# The control of relative humidity and air pollution in showcases and picture frames

# Tim Padfield

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#### Abstract

Absorbent materials such as wood, paper and cotton stabilize the atmosphere of showcases against the relative humidity changes caused by temperature variation and by exchange of air with the surroundings.

There are several exchange processes between the air in the case and the outside air: diffusion through porous coonstruction materials, air flow caused by temperature and pressure changes and air flow by convection in a showcase whose relative humdidity differs from that of it environment. The air changes about once a day in showcases made by conventional joinery techniques. The rate of exchange can be reduced to less than five volumes a year by sealing a showcase so that only one small hole is left for pressure equalization. A dust and sulphur dioxide filter can then be fitted to maintain a pure atmosphere within.

In heated rooms without air conditioning the RH may fall dangerously low in winter. A static method of RH control for showcases is described. This is a saturated solution of sodium bromide covered by a silicone rubber membrane.

## A note about this digital version of the article

This version shows each page, except this one, as a picture. The photographic illustrations are not well reproduced. As for the content, I would now add that wood is indeed a good humidity buffer, but it outgasses such a variety of chemicals that it should never be used in a sealed container. The appendices about practical experimental methods seem quaint now (June 2004) but give a good impression of the joys of experimental work in the analogue world of the nineteen sixties.

# TIM PADFIELD

# The Control of Relative Humidity and Air Pollution in Show-cases and Picture Frames

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#### ABSTRACT

Absorbent materials such as wood, paper and cotton stabilize the atmosphere of show-cases against the relative humidity changes caused by temperature variation and by exchange of air with the surroundings.

There are several exchange processes between the air in the case and the outside air: diffusion through porous construction materials, air flow caused by temperature and pressure changes and air flow by convection in a show-case whose relative humidity differs from that of its environment. The air changes about once a day in show-cases made by conventional joinery techniques. The rate of exchange can be reduced to less than five volumes a year by sealing a show-case so that only one small hole is left for pressure equalization. A dust and sulphur dioxide filter can then be fitted to maintain a pure atmosphere within.

In heated rooms without air-conditioning the RH may fall dangerously low in winter. A static method of RH control for a show-case is described. This is a saturated solution of sodium bromide covered by a silicone rubber membrane.

#### INTRODUCTION

Two recent articles [1,2] have shown the advantages of packing humidity-sensitive objects in cases containing materials, such as wood and silica gel, which have a stabilizing effect on the relative humidity.

Objects in display-cases, as well as those in transit, will benefit from this treatment. The use and performance of stabilizing materials in this role is one of the subjects of this article.

In buildings which are heated in winter but not fully air-conditioned the relative humidity RH) sometimes falls so low that wooden objects are damaged. Show-cases are not generally air-tight, and long periods of low humidity will eventually overcome the influence of the stabilizing material. A second

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theme of this article is therefore the problem of maintaining the RH within a display-case higher than that of its surroundings, without danger of condensation during accidental temperature changes.

There is also a brief discussion of air pollution within show-cases because most of the calculations apply to water vapour and pollutant alike, and a case designed to maintain a stable RH can easily be protected against entry of pollutants.

#### ATMOSPHERIC MOISTURE

The reader will need an understanding of the concept of relative humidity. A brief explanation is given below. Much fuller information is available in some of the textbooks listed in the bibliography [3,4].

At ordinary temperatures liquid water is in equilibrium with a definite concentration of water vapour in the space around it. This concentration is almost unaffected by the presence of other gases and depends only on the temperature. The movement of air distributes water vapour to spaces remote from a liquid water surface, where the air generally contains less than the equilibrium amount of water vapour. The actual concentration, expressed as a fraction or percentage of the equilibrium concentration, is the relative humidity (RH). The relation between the water vapour concentration (absolute humidity), relative humidity and temperature is shown in Fig. 1.

Why choose RH rather than water vapour concentration as the measure of atmospheric moisture? The reason is that moisture-



FIG. 1. The relation between absolute humidity, relative humidity and temperature. Based on hygrometric tables HMSO.

sensitive materials such as wood, paper, and textiles change their dimensions and moisture content as the RH around them changes, but are not much affected by changes of absolute humidity as long as the RH remains constant. In other words the moisture content—RH relationship is little affected by temperature. The moisture content—RH relationship of air, however, is very much affected by temperature, as Fig. 1 shows. The consequent interchange of water vapour between air and wood can be used to counteract the change in RH of air.

# EFFECT OF RH CHANGES ON MUSEUM Objects

The dimensional changes of absorbent materials are not uniform in all directions. Fibres swell more transversely than longitudinally and a log of wood swells less radially than circumferentially and very little longitudinally. Much of the trouble caused by RH changes is due to this unequal swelling. The warping of wood, for example, is caused by its different expansion in radial and circumferential directions. Laminated materials also warp. Even paper laid down on cotton cloth may cockle because, although the individual fibres of paper and cloth lengthen identically as the RH increases, the twisted cotton yarn may actually shorten. The progressive dissolution of creases in garments is due to the movement of the fibres as the RH fluctuates.

Dimensional changes are not the only result of RH fluctuation. Above certain values of RH some minerals and glasses become deliquescent and metallic corrosion and mould growth occur.



FIG. 2. Part of the absorption isotherm of soda-boiled cotton at 20°C (from Urquhart & Williams [5]).

It is always beneficial to maintain an unchanging RH around an object and sometimes it is necessary to maintain around a particular object a RH lower or higher than that prevailing in the gallery.

Old wooden articles were made from wood dried to equilibrium with air of over 70% RH. If these objects are subjected to much drier conditions the wood will warp and the structure may crack, according to the way in which the parts have been joined.

#### RH STABILIZATION BY ABSORBENT MATERIALS

The effect of cotton and wood in stabilizing a closed container against RH fluctuations caused by temperature changes has been lucidly explained by Garry Thomson in a recent article [I]. Briefly, the stabilization is due to the small effect of temperature changes on the moisture content of wood and the great amount of moisture contained in a small volume of wood compared with an

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equal volume of air. As the temperature rises the RH of the air tends to fall (Fig. 1). But the RH of the air in contact with the wood remains almost constant. If much wood is present its moisture content entirely determines the RH of the entire volume.

In a similar way the change in the moisture content of an absorbent material caused by a change of RH at constant temperature can be used to stabilize show-cases against changes caused by leakage of air into the case.

Fig. 2 shows the relationship between the moisture content of cotton and the RH of the air in equilibrium with it at 20°C. In Fig. 3 data from Figs. 1 and 2 are replotted to show how stabilization occurs. Consider a showcase of 1 m<sup>3</sup> volume with 400 g of cotton cloth laid on its floor. Initially the RH inside is 60% and the RH outside is 40%. The case is opened briefly so that all the air is changed but the cotton has no time to dry out appreciably. Then it is closed up again. The cotton will still be at A' but the air in the case will be at B. Water will now move from cotton to air. The position of the final equilibrium is governed by the condition that, in a closed container, the air must gain as much water as the cotton loses. Equilibrium is therefore reestablished at C (54% RH) where the two dotted lines are of equal length [6].





FIG. 4. Thin line: The effect of putting a bowl of water in an empty case (left) and in a case with 4 kg/m<sup>3</sup> of cellulosic material. The heavy line is the RH in the gallery. When the bowl is put in the empty case, the RH rises from around 50% to around 70%. The small-scale fluctuations are due to temperature changes. From the double vertical line the cellulose material is present. The change to high humidity has now become a slow drift.

When the leakage is slow and continuous the same sort of argument applies. A convenient rule of thumb can be obtained by calculating the weight of cotton whose isotherm has the same gradient as that of I m<sup>3</sup> of air. This is about 200 g. This amount of cotton can be considered equivalent in its moisture relations to I m<sup>3</sup> of air space. One volume change of air in a case of I m<sup>3</sup> containing 200 g of cotton will cause only half the RH change that would occur in the absence of cotton. One volume change in a case containing 2 kg cotton will cause only one tenth the RH change in the empty case. Wood is nearly twice as efficient as cotton but much slower acting.

The practical effects of using absorbent materials in showcase construction and furnishing are shown in Figs. 4 and 5.

## METHODS OF MAINTAINING A Constant RH

The best method of maintaining a constant RH in a show-case is to use absorbent material inside the case and a conditioned atmosphere outside it. Where this is impossible or too expensive, or where individual objects require a RH different from that in the gallery, three static, or almost static, methods of internal humidity control have been used.



FIG. 5. The effect of using absorbent material to stabilize the RH in a showcase. A and B: Temperature and RH in a gallery of the Victoria and Albert Museum. C: RH in an empty case. When the case is opened (arrows) it fills with air from the gallery. Through the week the RH drifts toward the average outside. D: RH in a case containing a wooden musical instrument and cloth-covered cork base. The RH is stabilized not only against the change of air when it is opened but also against changes due to temperature variation.

and changes due to temperature variation.

Cursiter [7] enclosed a panel-painting in a frame whose base contained a tray filled with a salt which reversibly changed its crystal structure, with evolution of water vapour, below a RH of 55% (at 15°C). Silica gel has been used as a moisture

Silica gel has been used as a moisture reservoir [8]. It behaves in exactly the same way as cotton or wood. The absorption isotherms vary considerably from one brand of silica gel to another, but the change of water content per 1% change of RH at 50% RH is about 6 g per kg dry weight.

Saturated salt solutions maintain, at a constant temperature, a constant RH in the surrounding atmosphere. The reason for this is that the concentration of the solution remains constant as the water evaporates, by precipitation of more salt. The equilibrium RH is less than 100% because the salt dilutes the water in which it is dissolved and hinders the escape of water molecules from the surface. The rate of return of water molecules to the surface depends only on the surface area and is unaffected by the dilution. Consequently the water vapour concentration above the solution diminishes until these two processes are in equilibrium. The slight temperature dependence of the RH is due to the change in solubility of the salt. For dilute solutions the lowering of water vapour concentration is given by Raoult's law:  $\delta p/p = n_a/n_b$  where  $n_a$  and  $n_b$ are the number of ions of salt and the number of molecules of water respectively. p is the concentration of water vapour over pure water.

As the concentration of salt increases, the interactions between the various ionic and molecular species increase so that the equilibrium RH becomes incalculable and must be experimentally determined. The published data for many salts have been collected by O'Brien [9]. An example of the use of this method is given in [10].

#### THE RATES OF THE PROCESSES CONTROLLING RH

So far I have described only equilibrium conditions and have ignored the rates of the

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various processes which control the relative humidity. These aspects of RH control are not important in the packing cases which were the subject of the earlier articles [1,2] because, although cases in transit are subject to greater and more rapid fluctuations of temperature and relative humidity, their thermal insulation and air-tightness is generally much better than that of show-cases. Also packing cases fit their contents more closely and equilibrium is rapidly established between the air and the materials in the case.

A sudden temperature change will rapidly affect the inside of a display case and the distances over which water vapour must move to restore equilibrium are much greater than in a packing case.

The effect of leakage will be to reduce the RH below the equilibrium value in a container provided with some method of humidification. With a silica gel or wood stabilizer the RH will slowly drift towards that of the outside air.

A knowledge of the rates of these various processes is very important in deciding how much stabilizer and humidifying apparatus must be provided and what surface area it should have.

# THE RATE OF LEAKAGE OF AIR

The most convenient and relevant tracer of air movement is water vapour. Its concentration can readily be determined by hygrometry.

To measure the rate of loss or gain of water vapour it is necessary to remove or cover all absorbent materials within a showcase, because a wooden base board, for example, will allow water vapour to diffuse through it. Furthermore, absorbent material inside the case may take months to reach equilibrium with the air and either delay or invalidate the results.

A shallow tray containing a saturated salt solution is placed in the case. The salt should be one whose saturated solution gives an equilibrium RH considerably greater or smaller than that of the ambient air. Several weeks are allowed to pass during which the residual absorbent materials (which are difficult to remove entirely) reach equilibrium. Then the rate of loss of water is measured while the RH inside and outside the case is recorded.

In one particular test the RH inside was 72% while the average outside was 55%. During one week the salt solution lost 24 g of water. The volume of the case was 1.25 m<sup>3</sup>. At 72% RH and 20°C the air within contained about 16 g of water while an equal volume of outside air contained 12 g. During one week therefore  $6 \times 1.25$  m<sup>3</sup> of air had come out of the case and been replaced by air from outside.

A number of experiments using various RH differences and several show-cases gave results of about the same magnitude.

Water vapour diffuses through air nearly twice as fast as oxygen and nitrogen and very much faster than dust particles. Diffusion is one of the processes responsible for air movement and so the data obtained with water vapour cannot strictly be extended to gases and particles of greater weight.

As a rule of thumb, however, one can assume that every day one volume of air is exchanged between a show-case of standard construction and its surroundings. Obviously less leaky cases exist, but unless they are scaled against pressure changes it is impossible to prevent air movement.

It has been argued that some ventilation is necessary to prevent excessive humidity changes during rapid changes of temperature and also to remove the gaseous emanations which are the product, and may in turn be the cause of deterioration. But this rate is too slow to prevent humidity changes and the rate of entry of pollutants must far exceed the rate of generation of decomposition products.

Nevertheless the protective effect of a showcase can be considerable. The air in a comparable unenclosed space changes every few seconds. Fig. 6 shows that even a small reduction in the rate of circulation of air can cause a considerable fall in the concentration of reactive gases.

# THE CAUSES OF AIR MOVEMENT

Air *diffuses* through some of the materials of the show-case—mainly through the wooden parts. It also diffuses through cracks and keyholes and the holes sometimes deliberately made in show-cases to 'let them breathe'.

Air *flow* is caused by changes of atmospheric pressure and temperature. This flow is almost entirely through cracks and holes and not through solid materials. Air flow by convection may occur when the RH, and therefore the density of the inside air, differs from that outside.

#### DIFFUSION

The rate at which one substance diffuses through another is given by Fick's law, which states that the rate of transfer of material through a plane is proportional to the concentration gradient perpendicular to that plane:

$$\frac{dm}{dt} = -AD\frac{\partial c}{\partial x}$$

where *m* is the quantity of material passing through the plane,  $\partial c/\partial x$  the concentration gradient, and *A* the area of the plane. *D* is the diffusion coefficient. The minus sign indicates that the transfer of material is in the direction of the region of lower concentration.

When the concentration gradient is constant the equation becomes:

$$\frac{lm}{dt} = -AD \, \frac{(c_i - c_0)}{l}$$

where  $c_i$  is the concentration inside the case,  $c_0$  the concentration outside and l the depth of the hole, crack or material through which the substance diffuses.

The diffusion coefficient of water vapour through air is about 0.24 cm<sup>2</sup>/sec. This is about twice the coefficient of the other gases



FIG. 6. Histograms of the daily average concentrations of SO2 and smoke outside the Victoria & Albert Museum (heavy line) and in a well-ventilated passageway within the museum. The close similarity of the daily smoke concentrations shows that exchange of air is rapid. Nevertheless the SO2 concentration inside is much lower than outside, presumably because of absorption and reaction on walls and furniture.

found in air. The coefficient for diffusion through wood is about  $1\cdot 2\times 10^{-4}~{\rm cm^2/sec}$  for water vapour and  $0\cdot 75\times 10^{-4}~{\rm cm^2/sec}$  for CO $_2$ [11]. This means that one square metre of wood allows as much air to diffuse as 3 cm<sup>2</sup> of hole through it and leaks water vapour as fast as a  $5 \text{ cm}^2$  hole.

The diffusion of pollutants such as sulphur dioxide through wood is complicated by absorption and reaction with the wood.

The rate of diffusion of water vapour

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through wood becomes important when static methods of RH control are used.

Consider a cubic show-case of glass with a wooden base of 1 m<sup>3</sup> area and thickness 2 cm. The air inside at 60% RH contains 10.5 g of water. An equal volume of outside air at 45% RH and 20°C contains 7.5 g. Then:

$$\frac{dm}{dt} = 10^4 \times 1.2 \times 10^{-4} \frac{(10.5 - 7.5) \times 10^{-6}}{2} \text{ g/sec}$$

This is a small fraction of the water lost by other routes in the cases tested which, if they were of similar dimensions, would have lost about 20 g. But in a carefully made case or frame the wooden parts might contribute significantly to leakage of water vapour. The wood should therefore be coated on the outside with aluminium paint or some other material of low permeability.

Diffusion into, rather than through, wood is sometimes important. Some wood intended for joinery is dried to equilibrium at less than 50% RH. This wood may be used to make show-cases or fittings within cases. Moisturesensitive objects may be damaged if they are put into these cases before the wood has reached equilibrium with the museum environment.

Another interesting situation arises when heating fails in winter so that a sudden rise in RH occurs inside a show-case [12]. Suppose that the RH in a case has suddenly risen to 100% while the surroundings are at 50%. To prevent damage to the contents show-cases are sometimes provided with a small ventilation hole to allow the damp air to diffuse out. If the hole is small and the diffusion rate slow the concentration of water vapour within the case will remain uniform throughout its whole volume.

At time t the concentration of water vapour within the case will be:  $(c_1 - m/V)$  where  $c_1$ is the initial concentration and m the weight of water which has escaped.

$$\frac{dc}{dt} = -\frac{\mathrm{I}\,dm}{V\,dt}$$

From Fick's law:  $\frac{dc}{dt} = \frac{DA\partial c}{V \partial r}$ 

$$\frac{dc}{dt} = \frac{DA(c_0 - c)}{Vx}$$
$$\frac{dc}{c - c_0} = -\frac{DAdt}{Vx}$$
$$ln(c - c_0) = -\frac{DAt}{Vx} + B$$

Integrate:

When t = o,  $c = 2c_0$  so  $B = \ln c_0$ 

Therefore:

This re-arranges to:

$$c = c_0 \left( 1 + e^{\frac{-DAt}{V\bar{x}}} \right)$$

 $ln(c-c_0) = -\frac{DAt}{Vr} + ln c_0$ 

This confirms, as one would intuitively expect, that the change of RH with time is exponential. As the RH difference becomes smaller the rate of change diminishes.

The quantity (Vx/DA) has the dimension of time and can easily be shown to be the time that would be taken for the concentration to drop from  $c_1$  to  $c_0$  at the initial rate. It is also the time at which  $c = 1.37 c_0$  and at about this moment therefore a satisfactorily moderate RH is re-established.

If: x = 2.5 cm, A = 10 cm<sup>2</sup>,  $V = 10^{6}$  cm<sup>3</sup>, D = 0.25 cm<sup>2</sup>/sec, the time constant is  $10^{6}$ sec = twelve days.

A 3.5 cm diameter hole is apparently insufficient to safeguard a case of 1 m<sup>3</sup> capacity. In practice there is always some absorbent material in the case and other causes of exchange and so the RH falls much more rapidly (Fig. 7).

The calculation of the size of hole needed to give a time constant of, say, two hours is very much complicated by the non-uniformity of the concentration at this high rate of diffusion.

It will become apparent later that a hole is not the best way to prevent a catastrophic change in RH.

#### AIR FLOW CAUSED BY PRESSURE AND TEMPERATURE CHANGES

Air is pumped in and out of a show-case by thermal expansion and contraction. Changes of atmospheric pressure also pump air between a case and its surroundings.

The relation between pressure, volume and temperature of a gas is defined by the gas equation, which for the present purpose is best written (PV/T) = constant, where T is the absolute temperature, which is the temperature in °C plus 273.

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FIG. 7. The change in RH inside a show-case after the air within had been raised to 100% RH. The case was almost cubic, of 0.25 m<sup>3</sup> with a hole 1.5 cm diameter through the base. (O) signifies that the hole was open; (S) shut. In A, B and C the RH was raised by blowing in steam to give theoretically saturated air. In D a bowl of water was left in the case for two days and then covered with oil without disturbing the air in the case. The heavy line is the RH outside the case.

- A: RH 50 cm above the floor of the case covered by 1 kg of cellulosic material.
- B: RH 15 cm above floor.
- C: RH 50 cm above floor of empty case.
- D: RH 50 cm above floor of empty case. The different curves of C and D are due to residual absorbent material which increases the slope of C and diminishes the slope of D from the correct value.

As the temperature rises from T to  $T + \triangle T$ a volume of air  $(V \triangle T/T)$  is forced out of the case. The change in the concentration of water vapour is  $c_1(\triangle T/T)$ . When the temperature falls the concentration increases again because of the entry of outside air. The concentration after one cycle is therefore:  $c = c_1 - c_1(\triangle T/T) + c_0(\triangle T/T)$ .

The main cause of thermal displacement of air in a large museum is the daily rise and fall of temperature (Fig. 4). When the concentration difference of water vapour between inside and outside is constant the daily loss is given by:  $V(c_1-c_0)(\triangle T/T)$ . When the concentration

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gradient falls as the exchange proceeds it is easy to show that after n days:

$$c = c_0 + (c_1 - c_0) \left( \mathbf{I} - \frac{\triangle T}{T} \right)^n$$

where  $\triangle T$  is the average daily variation.

This is a discontinuous function of time but it is, like diffusion, logarithmic in character: the rate of loss of water vapour decreases as it escapes.

In the inner galleries of the Victoria and Albert Museum, which is an unusually heavily built structure, the average daily rise and fall of temperature is about 2°C. One volume of air will

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FIG. 8. Atmospheric pressure over London during the spring and early summer of 1965.

therefore leave a show-case after about 140 days.

When the temperature change is less regular the exchange of air would have to be calculated for each change.

The same arguments apply to pressure changes. These each cause a movement of air of  $V(\triangle p/p)$ .

Fig. 8 shows the pressure over London during twenty-one weeks in the spring and early summer of 1965. These changes caused a movement of air equal to half the volume of a show-case. The average  $\triangle p$  was 10 mb [13].

These calculations become very tedious when the concentration is changing, but one can assume that when one volume of air has moved out of the case, over one-third of the original air, and therefore over one-third of the original water vapour, remains inside.

The slow variation of atmospheric pressure shown in Fig. 8 is accompanied by rapid small fluctuations of pressure. Fig. 9 shows typical microbarograph traces for calm, average and disturbed conditions (the instrument was enclosed in a show-case of the most modern design !).

The difficulty in estimating the rate of exchange of air caused by these small changes is that they are so rapid that the air forced through a crack by an increase of pressure has scarcely time to diffuse away into the interior before it is removed by the diminishing pressure outside.

A very approximate figure for the rate of exchange is two volumes per year. The pressure changes are of the order of 0.1 mb. Pressure changes of up to  $\frac{1}{2}$  mb in a few minutes occasionally happen. Exceptionally, changes of up to 5 mb in about ten to twenty minutes have been recorded [14]. According to Krogh [15] the greatest rate of change that must be anticipated is 1 mb in 10 seconds.

#### CONVECTION

Convection may be an important cause of air flow in cases which are maintained at a RH higher or lower than that of their surroundings.

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FIG. 9. Rapid pressure changes recorded in a gallery of the Science Museum, London. The microbarograph is only sensitive to rapid pressure changes and does not record absolute pressure. The traces are separated vertically merely for clarity and are typical of very calm, normal, disturbed and very gusty conditions respectively.

Moist air is lighter than dry air [16]. My experiments with various RH differences between a case and its surroundings failed to reveal this effect, but the experimental error was quite large and this process may contribute to the exchange of air. The rate would, of course, depend on the position as well as the size of the cracks.

Notice that those causes of exchange of air which are most difficult to prevent—the slow changes of temperature and pressure are the least effective. Scaling of show-cases to prevent diffusion and convection and to resist, or deform under, pressure changes up to 0.5 mb would very much reduce the leakage of air and would be a major contri-

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bution to the conservation of a wide variety of art objects.

The effect of slow changes of temperature and pressure should not be resisted because they would build up large stresses on the structure of the show-case. It is better to allow exchange of air through a small hole covered with a high-efficiency dust filter, such as glass-fibre filter paper, and chemical reagents to absorb pollutants.

Pollutant filters such as active carbon, which act by absorption, will release gases into a clean atmosphere because the process is reversible. On the other hand they absorb a much wider range of pollutants than any mixture of chemicals. A combination of both



FIG. 10. Six days' growth of salt creeping up the walls of a stainless steel dish. A 15 cm arc is shown.

methods would be better. In London the most noxious pollutant is sulphur dioxide. This can be rapidly removed from a show-case by impregnating part of the cloth furnishing with magnesium carbonate [17] or some other absorber [18].

# COMPARISON OF METHODS OF MAINTAINING A HIGH RH

The high leakage rate of ordinary show-cases means that during one winter any humidifying system must supply a large amount of water to the air in the case—about 1 litre per cubic metre of air space.

It is important to know how often the humidifying apparatus will need servicing and how bulky it will be. Here is a comparison

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of the weight of water released into the atmosphere by unit volume of each kind of apparatus.

r. Cursiter's method. The water-releasing process is:

$$ZnSO_{4}.7H_{2}O \stackrel{55\%RH}{=} ZnSO_{4}.6H_{2}O + H_{2}O$$

The density of zinc sulphate heptahydrate is 1.97 and the density of the loose crystals is probably a little over half this, say 1.3. One litre would contain about 1 300 g of the salt crystals. During the transition 80 g of water would be released. At 52% RH a further transition to the pentahydrate would release another 80 g.

2. Silica gel. The bulk density of dry silica gel crystals is about 0.7. At 50% RH a change of RH of 1% causes a change of

moisture content of 0.6% of the dry weight of the gel. Therefore when 1 g of silica gel changes from equilibrium at 55% RH to 50% the weight of water given out is 0.03 g. This corresponds to 21 g/l.

3. A saturated solution of sodium bromide. The process can be summarized as: NaBr solution  $\frac{58}{20}$  NaBr.2H<sub>2</sub>O+H<sub>2</sub>O. The solubility of sodium bromide in water is 116 g per 100 g water at 20°C. The density of the saturated solution is 1.55. One litre of solution weighs 1550 g, of which 720 g are water. Some of this water is taken up by the sodium bromide during crystallization and the amount available for maintaining the RH is 430 g. In practice it is advisable to have a container twice the volume of the solution (see below), so the available water would be about 200 g/l.

From the point of view of storage capacity per unit volume of apparatus the sodium bromide solution is best.

Salt solutions suffer from two defects: They are liquid and therefore messy, and also the salt tends to crystallize on the walls of the container and by constant repetition of solution and recrystallization slowly creeps out of its container (Fig. 10).

Both these problems can be overcome by covering the tray with a membrane permeable only to water vapour. Silicone rubber provides such a membrane, and by its use the defects of the salt solution are completely overcome at the expense of a reduction in the rate of evaporation of the water. Such a membrane will probably soon be available commercially through the efforts of several research laboratories which are exploring its potentialities in the fields of skin-diving, artificial lungs, etc. Until then I present in an appendix (p. 25) my own crude method of manufacture.

Unlike the other two processes used for RH control, the sodium bromide solution increases in volume during humid conditions. At 80% RH for example  $(\delta p/p) = (n_a/n_b) = \frac{1}{5}$ . This corresponds to a concentration of about 50 g /100 g water (remembering that  $n_a = 2[\text{NaBr}]$  because of ionization). The volume of the

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solution will more than double as it attains equilibrium at this RH. This is why a container twice the volume of the saturated solution is needed.

A saturated solution is not an efficient dehumidifier because diffusion in liquids is very slow, and the surface layers rapidly become dilute on absorption of water.

#### THE RATE OF DIFFUSION OF WATER FROM THE STABILIZING MATERIAL

The absorbent material and other devices used to control and stabilize the RH in display cases must generally be placed in the base of the case. How well do they control the RH in remote parts of the case?



FIG. 11. The way in which water vapour diffuses towards the base of a show-case 1 m high. The base is maintained at 50% RH. At zero time the air in the case is uniformly at 100% RH (Adapted from Carslaw and Jaeger [20], p. 98.)

In my experiments the RH difference between the top and bottom (about 1 m apart) was within the experimental error,  $\pm 3\%$ , despite the high leakage rate and a RH difference of about 20% between inside and outside. Water vapour must therefore be transferred rapidly to all parts of the case.

Convection and diffusion are the processes by which water vapour moves within a closed space. If the leakage is such that the inside air becomes drier, moist air will rise from the surface of the stabilizing material.

Convection is less likely when the inside air is damper than the stabilizing material in the base of the case. Diffusion is then the major cause of water vapour movement. The most dangerous situation for a static RH controlling system is therefore the rise in RH caused by a sudden fall in temperature.

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The mathematics of diffusion through two different materials is very complicated when the concentration gradient is continually changing. A small error must therefore be introduced by making the simplifying assumption that the stabilizer attains equilibrium with the surrounding air much more rapidly than water vapour diffuses to it [3,19].

An analogous problem in heat flow is described in a standard textbook [20]. Fig. 11 shows the vertical movement of water vapour in a show-case of infinite horizontal extension, 1 m high, with the base covered with several layers of cotton cloth as stabilizer. Initially the whole of the inside air is at 100% RH, but the cotton cloth is in equilibrium with air at 50% RH. This situation could easily arise when there is a failure of heating in a room and the temperature falls rapidly by about 10°C. Fig. 11 shows the way in which the RH at any point above the cotton decreases with time.

When the case has one or more absorbent sides as well as base the RH at any point can be calculated approximately from published solutions of the diffusion equation [21].

In general one can assume that any diffusion process of this kind takes a time of the order of  $(l^2/D)$  to approach completion where l is the greatest distance over which diffusion takes place.

This can easily be confirmed by stringing small pieces of filter paper impregnated with cobalt chloride along a horizontal tube (to avoid convection currents). One end is closed, a small quantity of dry silica gel is put at the other end and a bung inserted. The papers will slowly turn blue in order from the end nearest the silica gel. In practice the mixing of air by diffusion is probably aided by mass movement in convection currents caused by the heating of dark areas through absorption of light and infrared radiation from lamps. Convection may also be caused by slight temperature changes due to the play of draughts around the case.

Whatever the reason, equilibrium is reestablished much more quickly than the theory of diffusion predicts (Fig. 7).

# THE EFFECTS OF TEMPERATURE CHANGES AND GRADIENTS

An objection sometimes raised to the exhibition of objects in almost closed containers is the danger of condensation on glass or object when the temperature suddenly falls.

It is obvious from the calculations and experiments already described that a very large area of ventilation hole must be provided to equal the stabilizing performance of absorbent materials. There are some situations, however, in which the presence of a large amount of stabilizer can do more harm than its absence.

If the absorbent material is continually at a higher temperature than the glass of the case there will be, at equilibrium, a relative humidity gradient between glass and absorbent because the water vapour concentration will be uniform and, as a finger drawn horizontally across Fig. 1 will show, the RH will increase towards the glass surface. Hazeu and Hueck have confirmed experimentally the validity of assuming a uniform concentration of water vapour in a container subjected to a temperature gradient [22].

For example, if the inside temperature is  $20^{\circ}$ C, the RH 55% and the temperature of the glass  $15^{\circ}$ C, the RH at the glass will be 75%. A piece of paper close to the inside of the glass would then be in danger of mould growth. Fig. 12 shows part of a print mount which cockled sufficiently to bring parts of the paper close to the glass. At these ridges occasional high humidity has encouraged mould growth.

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FIG. 12. Mould growth on the ridges of a cockled, thin paper print mount.<sup>1</sup> The RH on the ridges is greater than that in the hollows while the temperature of the paper is higher than that of the glass.

If the temperature of the glass is  $10^{\circ}$ C the RH will be 100% at its inside surface and dew will form. This process will continue until the absorbent material has lost enough water to bring the moisture content of the air below that giving 100% RH at the glass surface. At a glass temperature of  $5^{\circ}$ C, for instance, this condensation will continue until the RH around the cotton drops to 38%. This means that 1 kg of cotton or paper will give off 15 g of water. Nearly all of this will be misting up, or running down the glass.

This process does no damage to the contents of the case as long as they are remote from the glass and not splashed by dripping water. In fact the contents will be more subect to damage by dehydration than by soaking. The danger of drips from the top of a glazed case can be minimized by fixing close beneath the glass a sheet of transparent absorbent material such as cellophane.

This distillation process should be rare in museums but it is common in glazed outdoor notices.

One occasionally comes across framed prints and water colours where circumstances have combined to cause damage by water. The ratio of the weight of absorbent material to the volume of the container is high and the distance between paper and glass is small. The paper may be mounted in such a way that changes of RH will cause it to cockle and press against the glass. If now the temperature of the glass falls below the dew point the distillation process will proceed vigorously because of the high temperature gradient. The condensed water will be absorbed by the paper where it touches the glass and will pass through the paper by capillary action until, at a point remote from the glass, it evaporates again. At the limit of water movement a brown line appears—a mysterious but very noticeable phenomenon [23].

More commonly the water falls to the bottom and is absorbed by the mount which shows an irregular brown line where the water evaporated during the last episode of this kind.

It is interesting to note that a similar distillation process is used to provide water in arid regions. Salt, or brackish water, is led into shallow channels of some black material. The channel is covered by a cloche of glass or polythene film. Sunlight heats the channel and the water evaporates. The vapour condenses on the glass which does not absorb solar

<sup>1</sup>The mould growth is, in fact, in the hollows of the print mount and therefore does not illustrate the effect described-



FIG. 13. The effect of using a saturated solution of sodium bromide to raise the RH in a show-case. The heavy line is the RH in the gallery. The upper thin line is the RH in a case containing absorbent material and a tray of saturated solution of area 500 cm<sup>2</sup>, under a false floor in a case of 1.25 m<sup>3</sup>. The lower line is the RH in a case containing absorbent material only. Both cases were initially conditioned to 56% RH. For the sake of clarity the temperature record is omitted. It varied between 16° and 19°C.

energy and so remains fairly cool. The distilled water dribbles into gutters and is collected [24]. The process can even be performed with moist materials such as bruised leaves.

The radiant energy from tungsten lamps in well-designed installations need not cause a temperature difference of more than 2°C between any part of a show-case and its surroundings. Fluorescent lamps cause an even smaller rise in temperature. Lighting probably aids air circulation by generating convection currents above dark surfaces.

If direct sunlight is allowed to shine on a case containing absorbent material the temperature and absolute humidity will rise (the RH remaining almost constant) as in a glasshouse. During the evening, cooling may cause a rise in RH which the absorbent material cannot correct quickly enough to prevent dew formation. This phenomenon has generally been prevented by boring holes in the case. These allow the heated moist air to dissipate by convection during the period of illumin-

by convection during the period of illumination.

Holes in show-cases are therefore effective deterrents against dew formation during a rapid fall of temperature following irradiation by sunlight, but are rather ineffective against dew formation through a slow fall of temperature in a case without absorbent material. This apparently paradoxical result is a consequence of the ineffectiveness of diffusion through holes compared with air flow by convection.

It is now generally accepted that no art object should be exposed to direct sunlight. There should therefore be no need for holes to aid convection.

Obviously it is sensible to choose the lowest acceptable RH for show-cases subject to sudden changes of temperature. For this reason I have chosen sodium bromide solution as the best RH-governing material for show-cases containing wooden objects in countries with low winter temperatures. The RH should not fall below 50% in a moderately well-scaled case (Fig. 13). On the other hand a sudden fall of temperature of over 10°C must occur before dew begins to form.

# SUMMARY AND CONCLUSIONS

A stable relative humidity is guaranteed by using an abundance of unvarnished wood, paper and cotton cloth in the construction and furnishing of display cases and picture frames. These materials stabilize the RH very effec-

tively except under the exceptional circumstances of a rapid temperature change of over  $10^{\circ}$ C or a continuous temperature difference of the same magnitude between different parts of the case.

Seasonal variations of RH will affect the atmosphere within cases containing such materials because air is continually exchanged between a case and its environment.

There are several causes of this exchange:



FIG. 14. One of the experimental show-cases. Some boards and their cloth cover have been removed to show the saturated salt solution creeping out of its container. The floor is covered with aluminium foil.

diffusion, convection, flow caused by pressure and temperature changes. The last two processes cause a slow exchange of the order of two or three volumes per year. Show-cases of conventional construction show a rate of exchange of about one volume per day. This leakage presumably occurs through the first two processes. Such efficient ventilation is unnecessary and allows gaseous pollutants and some dust to enter the case. The conservation of the contents would be improved by building cases to resist, or deform under, pressure changes of up to 0.5 mb. Small holes covered with filters against dust and pollutants would allow slow equalization of pressure. In this way the exchange of air would be limited to less than five volumes per year.

The conservation of wooden material in rooms which are heated but not air-conditioned often demands an artificially raised RH in individual show-cases.

A saturated solution of sodium bromide may be used to maintain the RH within a case higher than that outside. The salt solution must be covered by a semi-permeable membrane to allow the passage of water vapour but prevent the salt from creeping out of its container. The solution is much less effective in reducing the RH, so this method must be used in combination with a large amount of absorbent material. A saturated solution of surface area 1 000 cm<sup>2</sup> for every cubic metre of air space will maintain the RH above 50% without the need for forced air circulation, even in a case with a leakage of one volume per day. The apparatus may even be concealed beneath a porous false floor (Fig. 14).

The manufacture of the membrane as described in the appendix is rather tedious, but I have written this article anticipating that a suitable membrane will soon be available commercially.

# STUDIES IN CONSERVATION

# APPENDIX

HOW TO MAKE A SILICONE-RUBBER MEMBRANE



1. Take two sheets of uncoated cellophane of about 0.05 mm. thickness. Two strips of the same material are used as spacers.



3. Turn back the top sheet and squeeze out a worm of Silastoseal A (Midland 4. Use a stiff metal Silicones Ltd., Barry, Glamorgan, U.K. a bevelled edge +



6. Soak in water for several hours

7. Peel off top sheet & spacers.

- 8. Lay the bottom sheet on glass and fix it down with gummed paper.
- 9. Carefully sponge away surplus water from the surface of the rubber.

10. Take a piece of Nylon or Terylene curtain netting and lay it on a layer of Silastoseal A freshly spread on some disposable surface. Rub gently to ensure even coating of yarns. Lift the net and place it carefully on the rubber. Rub with the edge of a microscope slide or a similar instrument to ensure contact all over.

11. Allow to set for 2 days.



2. Lay the *cellophane* on a very clean plate-glass table. Use adhesive to fix down one edge of each sheet and the end of each spacing strip.

a bevelled edge to squeeze out the silicone

between the sheets.

 Pull off cellophane to reveal complete silicone-rubber membrane.

The membrane is attached to the tray of saturated salt solution by coating the edge of the glass tray with Silastoseal A and laying the membrane with the smooth side against the glass. Press down all round to ensure a good scal.

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FIG. 16. Bowl of saturated sodium bromide solution covered with the silicone rubber membrane. The curvature of the membrane is caused by osmosis (see text).

# Test for continuity of the film

The silicone rubber is pressurized gently by putting the tray in a dry environment. In a day or two the membrane will bulge upwards if it has no holes (Fig. 16). This is because the water in the air inside the covered dish reduces the concentrations of oxygen and nitrogen below those in the dry air outside. Osmosis will occur: oxygen and nitrogen diffuse through the membrane to increase the internal pressure until the concentration of these gases is the same inside as outside.

# Permeability of the film

Films made in this way cannot be expected to show a uniform water-vapour permeability. I have tested several films without net rein-

STUDIES IN CONSERVATION

forcement. Using an RH outside of 32%, and 58% within, the average permeability was 80 g/day/m<sup>2</sup>. Assuming that the diffusion rate is proportional to the RH difference, the rate of movement of water vapour in still air is  $3 \text{ g/day/m^2/1\%}$  RH. Some films showed a much higher permeability: up to 10 g/day/m<sup>2</sup>/1% RH. The rate of evaporation from an uncovered dish in still air is two to five times as fast. The net reinforcement will further reduce the permeability.

When the solution has dried up it may be regenerated in two ways. If a filling hole has been made in the tray it is simply necessary to add water. If there is no hole the tray may be left in a box with the correct amount of water in it. Over a period of several weeks the water will diffuse into the tray containing the salt. For very small display cases it is possible to make a sachet entirely of the rubber membrane, using Silastoseal A as an adhesive. The saturated solution, or simply dry crystals, may be inserted before the last seam is sealed.

It is important that some solid crystals should always be present in the dish of solution because supersaturation occurs easily in sodium bromide solutions which are protected from dust.

#### Experimental details

The RH data were obtained from conventional hair hygrographs. These are not very accurate. Actual values of RH are likely to have been within 2% of the results shown on the various graphs except where the indicated RH is very high. In this case the instrument is calibrated to read low.

The data on the weekly charts were compressed in the time scale by using a photographic device. This is described in detail below because it was useful for showing up slow environmental changes recorded over many yards of weekly charts.

The thermohygrograph charts are joined together to form a continuous strip. This strip is driven over a narrow slit. Underneath the slit a strip of photographic film is driven at a much slower speed. In this way a bunchedup reproduction of the original trace is recorded on the film (Figs 17 and 18).

#### ACKNOWLEDGEMENTS

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Tim Padfield

Department of Earth Sciences, The University of Leeds

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# LA RÉGLEMENTATION DE L'HUMIDITÉ RELA-TIVE ET DE LA POLLUTION ATMOSPHÉRIQUE DANS LES VITRINES ET LES CADRES DE TABLEAUX

Les matériaux absorbants, comme le bois, le papier et le coton, stabilisent l'atmosphère des vitrines contre les changements de l'humidité relative provoqués par des variations de température et des échanges d'air avec l'atmosphère ambiante.

Plusieurs processus d'échange se produisent entre l'air de la vitrine et l'air extérieur: la diffusion à travers des matériaux de construction poreux, les courants d'air provoqués par la température et les changements de pression et ceux provoqués par la convection dans une

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vitrine où l'humidité relative diffère de celle de son milieu ambiant. L'air se renouvelle environ une fois par jour dans le vitrines faites selon les techniques d'ébénisterie conventionnelles. Le taux d'échange peut être réduit à moins de cinq volumes par an en scellant la vitrine, afin qu'il ne reste qu'un petit trou pour égaliser la pression. Un filtre à poussière et à anhydride sulfureux peut alors être installé pour maintenir la pureté de l'atmosphère à l'intérieur.

Dans les chambres chauffées sans climatisation, l'humidité relative peut baisser dangcreusement en hiver. On décrit une méthode astatique de réglementation de l'humidité relative. Il s'agit d'une solution saturée de bromure de sodium, recouverte d'une membrane de caoutchoue à la silicose.

# IL CONTROLLO DEL L'UMIDITÀ' RELATIVA E DELL'INQUINAMENTO DELL'ARIA NELLE BACHECHE E NELLE CORNICI PER QUADRI

I materiali assorbenti come il legno, la carta e il cotone stabilizzano l'atmosfera nelle bacheche contro i cambiamenti nell'umidità relativa provocata dalle variazioni di temperatura e dal ricambio dell'aria con l'ambiente.

Si verificarono vari processi di ricambio tra l'aria nella bacheca e quella esterna: la diffusione attraverso i materiali porosi di costruzione, il flusso d'aria provocato dai cambiamenti di temperatura e di pressione e il flusso d'aria per convenzione in una bacheca la cui umidità relativa differisca da quella dell'ambiente.

Nelle bacheche costruite secondo le tradizionali tecniche della falegnameria si ha un ricambio d'aria circa una volta al giorno. Il tasso di ricambio può venire ridotto a meno di cinque volumi all'anno ermetizzando una bacheca e lasciando solo un forellino per la compensazione della pressione. Per conservare un'atmosfera pura all'interno si può allora montare un filtro contro la polvere e l'anidride solforosa.

<sup>°</sup> Nelle sale riscaldate senza il condizionamento dell'aria, l'umidità relativa può scendere a punte pericolose d'inverno. Si descrive il metodo astatico per il controllo dell'umidità relativa. Si tratta di una soluzione saturata di bromuro di sodio coperta da una membrana di gomma siliconica.

# KONTROLLE DER RELATIVEN LUFTFEUCH-TIGKEIT UND DER LUFTVERUNREINIGUNG IN AUSSTELLUNGSKÄSTEN UND BILDER-RAHMEN

Absorbierende Materialien wie Holz, Papier und Baumwolle stabilisieren die Atmosphäre von Schaukästen gegen Schwankungen der relativen Feuchtigkeit, verursacht durch Temperaturschwankungen und durch den Luftaustausch mit der Umgebung.

Es spielen sich zwischen der Aussenluft und der Luft in dem Schaukasten verschiedene Austauschprozesse ab: Diffusion durch poröss Konstruktionsmaterialien, Luftaustausch verursacht durch Temperatur- und Druckschwankungen und durch Konvektion in einem Schaukasten dessen relative Feuchtigkeit von der seiner Umgebung verschieden ist.

In einer, mittels der gebräuchlichen Tischlermethoden hergestellten Ausstellungsvitrine findet ein vollständiger Luftaustausch ungefähr einmal im Tage statt. Wenn man die Vitrine versiegelt, kann die Austauschgeschwindigkeit auf weniger als fünf Volumen pro Jahr herabgesetzt werden. Jedoch muss man ein kleines Löchlein anbringen, damit sich die Druckunterschiede ausgleichen können. Obendrein kann man dann auch noch ein Staub- und Schwefeldioxydfilter einbauen, um die Reinheit der Luft innerhalb des Schaukastens sicherzustellen.

In geheizten Räumen ohne Klimaanlage kann die relative Feuchtigkeit der Luft im Winter auf eine gefährlich niedrige Stufe absinken. Es werden astatische Kontrollmethoden für die relative Feuchtigkeit beschrieben. Dieses bestehen aus einer gesättigten Lösung von Natriumbromid, die mit einer Silikongummimembran abgedeckt ist.

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