The Hunt Ball

A recent chance observation on a local railway station cleared up a mystery that had perplexed me ever since my college days.

Oxford University in the early sixties was mostly a man's world, with about ten percent women. The inequality was compensated by a number of finishing schools for the daughters of the gentry. One of these ladies played the flute in an amateur orchestra and we first exchanged words when I inadvertently emptied the accumulated condensation in my bassoon down her neck, as she fluted serenely on the next step of the steeply sloping orchestra stage.

The relationship dried out later, but not before she had invited me to a party at her daddy's country house, a modest mansion with forty bedrooms and an impressive collection of ancestors in oils.

The collection was about to be augmented by a portrait of the present master of the house, who was also a retired Major in the Frightfulshire light infantry, a baronet, master of the local foxhounds and was exactly 50 years old. The painter, who had attended the same chemistry classes as me but had left to go to an art school, invited me into the temporary portrait studio. He had decided to protect the painting with glass, because he had only just finished it and was afraid that the guests would touch, or brush against the portrait and destroy it.

Now it was time for the presentation. It had been a successful hunt that day, two foxes had been killed and the ritual daubing of the youngsters with the blood of the severed tails had been performed with parental fondness. The guests gathered in the evening sunshine on the lawn outside the ballroom to honour the birthday baronet. The portrait was superficially a touch flattering but had nevertheless caught the personality of its subject, because as the afternoon sun illuminated the portrait, blood began to ooze from the mouth and nose and dribble down the tunic.



There was considerable embarrassment, particularly as the photographer from 'Country Life' had been invited and also the mayor and the bishop, eager huntsmen all. Suspicion first fell on the painter, who had also, unknown to me, been collected by the flute player. He pointed to me, saying that I had had access to the painting and was a chemistry student, capable of all sorts of cunning tricks. The suspicious interest of the guests was fortunately snuffed out by the Bishop, who said that the painting must be exorcised at once in the chapel and led the way, while I was left to wonder if it was wiser to flee or to stay.



Figure 2. The condensation behind the glass covering a poster is concentrated over the white parts of the image.

The story now jumps to an event nearly forty years later, where I was again the object of suspicion.

I was standing on the platform of a suburban station in north Copenhagen when I noticed a poster in a glazed frame lit by the failing sun of a winter afternoon. The subject of the poster was crime: a dire and crudely expressed warning against copying CDs. What had caught my attention, however, was the pattern of condensation behind the glass. The close up, outlined in orange on the left, shows the close association of condensation with the white letters.

It is not only a crime to copy a CD, it is forbidden to photograph the property of the Danish State Railways. A railway employee came rushing along the platform, waving the brush he had been using to sweep the same and explained the seriousness of my action. Fortunately the train was just pulling into the station. I waited for the warning tralala and stepped smartly into the carriage as the doors slid together.

The shock to a timid middle class citizen on being accused of a crime while innocently observing the passing scene jerked my mind back to that long ago afternoon when I, for the only time in my life, sipped champagne with the Landed Class of England.

As I huddled down in the seat, preparing to pretend not to be there if the railway police boarded the carriage at the next station, I combined my two observations with my knowledge that many organic dystuffs have such an intense colouring power that they can be dusted sparsely onto the surface of glass as a dry powder which is almost invisible. When these tiny particles come into contact with water they dissolve to give an intense stain. Methylene blue, for example, is used in this way to detect pinhole defects in waterproof rubber enclosures. Why is the condensation so closely tied to the pale areas of the pictures? It must be that the dark areas heat up more in the sunlight and some of this heat is released as long wavelength radiation which is absorbed by the glass. The pale areas absorb less light and also emit less long wave radiation. The reflected light passes unhindered through the glass. Therefore the glass will be cooler in front of the pale areas, so that will be the first place to suffer condensation. All this of course depends on there being some water present. That could easily





be arranged by varnishing the painting with hydrophilic gelatin instead of the usual hydrophobic resin varnish. The shine is the same.

The deeper explanation for the blood flowing from the face in the portrait must be that my former colleague was jealous of losing the flute player to an insignificant person who played such a scarcely used orchestral instrument that during a forty bar rest I had rested the instrument on my knee, with such fateful consequences. The fact that he was also a fanatical opponent of blood sports hardly dulls my piquant thrill at being the object of a cunningly prepared crime of passion.

The reader will perhaps be sceptical that there could be enough water in the system to produce such a dramatic result. There always is! The picture on the left was taken through a supposedly sealed double glass window pane in my house. The low afternoon sun is swinging round from the left of the picture and shining on the glass to the right. The limit of the shadow cast by the brickwork is visible as a dark line up the centre. Water is being distilled from its absorption sites on the two inner glass surfaces that are being warmed by the sun, into the cold shadow, where it is confined to a steadily narrowing volume, from which it condenses as fine droplets, so fine that they give a smoky brown transmission colour. The total amount of water is tiny, just that which can be absorbed invisibly on the glass surfaces within the once sealed double glass pane when it is at a uniform temperature.

I present one more example, on the left, which shows that the phenomenon also has economic consequences. In well ordered countries, a menu with prices outside the restaurant is required for a licence to sell food. The cunning chef knows that if he frames the menu behind glass with a metal frame, condensation will occur every evening at the edge of the glass, which cools first and condenses water released from the paper, which is fastened to the warm wall behind. The mouth watering descriptions of the food will be clearly visible while the prices will be obscured by condensation. The coffee and desert may well be entirely covered by fungi and bacteria, on the menu at least, but the customer is already hooked.

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Figure 6. When a stack of film cans is taken out of cold storage, water vapour will diffuse within the film can, from the rapidly warming exposed surface to the parts that are still cold..

The high risk behaviour of enclosures in a temperature gradient presents unexpected dangers in conservation. One unavoidable cause of a powerful transient temperature gradient is the removal of a film from the deep freeze archive which has become the normal environment for preserving this art form.

Most conservators are aware that the film must be kept away from the room air while it warms up, because of the condensation that would otherwise form on the outside of the container, and threaten to creep in to damage the contents. There is however a more subtle threat of internal condensation, where water vapour migrates from a warming part of the package to the still cold interior. The process is shown in figure 6.

A good old fashioned Hollywood five reeler will hold a cold core temperature long after the happy ending has warmed up. Let us suppose that the warm end is at 5°C and that the film has a water content corresponding to 50% RH. The dew point of the air at the surface of the film roll will be about minus 5°C. If this water vapour has a chance to diffuse to a part of the parcel that is colder than this, ice will form there. As the packet continues to warm, the ice will melt and wet the immediately adjacent film.

It is therefore important to enclose the warming package in an airtight container that is also thermally insulating. There should never be more than about 7 degrees temperature difference between the hottest and the coldest part of the assembly. This is yet another illustration that the key to humidity control is temperature control. One could add that the film should be equilibrated to the lowest acceptable RH before enclosure and committment to the cold store.

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The examples given so far involve processes that occur in a changing environment. It is also possible to provoke steady moisture movement in an environment with a permanent temperature gradient



Figure 7. Section through a wall and a framed picture, showing the temperature gradient and consequent RH differences.



Figure 8. Sorption curves of cotton, showing the very small influence of temperature.

I illustrate this by considering the environment of a picture hung against the inside surface of an uninsulated outside wall.

The steady temperature gradient is the blue dotted line. The paper print has been tinted with watercolour so that it is now buckled. The high points touch the glass and the low points touch the impermeable back, of polystyrene channel plate, for example.

If the paper were not there, the climate within the enclosure would show an extreme RH gradient: from 68% at the inner surface of the glass to 100% at the surface of the backboard. The water vapour concentration is uniform throughout the enclosure, it is only the relative humidity that shows a steep gradient.

Paper is, however, a humidity buffer. Assume that the paper starts at equilibrium with the room climate. It will have a uniform water content of about 6.5% by weight (see figure 8 below). The paper near the backboard will absorb water to about 20% by weight, reducing the RH at the back so that condensation does not now occur. The water vapour concentration close to the paper is now falling, so water vapour migrates through the air from the warm side of the enclosure. A lower RH therefore develops next to the glass. Paper is, however, a humidity buffer and therefore releases water vapour to the air. The result is that the paper becomes drier at the glass than at the backboard. Two opposite moisture gradients have developed: moisture is through the air towards moving the backboard, and is moving through the paper in the opposite direction. This reverse flow is relatively slow: the water molecules have to hop to vacant sites for hydrogen bonding to the cellulose molecules. This process requires activation energy and is therefore retarded at low temperature. The rate of diffusion through the air is, however, not so much influenced by temperature and is in any case much faster.

That is why mould appears in the troughs, where the water content is highest and the temperature is maybe a bit chilly but acceptable to many fungal and bacterial species.

Ah! You will say, but sometimes there is fungus growing where the paper touches the glass! To which I will suggest that you redraw the diagram to show the situation early on a spring day when the room is still cool but the sun is warming the wall.

How to prevent this uneven moisture content

The essential action is to reduce the temperature gradient.

Insulating the backboard is a good idea. Using a water absorbent backboard without thermal insulation is dangerous. It is important to understand that humidity buffers only function when they are always at the same temperature as the object they are intended to protect, otherwise they actively de-stabilise the climate around the object.

Thermal insulation depends mostly on the thickness of the bubbly or fibrous material, and there is a limit to the æsthetically pleasing insulation thickness. One can also just establish a gap between backboard and wall, so the question is which is more effective: an air space where room air can flow past to warm the back of the picture or an equal thickness of insulating backboard? The choice depends on the thermal conductivity of the wall and the size of the picture, because the circulating air will cool according to the distance it must travel through the crevice between cold wall and backboard. If in doubt, an insulating backboard is a wise choice, unless you are in doubt about the wisdom of using backboards at all.

Getting the quantitative proof

There is a "Backboard Project" with an international cast of experts whose aim is to define the ideal protection for the back of an oil painting. So far the project team has published an advanced mathematical analysis of the situation behind unglazed paintings subjected to a sudden change of RH in a constant temperature environment (1). I look forward to having to concentrate hard on their corresponding treatment of what happens in a fluctuating temperature gradient.

There are considerable practical difficulties in measuring what actually happens in detail. The temperature gradient can rather easily be measured continuously with a data logger and some very fine thermocouples embedded discreetly in a test picture. The moisture content is a much more difficult matter. The smallest easily available relative humidity sensor for measuring RH in an air space is about $5 \times 3 \times 1.5$ mm. The thickness is rather large for testing the theory of uniform water content and varying RH, but it can maybe work if one deliberately makes a very wavy picture in a deep frame.

The moisture content of the paper is very difficult to measure accurately. A really high water content can be estimated by measuring the electrical resistance between two electrodes woven into the paper. Episodes of dew formation on the paper can be revealed, irreversibly, by dusting the paper with methylene blue dye before assembling the specimen, as mentioned earlier.

I am, at the time of writing, building an experimental device to measure the relative magnitude of the two opposing flows of moisture through porous materials in a temperature gradient.

Postscript

I need scarcely remind paper conservators of the peculiarly relevant and curious story of the Dada artist Georges Renouilles, who invented a variant of Max Ernst's *decalomania*. He took plain sheets of paper and squeezed them into frames so that they buckled. He then exposed them on the outside of a wall so that moulds of various colours grew in the hollows, or the ridges, and dark wavy lines formed at the limit of evaporation from the bottom of the frame. He then dried these papers out and pressed them flat, sometimes returning them to the frames buckled in the other direction, so that he got some pictures that resembled Scots tartan. Andre Breton refused to let Georges into the surrealist club on the grounds that it was not truly automatic art but calculated scientific processing. Renouilles' art is hardly known now because, in his disappointment, he packed all his production away in a cellar in Paris' 19th arrondissement. When the boxes were opened after his death, the pictures were found to have suffered the ironic fate of rotting away uniformly in the moist cellar. As the ageing, but still sharp, Andre B remarked: this proved that it was scientific art because it was typical of a scientist not to apply to his personal life the lessons learned in his professional life.

Reference:

1. Giovanna Di Pietro and Frank Ligterink, 'Prediction of the relative humidity response of backboard protected canvas paintings' *Studies in Conservation* **44** (1999) 269-277.

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