

SUMMARY

A woven silk picture transferred its image to the glass against which it had been pressed for fourteen years. The image was formed from salt, which occupied the areas where the silk had not touched the glass. Salt impregnation increases the water absorption of silk at a relative humidity below the value at which pure salt deliquesces. A salt solution had formed in the fabric at a moderate relative humidity and then migrated to the glass where the salt precipitated because the relative humidity was below the deliquescence point of pure salt. The process has been replicated.



THE SPONTANEOUS TRANSFER TO GLASS OF AN IMAGE OF JOAN OF ARC

Tim Padfield and David Erhardt
Conservation Analytical Laboratory
Smithsonian Institution
Washington DC 20560 USA

It is not unusual to find on opening the glazed frame of a picture that an image of the original has been imprinted on the inner surface of the glass. Here we propose an explanation for one example of this phenomenon.

The silk picture shown in Figure 1 was woven by the Jacquard process in France around the beginning of this century. It now belongs to the National Museum of American History in Washington DC [1]. This picture and six others from the same source were framed pressed against glass. They hung for seven years in a curator's office, after which they were put into a store room for a further seven years. When the frames were dismantled each glass was seen to have acquired a copy of the original picture.

The image, shown in Figure 2, results from the scattering of light by fine crystals of salt, sodium chloride, which form an adherent film on the inner surface of the glass. The salt is mixed with a small amount of an organic substance with surfactant properties. The dark areas are clear glass. The white areas of salt on the glass match the white areas on the picture almost exactly. There is, however, a notable exception: the sleeve of the left arm (Figure 3, top). Here a dark mark on the glass (Figure 3, middle) corresponds to a glossy white area on the woven image. Figure 3, bottom, is a relief image of the cloth which shows that all the dark areas of the picture, but only a few of the white areas, including the highlight on the sleeve, are raised. The salt image does not match the pattern of the colour but instead follows the relief of the original. The salt is found on the glass only where the cloth did not touch it.



Figure 1: The woven silk picture of Joan of Arc. It measures 520 by 320 mm.

Figure 2: The image on the glass which was pressed against the picture. The pale areas are formed by light scattered from fine salt crystals.

Figure 3 (left): An enlarged portion of Figure 1 (top) with the salt image (middle) and the surface relief of the silk (bottom).

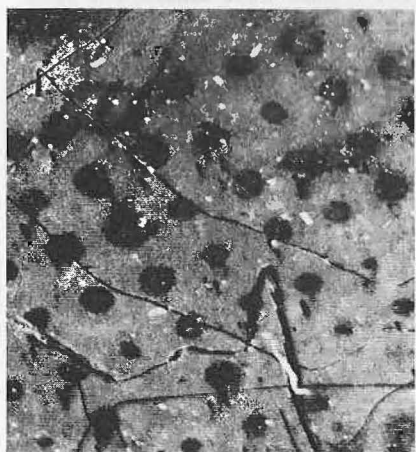
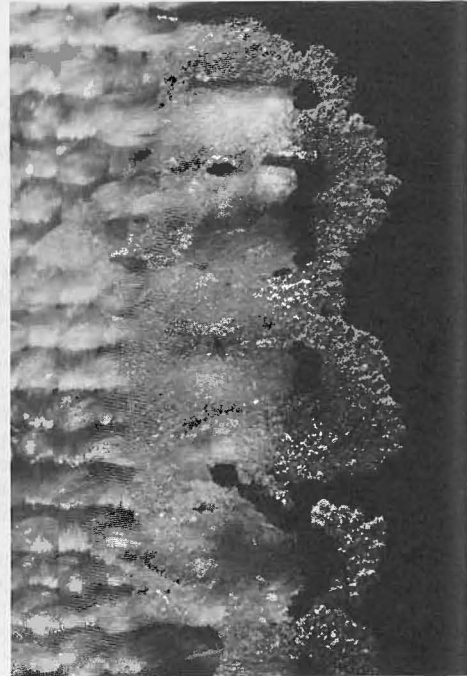
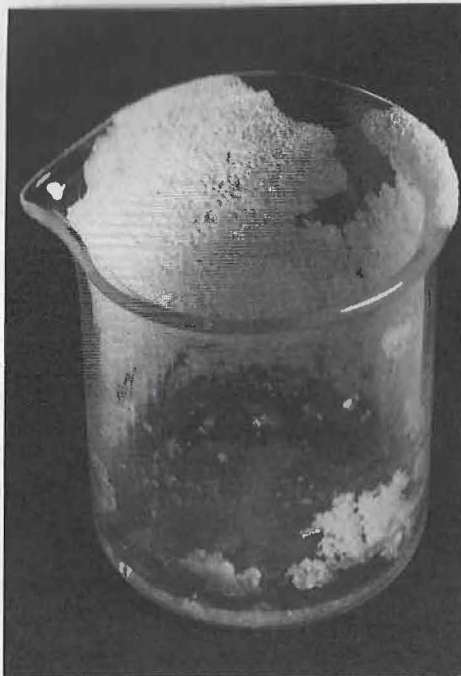
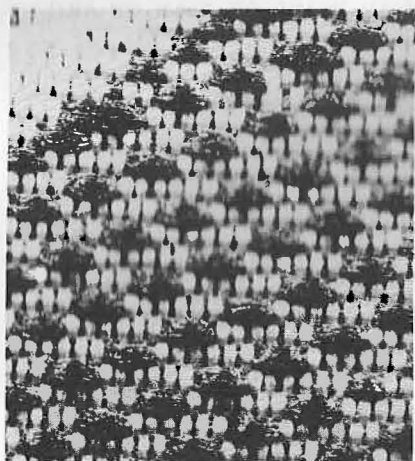


Figure 6: A portion, 10 mm across, of a companion picture to Joan of Arc (top), and the corresponding salt image.

Figure 4: The crystallization pattern of an evaporating salt solution with surfactant.

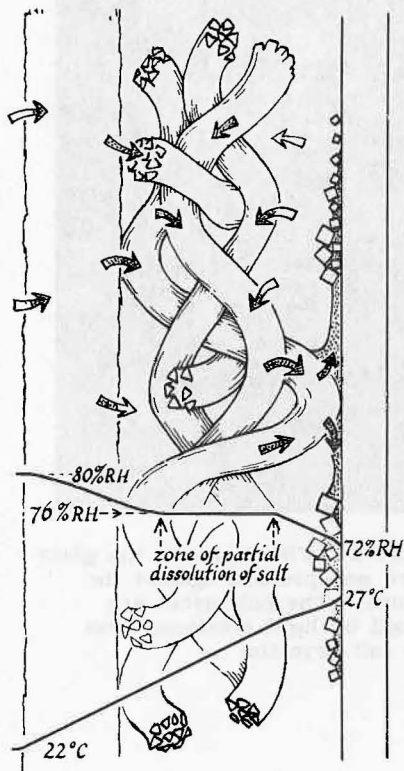
Figure 5: The pattern of salt formation on glass resulting from migration and evaporation of solution from saturated silk.

The image on the glass is consistent with crystallization from a salt solution containing a trace of surfactant [2]. Figure 4 shows how crystals form over the glass of a beaker containing such a solution. Note how there is a gap between the surface of the solution and the lowest crystals on the glass. This gap is shown more clearly in Figure 5. Here a piece of silk, saturated with salt solution, is placed against a piece of glass. As evaporation proceeds crystals form on the glass at a small distance from the point of contact of glass with silk. Figure 6 shows a portion of a companion picture to Joan of Arc and the corresponding salt image. The clear area on the glass around the point of contact with the silk is clearly shown.

Salt is widespread in the picture assembly. It is in the silk cloth, in the linen behind the silk and in the card backboard. The salt could have transferred to the glass during a period of high relative humidity (RH). Above 76% RH pure salt deliquesces: the crystals absorb water vapour from the air and dissolve to form a saturated solution.

A possible sequence of events within the frame of the picture of Joan of Arc is illustrated in Figure 7: as humid air diffuses slowly into the picture from the back, water absorption by the salt crystals buffers the relative humidity so that until all the salt has dissolved the relative humidity of the air within the enclosure cannot exceed 76%. Suppose now that a temperature gradient forms within the picture because its back is against a cool outside wall or because the front is warmed by a spotlight. The relative humidity at the back of the picture will be buffered to about 76% by the action of the salt, whose deliquescence point is not affected by temperature. However, the relative humidity at the warmer inner surface of the glass will be slightly below 76% because in an empty, closed space it is the water vapour concentration which tends to become uniform, not the relative humidity. Under these conditions the salt solution in the fibres will move by capillary flow among the fibres and then migrate from the point of contact across the glass. The salt solution begins to dry out as it traverses the glass, eventually depositing salt at a small distance from the point at which it emerged from the fibres. The evaporated water diffuses back through the picture and the cycle of deliquescence, capillary movement, evaporation and precipitation continues. The first deposit of salt crystals on the glass forms a capillary network allowing the solution to flow outward from the point of contact protected from evaporation. Fresh salt precipitates outside the existing fringe of salt. Over several years even a feeble movement of salt driven by intermittent imposition of a high relative humidity and a small temperature gradient may indeed have generated the image found on the glass.

Figure 7: The process of salt transfer caused by a temperature gradient at high ambient relative humidity.



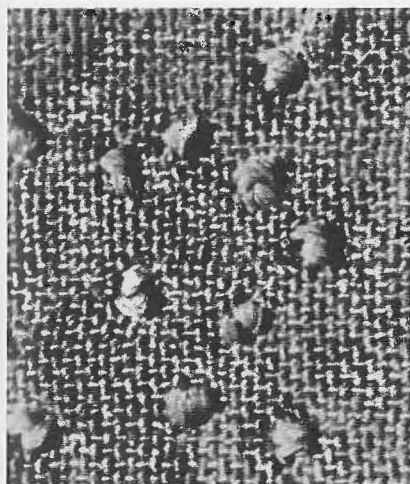


Figure 8: The experimental silk cloth with the image formed on the glass (10 mm across).



Figure 9: The faint salt image on glass formed over two weeks in a constant environment of 65% RH and 22°C. The image is 3 mm across. The bright discs are unfocussed dust particles.

Figure 8 shows the result of a laboratory simulation of the image transfer process proposed in Figure 7. A piece of silk cloth was made uneven with loops of silk thread. This cloth was put in a glazed frame with linen backcloth and card to imitate the construction of the original, except that an impermeable back was added. The silk alone was impregnated with salt. All the components were pre-conditioned to 76% RH by suspending them over saturated sodium chloride solution. After this the pieces were assembled and set on the laboratory bench. The glass was overlaid by a sheet of black paper which was warmed by a lamp. The back of the picture was maintained at the 22°C ambient temperature by fanning air over it. The slight increase in temperature of the silk would, if no salt were present, cause a small increase in the relative humidity of the air in the enclosure. In this case, however, the salt buffered the relative humidity by absorbing the water vapour released by the silk. After fourteen days the piece was disassembled and photographed. Figure 8 (bottom) shows the image on the glass. The similarity to the genuine effect is close, though the process has been arrested at an early stage in the spreading of the fine-grained salt layer out from the clear portion close to each point of contact.

This salt image was formed quite rapidly at about 76% RH, the minimum value at which pure salt deliquesces. However, a relative humidity as high as 76% should never have occurred, at least not for long, in an air conditioned museum. We therefore set up an experiment to see if image transfer could occur at a lower relative humidity and at a uniform temperature.

In this second experiment the test picture was conditioned to 65% RH and then assembled as before. After two weeks of incubation at 22°C salt transfer was again observed. The effect was weaker; indeed the salt was scarcely visible. The image shown in Figure 9 was photographed in a humidity chamber so that the fine salt deposit deliquesced to give liquid droplets which scattered light better.

The silk was examined to determine the distribution of the salt, originally homogeneously distributed within the fabric. We found that it was now concentrated at the high points of the weave, where the cloth touched the glass. It is not obvious why this should be so. However, the authentic images, such as Figure 6, show a small pip of salt at the point of contact, surrounded by the clear halo. Whatever the process at work, there is no inconsistency between the original and the reproduction.

How can salt move, apparently in solution in water, within cloth that is dry to the touch, at a relative humidity well below the deliquescence point? To gain more evidence we measured the water absorption of salt-impregnated silk as a function of relative humidity. The results were surprising. It seems that salt-impregnated silk does not behave like a simple mixture of salt and silk. The diagrams in Figure 10 show what happens. In the case of clean silk there is a continuous absorption of water as the relative humidity increases. The shape of the graph for pure salt is completely different: there is negligible absorption of water as the relative humidity rises until the critical value of 76% RH is reached. At this point the salt absorbs water from the air and dissolves in it to form a saturated solution. As the relative humidity rises further the salt solution continues to absorb water, theoretically reaching infinite dilution at 100% RH. One might expect to describe the behaviour of a mixture of salt and silk by adding together these two curves to produce the composite curve in box C. In fact, however, the step in the curve is smoothed out so that the contaminated silk absorbs more water than expected at a low relative humidity, as shown in box D. Above 76% RH the water absorbing capacity of the mixture is less than expected.

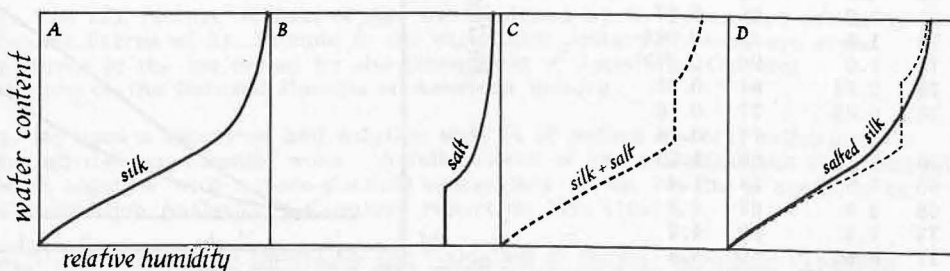


Figure 10: Comparison of the water absorption of silk and of salt: separate and mixed.

Table 1: Water content of silk (percent of dry weight) at 25°C.

RH	clean silk	silk plus 46% salt
9	2.1	2.3
26	4.7	5.1
35	6.0	6.7
45	7.5	8.5
56	9.2	10.9
67	11.4	15.2
70	12.8	20.0
72	13.5	30.7
73	13.9	67.3
67	13.5	21.0
56	11.7	14.1
45	9.9	10.8
35	7.8	8.2
26	6.5	6.6
9	3.3	3.3

RH	clean silk	silk plus 3% salt
15	4.4	4.3
20	5.2	5.1
26	6.0	5.9
32	6.8	6.7
38	7.8	7.6
47	8.5	8.6
54	9.4	9.5
58	9.7	9.9
64	10.4	11.1
71	11.6	13.7
78	13.5	17.8
83	14.5	20.4
93	20.0	33.5
84	17.6	23.0
78	15.8	19.6
75	15.3	18.4
72	14.7	17.3
68	14.1	16.2
65	13.8	15.5
63	13.1	14.3
58	12.5	13.2
53	11.9	12.2
40	9.9	9.8
29	8.4	8.2
20	6.6	6.5

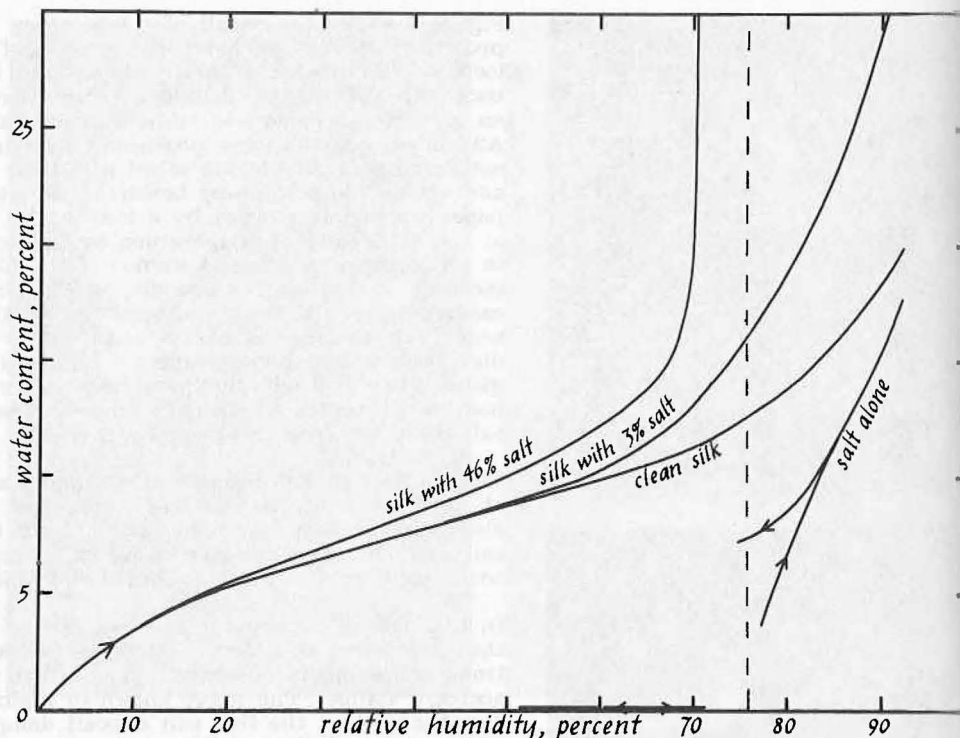


Figure 11: Water absorption isotherms at 25°C of pure silk and of salt weighted silk. The isotherm of pure salt is expressed as grams of water per 3 grams of salt to match the data for 3% salt loaded silk.

Some of our experimental results are shown in Figure 11 (all the measured values are given in Table 1). With very heavy salt contamination the extra water uptake becomes measurable at 25% RH. A three percent loading of salt causes separation of the two curves at about 55% RH.

This extra water is not necessarily mobile. To confirm the existence of an ionic solution we measured the relative humidity dependence of the electrical resistance of silk containing 2.4% salt (Table 2). The results are plotted as conductivity in Figure 12. The electrical conductivity is enhanced in a manner very similar to the water absorption. There is no sudden change of conductivity at 76% RH. Electrical conductivity of the contaminated silk becomes measurable at a relative humidity well below the deliquescence point of salt while that of clean silk remains very small.

It is quite clear from these measurements that salt and silk interact when mixed to form a system with a response to atmospheric moisture unlike that expected from adding the separate contributions of the components.

Table 2: Electrical resistance of silk containing 2.4% of salt.

RH	Mohm	RH	Mohm
37	>7	37	>7
47	>7	60	5.4
53	7	66	3.3
57	6.8	71	2.3
61	5.4	75	1.1
63	4.5	80	0.46
66	3.0	85	0.17
73	1.6	89	0.084
74	1.0	90	0.072
75	0.72	84	0.21
76	0.62	77	0.76
		74	0.74
36	>7	69	1.25
60	6.5	68	1.4
68	3.6	63	2.6
73	1.6	60	4.2
77	0.65	59	4.8
79	0.52		
87	0.12		
80	0.36		
76	0.74		
73	0.64		
72	0.77		

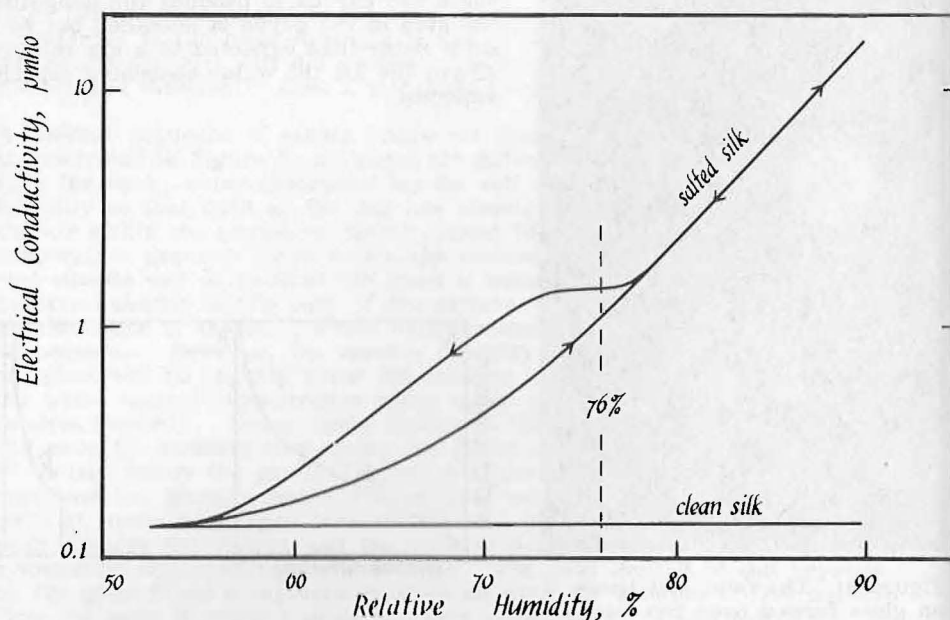


Figure 12: The electrical conductivity of a silk strip impregnated with 2.4% salt, measured at 20°C. The strip was 16 mm wide by 85 mm long and weighed 330 grams per square metre.

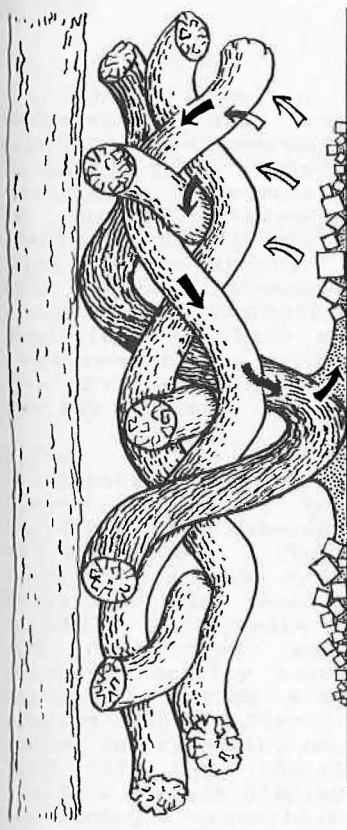


Figure 13: Diagram of the salt transfer process at constant and uniform temperature.

These results suggest a mechanism for salt transfer that needs no external driving force such as a temperature gradient. This is summarised in Figure 13. The salt-contaminated silk absorbs more water from the atmosphere than pure silk. An electrolyte solution is formed within and among the fibres which is sufficiently mobile that it permeates by capillarity, or by surface diffusion, throughout the entire system. At the point of contact between fibre and glass the solution creeps over the glass. Once free from the fibre the normal deliquescence point of pure salt reasserts itself and the low relative humidity (that is below 76%) causes the solution to evaporate. The salt remains on the glass, the water vapour diffuses to the fibre and the cycle repeats itself. The end result is a transfer of salt from fibre to glass.

The ability of salt to move in solution within a protective capillary network at quite a low relative humidity is demonstrated by the crystals forming in an ambient 50% RH outside the rim of the beaker shown in Figure 4. A salt image, though slow to form at a low relative humidity, is more likely to endure under these mild conditions because the salt separated out on the glass has no tendency to revert to a liquid form unless the local relative humidity exceeds 76%. This second, isothermal mechanism, though slow, is the more plausible explanation for the image of Joan of Arc.

The two mechanisms for salt transfer both require that the glass surface be below 76% RH. They differ in the way a salt solution develops in the fibres. The first mechanism relies on a temperature gradient to produce a relative humidity of 76% in the fibres, a condition which causes even pure salt to deliquesce. The second, isothermal, mechanism depends on the formation of a solution in salted silk below 76% RH. This development of an ionic solution at a low relative humidity is not unique to silk. Cotton contaminated with salt also shows enhanced water absorption. This property may turn out to be a general attribute of hygroscopic solids contaminated with inorganic salts.

The presence of an ionizing liquid has long been known to accelerate reactions on the surface of materials. For example, salt solutions enhance corrosion of metal surfaces [3]. We have found that contamination with a salt solution accelerates corrosion of marble by acetic acid vapour [4]. These reactions occur upon the surfaces of materials that are basically impermeable even though they may be porous on a gross scale. Here the normal deliquescence point of a salt applies. The same acceleration of degradation reactions may occur in hygroscopic organic materials, but at a relative humidity much lower than the deliquescence point of the pure salt. Contaminants which would normally be considered dry and inert at normal museum humidity may really be mobile and reactive, without showing symptoms such as sweating and darkening which occur when salts deliquesce in non-hygroscopic materials.

Deliquescent inorganic salts are widespread in museums. They may be original components of objects, contaminants acquired from use, reaction products of gaseous air pollutants, deliberate additions during treatment or the unconsidered by-product of preservative treatment. Their presence must have an important effect on the permanence of materials.

Acknowledgements

Walter Hopwood, Martha Goodway, Joan Mishara and Harold Westley helped with the analytical work on the silk pictures. We are grateful for help from Rita Adrosko and Kathy Dirks of the National Museum of American History.

NOTES & REFERENCES

1. The silk picture of Joan of Arc was designed by G. Doyen and woven by Neyret Frères of St. Étienne in the early 20th century. There are seven pictures in the set owned by the Department of Social and Cultural History of the National Museum of American History.
2. We used a saturated salt solution with 1% of sodium di-octyl sulfosuccinate for all the experimental work. A full account of the analytical and experimental work together with a more detailed commentary on the results is available as Conservation Analytical Laboratory report no 3349 (1987).
3. U.R. Evans, The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications (London: Edward Arnold Ltd., 1960) pp. 486-501.
4. Work in progress in our lab. Acetic acid vapour in a stream of air at 70% RH reacts much faster with a piece of marble which is contaminated with a small amount of sodium bromide solution than with pure marble. Sodium bromide deliquesces at 54% RH.

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