.

The presence of starch, in particular amilose, on the shroud was confirmed by the fact that during testing for sulfoproteins in blood areas with an iodine-azide reagent (which bubbles vigorously when sulfur is present), a reddish background was formed. Image colour does not appear under the bloodstains when they are removed with a proteolytic enzyme. Whatever process produced the image, colour must have occurred after the blood flowed onto (or was painted onto) the cloth, and the image-producing process did not destroy the blood (Heller and Adler, 1981).

Saponaria officinalis, also called "soapweed," reduces the surface tension of water making it a good wetting agent. Both hydrophobic and hydrophilic materials on a newly woven cloth are put into solution or suspension by *Saponaria*. After been washed in a *Saponaria* solution, ancient clothes were "laid out on bushes to dry" (Donadoni, 1978) Under such conditions, materials that are in solution or suspension in the wash water will concentrate at the drying surface. We hypothesize that evaporation / concentration can explain the superficial nature of the image.

The commercial production of linen started during Medieval times: most commercial bleaching in Europe took place in "bleach fields" in the Low Countries, where completed pieces of cloth were spread out for bleaching. These medieval linens are homogeneous, whereas the shroud shows bands of different densities.

Experimental production of image-like colours.

Tests of image-formation hypotheses needed fresh material. However, modern linen is useless for experimental image-production purposes because it is vigorously bleached and been coated with sizing compounds and fluorescent fabric brighteners.

Kate Edgerton (deceased, Norwich, CT) grew flax and made some linen, using both starch and *Saponaria*. Unfortunately, she ironed the samples with a "warm iron" which coloured the cloth and changed the *Saponaria* glycosides. Edgerton's samples could be bleached to remove most of the colour by soaking in 3.5% hydrogen peroxide. This treatment did not remove the natural waxes. That material was used in the reported experiments.

Because Edgerton's linen was scarce, many preliminary tests were performed on pure-cellulose filter paper. These experiments were done by placing drops of test solutions on a dry plastic plate and laying a piece of Whatman's #4 filter paper over them. The liquid migrated

through the paper and evaporated at the surface. No colour could be observed in either sunlight or ultraviolet illumination with *Saponaria* alone or with the model saccharides. The different samples were treated with ammonia vapour for different times. Light colours developed slowly on the tops of samples that contained reducing saccharides.

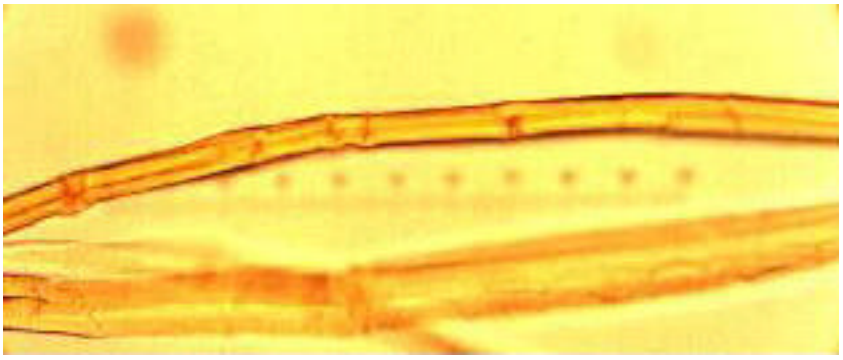
A technical grade dextrin, that reduced Fehling's solution, was used to test crude-starch reactions. Paper was laid over different numbers of drops of dextrin, and the liquid was allowed to migrate into circular spots and evaporate. Samples were then laid over drops of *Saponaria* solution, which caused the polysaccharides to move radially, as in a circular paper chromatogram. Afterwards, these samples were treated with ammonia that produced the development of a brown colour, which was more intense where the dextrin had been concentrated by migration at the *Saponaria*-solution front and on the paper's surface.

Very little colour was obtained when the same experiments were repeated with purified starch or plant gum. It was evident that colour development required both reducing sugars and amines.

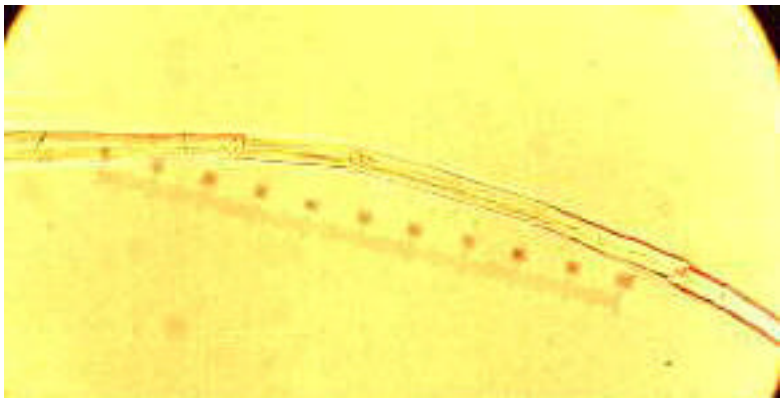
After these successful experiments, a sample of Edgerton's bleached linen was placed on four drops of dextrin solution on a plastic plate. A round spot was obtained and the water was allowed to evaporate from the cloth: at this point no colour could be seen on either surface. The middle of the same sample was placed on four drops of *Saponaria* solution. The wet spot expanded radially through the cloth. The water was allowed to evaporate, and no colour could be observed. The sample was then treated for 10 minutes with ammonia vapour: a very light colour could be observed on the top surface after standing 24 hours at room temperature. To increase the reaction rate, a sample was treated at 66 ºC for a few minutes (Figure 2 above). In these

conditions the development of colour is very clear and the most intense colour appears in the ring on top. Some colour appears around the ring on the back surface; however, the centre of the back is nearly white.

Experimental manipulations of concentrations and one-dimensional migration of solutions, as in a large cloth, could produce the same front-to-back colour separation as observed on the shroud.



When observed under a microscope, the fibres on the top-most surface are the most coloured and the colour is a golden yellow similar to that on the shroud (Figure 3 above).



The coating of brown products is too thin to be resolved with a light microscope, and it is all on the outside of the fibres. There is no coloration in the medullas: the colour does not scorch the cellulose. There is essentially no colour on fibres from the middle of the back surface (Figure 4 above).

DISCUSSION

A large number of attempts have been made to reproduce the Shroud image by different methods, and many "theories" have been proposed (Vignon, 1970). All have failed when compared with observations and measurements on the Shroud and none of them was able to explain the experimental fact that only the surfaces of the fibres are coloured .

Studies on contact and material-transfer hypotheses (Pellicori & Evans, 1981) eliminated hypotheses based solely on vapour-diffusion and/or material-transfer mechanism. Vapours and

liquids penetrate the cloth: materials that will colour the surface will also diffuse into and colour the inside of the cloth.

Hot irons, statues, etc., must be ruled out, because different colours can be seen as a function of the depth into the cloth. Colour penetration is different for contact and non-contact areas, and fibres are coloured through their entire diameter.

Other "theories" and attempts at image production have ranged from pseudoscience to the lunatic fringe. Many have involved unknown physics, some involving ionising radiation, postulated at the time of the Biblical resurrection (Antonacci, 2000).

This is certainly the first report of colour development with features very similar to the Shroud obtained by a natural process on a cloth prepared following the procedure that was in use about 2000 years ago as it was described by Pliny the Elder. This ancient technology used to leave residues of reducing sugars on the cloth both deriving from crude starch and *S. officinalis*.

The amino reactants required to develop colour may derive from a corpse. In fact decomposing bodies start producing ammonia and amines, e.g., cadaverine (1,5-diaminopentane) and putrescine (1,4-diaminobutane), fairly quickly, depending on the temperature and humidity. The ammonia and many of the amines are volatile, and they rapidly undergo Maillard reactions with any reducing saccharides they contact. It is well known that browning rates depend on pH: rates peak in the neutral to basic pH range, but rates are still rapid in the 3-7 pH range (Ledl and Schleicher, 1979)[1]. Human sebaceous secretions are about 28% free fatty acids; therefore, human skin is normally slightly acid, but the developing amines should neutralize the medium increasing the reaction rate.

Melanoidins, the brown polymeric materials coming from the Maillard reaction, although their structures are still rather elusive (Arnoldi et al, 2002), have certainly a highly unsaturated structure as observed for example by Cammerer and Kroh (1995). This seems in good agreement with the fact that image fibres could be decolourised with strong reducing agents, indicating the presence of conjugated double bonds (Heller and Adler).

Such sugar-amine reactions may offer a simple, realistic, natural explanation for the colour on the shroud.

Several Shroud researchers have wondered why there is no mention of an image on the "cloths" reportedly found in Jesus' tomb. Assuming historical validity in the accounts, such a situation could be explained by the delay in the development of the Maillard reactions' colours at moderate temperatures.

Another important observation is the fact that the image-forming process produced slightly different colour densities on the different lots of thread (Jumper et al., 1984). The density-density of the image is not simply a function of the chemical properties of cellulose: it also depends on the individual properties of the threads. The observed effects must have been caused by different amounts of impurities that originally coated the surfaces of the threads as a result of slightly different production conditions.

Slightly different amounts of impurities on the linen threads would cause slightly different surface energies. Liquids would wet the threads as a function of the difference between the surface tension of the washing solution and the surface energy of the specific linen thread. This would explain the "banded" appearance of the Shroud.

The chemistry of the colour does not answer all questions about how the "photographic" image formed. The image seems to show the body of a man, and it is darkest in areas that should have been closest to the body's surface.

Vapour diffusion parallel to the cloth's inner surface would follow Graham's Law, and high Maillard reaction rates would limit the spread of reactive amine vapours. Gaseous reactive amines can be lost by diffusion through the porous cloth, reducing concentrations and reaction rates inside the cloth. The surface area of cloth is large, and decomposition amines adsorb strongly. All of these phenomena would cause a rapid reduction in amine concentrations away from contact points.

Postmortem body temperatures can reach 41ºC (Irvine, 2001), and steep temperature gradients would exist across the cloth as a result of the low thermal diffusivity of linen and the angular dependence of radiant heat flow from a nonmetallic surface (Gubareff et al, 1960). The temperature gradients will have a large effect on Maillard reaction rates. These combination of factors could produce a distribution of reaction products with the appearance of the image.

The problem of radiocarbon age determination.

In 1988 Damon et al. (1989) reported result of a radiocarbon age determination as 1260-1390 with at least 95% confidence. The instruments and methodologies applied were certainly the best that could be used in the world, however that datation does not reflect the STURP observation on the linen-production technology and the chemistry of the fibres. A detailed description of the characteristics of the fibres used for determination has not been reported, however the sample was cut very near to another sample given in 1973 to Professor Gilbert Raes of the Ghent Institute of Textile Technology.

Some of the fibres of this latter sample are in the hands of R. Rogers who has observed a series of very peculiar characteristics that indicate very clearly that this sample is incoherent with the general features of Shroud. The most important experimental observations are the following (Rogers and Arnoldi, 2002):

a) An evident contamination with cotton fibres (easily recognizable from linen at the microscope), which do not appear in the other parts of Shroud. Cotton was practically unknown in ancient times and was introduced in use only around 1350.

b) Linen fibres in the Raes sample show at the microscope only traces of lignin at the nodes in comparison with the rest of Shroud, indicating a more modern technology for cloth preparation, which is confirmed by the chemical quantitative determination of lignin.

c) All Reas threads show coloured encrustations on their surfaces that are lacking on the rest of Shroud.

All these observations suggest that the sample for the radiocarbon age determination came from an area, which had been darned, a phenomenon that must not surprise, because the Shroud may have been restored during his complicate history, especially after it was damaged by a fire in 1532. Therefore the 1988 radiocarbon age determination, which indicated that the Shroud was Medieval, seems highly unreliable. A second radiocarbon analysis should be very advisable, at least on the charred materials removed during the June-July 2002 restoration (Ghiberti, 2002).

CONCLUSION.

The chemical analyses performed by the STURP (Schwalbe and Rogers, 1982) are in good agreement with the Pliny description of ancient cloth technology, as extensively discussed recently by us (Rogers and Arnoldi, 2002):.

We can now formally propose a completely natural hypothesis for image formation. Impurities in ancient linen could have been suspended by the surfactant property of a *Saponaria officinalis* washing solution and they would be concentrated at the cloth surface by evaporation. Reducing saccharides would react rapidly with the amine decomposition products of a dead body.

This hypothesis is the first one, which can explain the very peculiar distribution of colour on the Shroud fibres. Such a natural image-production process would support the hypothesis that the Shroud of Turin had been a real shroud. However, these observations do not *prove* how the image was formed or the "authenticity" of the shroud.

References.

Antonacci, M. *The Resurrection of the Shroud.* M. Evans and Company, Inc., 216 East 49th St., New York, NY 10017. (2000).

Arnoldi, A. Thermal processing and foods quality: analysis and control, in Richardson P, *Thermal Technologies in Food Processing.* Cambridge UK, Woodhead Publishing, pp. 138-159 (2001).

Arnoldi, A., Boschin, G. & D'Agostina, A. Melanoidins in foods. *Res. Adv. Food Sci., 3*, 1-10 (2002).

Cämmerer, B. & Kroh,. L. W. Investigation of the influence of reaction conditions on the elementary composition of melanoidins. *Food Chem.* **53,** 55-59 (1995).

Damon P.E., Donahue, D.J., Gore, B.H.; et al. Radiocarbon dating of the Shroud of Turin. *Nature*, **337**, 611-615 (1989).

Donadoni A. M. (1978) personal communication.

Ghiberti, G. *Shroud Images 2002*. Opera Diocesana Preservazione Fede, Turin, 2002.

Gilbert, R. Jr.& Gilbert, M. Ultraviolet-visible reflectance and fluorescence spectra of the Shroud of Turin. *Applied Optics* **19**, 1930-1936 (1980).

Gubareff, G. G., Janssen, J. E. & Torborg, R. H. *Thermal Radiation Properties Survey*, (Minneapolis. Honeywell Research Center, Minneapolis-Honeywell Regulator Co., 1960).

Heller, J. H. & Adler, A. D. A chemical investigation of the Shroud of Turin. *Canadian Society of Forensic Science Journal* **14,** 81-103 (1981).

Hochberg, B. *Handspinner's Handbook*, summarized as Events in Textile History, Edgerton, K. & Knott, L., Eds. (Windham Center, CT, 1980).

Irvine, R., Pathology Section, Office of the Medical Investigator, University of New Mexico, Albuquerque NM 87131, Personal communication (2001).

Jumper, E. J., Adler, A. D., Jackson, J. P., Pellicori, S. F., Heller, J. H. & Druzik, J. R. A comprehensive examination of the various stains and images on the Shroud of Turin. *ACS Advances in Chemistry, Archaeological Chemistry **III*** **205,** 447-476 (1984).

Ledl F. & Schleicher, E. New aspects of the Maillard reaction in foods and in the human body. *Angew. Chem. Int. Ed.,* **29**, 565-706 (1990).

Pellicori, S. F. & Evans, M. S. The Shroud of Turin Through the Microscope. *Archaeology*, January/February 35-43 (1981).

Pliny the Elder *Natural History*. Book 19, §48 (AD 77)

Rogers R. N., Arnoldi A. Scientific method applied to the Shroud of Turin: a review. http://www.shroud.com/pdfs/rogers2.pdf.

Rogers, R. N. Supportive comments on the Benford-Marino '16th century repairs' hypothesis. *British Society for the Turin Shroud, Shroud Newsletter* **54**, 28-33 (2001).

Schwalbe, L. A. & Rogers, R. N. Physics and chemistry of the Shroud of Turin, a summary of the 1978 investigations. *Analytica Chimica Acta* 135, 3-49 (1982).

Vignon, P. *The Shroud of Christ* (1902), reprinted by University Books (1970).

Ya Chirva, V., Kintya, P. K. & Lazur'evskii, G. Triterpene glycosides from *Saponaria officinalis. Khim. Prir. Soedin*. **5,** 59-60 (1969).