Introduction:

In European and North American collections, it is common practice to store objects in protective containers. These containers are meant to protect objects against mechanical damage and to prevent dust from accumulating. Moreover, they should also stabilize external temperature and humidity fluctuations. The use of protective containers dates back to Antiquity. Contemporary sources reveal that scrolls were kept in cylindrical containers made of wood or ivory already in ancient Egypt, Greece and the Roman Empire (Albrecht-Kunszeri et al., 2001). Protective containers have also been used in Eastern Asia for a long time, a noteworthy example being Japanese boxes made of Paulownia wood (called INRO boxes) which provide a particularly effective protection against external relative humidity fluctuations mainly because of its hygroscopic characteristics (Fig. 1, Miura, 1977). In addition, various techniques were used to stabilize the microclimate inside the boxes, for instance the addition of hygroscopic materials such as straw (Wills, 1977). Wills reports that these wooden boxes can even withstand flooding. The wood swells in water, thus closing the boxes tightly which in result made them float on the water. The enclosed objects remain unharmed (Wills, 1977). Nowadays, protective enclosures are mostly made of archival quality cardboard (either solid or corrugated) which must meet the standards of ISO16245-2009 or DIN/ISO 9706-2009. Generally, boxes made of corrugated cardboard are not designed to withstand catastrophes caused by fire, water or the collapse of a building. However, with appropriate construction and utilization of the correct materials i.e. cardboard of at least 300 g/m² and a water-resistant coating of the inside as well as a reinforced outer surface they can protect against a limited amount of water leakage in storage depots. They do so by absorbing liquid water, thereby becoming less solid (Fig. 2), but nonetheless preventing the water from penetrating into the enclosed object.

Fig. 1: The interior of a box of a box made of Paulownia wood (an INRO box) used to store hanging scrolls; it is supplemented by an outer box, which is often lacquered (a daisashi box). This type of box construction offers efficient protection against water damage (Miura, 1977).

Fig. 2: A corrugated cardboard enclosure without water-resistant coating damaged by local water leaks. The stability of the box was dramatically reduced due to the absorption of water. The collection material enclosed in the box remained unaffected because liquid water did not penetrate the box, the moisture content of the objects, however, increased.
Table 1: Box materials that were investigated, product names, thickness and grammage.

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Effect of climatic fluctuations on paper: Until today the impact of external environmental fluctuations on protective enclosures has hardly been investigated; this pertains to both temperature and humidity fluctuations. Bogaard and Whitmore (2002) dealt with the effect of climate fluctuations on the stability of paper. They exposed cotton filter papers (Whatman # 42) at a temperature of 23°C in a chamber and a relative humidity that alternated between 25% and 75% every 2 hrs. over a period of 42 weeks. This led to a reduction of the polymerization degree of the cellulose by one third after only 10 weeks, and by one half after 30 weeks, in addition to a significant reduction of the paper strength. The degradation of cellulose caused by humidity fluctuations was attributed to the hydrolytic splitting of the cellulose molecules. The experimental design did not allow concrete definitions of a climate fluctuation range that can be regarded as safe for paper based objects. However, it could clearly be shown that cellulose undergoes hydrolysis caused by repeated absorption and desorption of humidity over a longer period. J. Hofenk de Graaf (1994) addressed the problem of browning that can be observed on drawings and prints mounted on mats. The author was able to attribute these changes to thermally induced absorption and desorption of water by the paper carrier in the window mat during storage. Both examples show the importance of the material characteristics that storage enclosures should possess when it comes to regulating external climate fluctuations. The work of Hofenk de Graaf (1997) emphasises the particular importance of maintaining a constant temperature for long-term stability of collection materials stored in a protective packaging.

Experimental set-up – Materials: The microclimate in boxes constructed from various materials was measured under the influence of external fluctuations in temperature and relative humidity. The internal measurements of the boxes (~360 x 220 x 85 mm) correspond to a volume of ~6,730 cm³. The standardized box is constructed as two-piece box with single thickness for base and lid. Both base and lid have a double thickness on either side, so that, when the box is closed, all sides have a triple thickness, the variety of materials used for constructing the boxes is listed in table 1; all materials were supplied by KLUG-CONSERVATION, who also manufactured the boxes. Corrugated cardboard E-flute and B-flute are three-layered board materials, in which a corrugated layer is laminated on both sides with thin cardboard.
Depending on the composition of the materials, they conform to the requirements for durable papers DIN ISO 9706-1995. The two corrugated cardboards differ from one another in the thickness of the corrugated wave, which, for the B-flute board (3 mm), is almost double the thickness of that of the E-flute board (1.7 mm) Figures. 3a, 3b, 3c. “Solid grey board” is a type of cardboard made from rags, chemical wood pulp and recycled paper, and does not conform to the norms for age-resistant materials. Twinwall Polypropylene sheet is a non-cellulose-based box material that does not conform to current ISO16245-2009 or DIN ISO 9706-2009 standards. All measurements were taken in a climate chamber (Heraeus-Vötsch, type HC 0020) (Fig. 4), where cycling fluctuations of temperature and humidity can be programmed. The temperature and relative humidity within the boxes was measured using Driessen and Kern Sensmitter SHT 75 micro sensor data loggers (Fig. 5), which record data at two minute intervals. The accuracy of the instruments was ± 2% RH and ± 0.5˚C. Some boxes were filled with stacks of Novo® paper (90 gsm). Novo® paper is an acidic test paper produced by KLUG-CONSERVATION. It is composed of 50 – 65 % ground wood pulp, 25 – 35 % bleached sulphate pulp and 12 – 15 % china clay as a filler. The paper has a pH of 4.5 which is achieved by adding aluminium sulphate to the sizing. Novo® paper was cut in sheets and piled to stacks measuring 200 x 350 x 80 mm (5600 cm³). In order to position a micro-sensor in the centre of each paper stack without contact, a space of exactly the sensor’s dimensions including space for its cable was allowed in the centre of each box. The stack was made up of equal numbers of whole pieces of paper both above and below the sensor. All boxes (both empty and filled with a stack of Novo® paper) were opened and pre-conditioned in a climate chamber at 50 % RH and 23 °C for 24 hours according to DIN ISO EN 20 187 prior to the experiment.

Fig. 4: The climate chamber was big enough to condition and subsequently treat three boxes simultaneously. During the treatment the boxes provided with climate sensors were placed on an open aluminium frame with a distance of 17 cm from each other. Reference data was collected by a humidity and temperature sensor (arrow) inside the climate chamber. (red arrow).

Fig. 5: Mounting a temperature and humidity sensor in an empty box made of E-flute. The sensor was positioned in the centre of the box using a perforated aluminium plate that was attached with Filmoplast™ PP0 (Neschen AG) to the base of the container.
Results – empty boxes:

The levels of relative humidity in the climate chamber fluctuated from 50% – 77% – 52% over a period of 12 hours. These fluctuations reached the interior of each box with a delay that depended on the kind of material used for the box as well as for its lining (table 1). Inside boxes made of corrugated cardboard (with or without paper laminating), of cardboard or of "grey cardboard", an average RH of 65% established itself within less than 20 minutes when relative humidity was increasing. The adjustment occurred more slowly when the relative humidity in the climate chamber was decreasing; 65% RH inside the boxes was only attained after an hour or an hour and a half. The measuring points are well lined up and are represented by the curve (2) illustrated in (Fig. 6). As for the boxes laminated with textiles (acrylic coated book cloth qualities, i.e. English Buckram™ or Durabel™, see table 1), the attenuation of external fluctuations in humidity was significantly higher, as the flatter curve and the 3% – 5% lower humidity equilibrium show (Fig. 6, curves 3 and 4). This can be explained by the fact that the impregnated, relatively thick bookbinding textiles used in these boxes are less permeable to humidity.

The behaviour of the Twinwall Polypropylene box did not conform to our requirements. The same relative humidity as in the surrounding climate chamber was measured inside the box for the entire duration of the experiment (Fig. 6, curve 5). The construction of the Twinwall Polypropylene box might have allowed levels of relative humidity to equalize through openings in the plug connections.

Fig. 6: Transfer of the relative humidity over a 12 hour cycle fluctuating between 50% – 77% – 52% RH at a constant room temperature of 23°C:

1 (dotted black line) RH in the climate chamber
2 (dark blue) RH in the E-flute box
3 (blue) RH in E-flute box, covered with "English Buckram" cloth
4 (light blue) RH in E-flute box covered with "Durabel" cloth
5 (yellow) RH in a box made of Twinwall Polypropylene material
Water movement in the paper stack:

When observing the interior climate of protective enclosures, it is important to observe the behaviour of paper stacks. Paper is a hygroscopic material, absorbing and desorbing water depending on the relative humidity of the surrounding atmosphere (Fig. 7). In a stack of paper, these absorption and desorption processes take place spontaneously only at the sides of a stack and on the uppermost sheet of paper that is exposed to the atmosphere (Fig. 8, 9). The equalization of humidity in the interior of the stack takes place via the slow process of diffusion, a mechanism that requires days or even weeks, depending on the permeability of the paper and the size of the stack. This equilibrium cannot be attained during short cyclical fluctuations (Fig. 10).

A paper stack, 8 cm high, stacked up with A4 sheets 80 gsm, weighs approximately 4 kg. At 20 °C and with a relative humidity of 50 %, paper contains on an average approximately 6% water. If under the above mentioned conditions, such a stack of paper were to be stored, it would contain 240 g of water.

Fig. 7: Absorption and desorption isotherms of water vapour for cotton cellulose at 24.6 °C (according to Nimz 1988).

Fig. 8: A moist stack of paper releases the absorbed water into the more dry surrounding atmosphere through the top most page and the sides of the stack until equilibrium is reached between the relative humidity of the air and the water content of the paper. The release at the interface between paper and air occurs quickly (large arrows), the migration of the water into the interior of the stack occurs by diffusion and occurs slowly (small arrows).

Fig. 9: Exposed to a damp atmosphere, a paper stack absorbs water at the interface between paper and air until an equilibrium is reached between the relative humidity of the air and the water content of the paper stack. Sorption of water at the boundary layer between air and paper happens quickly (large arrows), whereas the migration of the sorbed water into the centre of the stack occurs by diffusion and occurs slowly (small arrows).

Fig. 10: Effect of external fluctuations of the relative humidity (RH) between 40 % and 80 % in a 24 hour cycle (1) on the RH in the pore volume of a paper stack. The top sheet displayed a gradient that is almost the same as the humidity fluctuations of the surrounding atmosphere (2). At a depth of 1 mm, the cyclical fluctuation of the RH is already reduced by 20 % (3). This is approximately half the RH fluctuation in the pores of the top page. The grey line (4) indicates that the RH in the pore volume of the paper 3 mm below the top page is almost constant (after Patfield, 2009).
A certain amount of this stored water must be released if the relative humidity of the surrounding environment decreased, until an equilibrium between the humidity of the environment and the water absorbed by the paper is established. If the humidity levels in the surrounding environment increases, a corresponding amount of moisture will be taken up through the sides of the stack and through the top-most page. By changing the temperature, changes in the water content of the paper can be induced, because the absorbed water cannot be retained in the same quantity at higher temperatures and therefore evaporates. Although the water content of paper does not primarily depend on temperature, one can assume that, with a temperature increase of 10 °C, the mass of water absorbed by the paper will spontaneously be reduced by approximately 1 %. This means that 2.4 g of water must be released into the surrounding atmosphere through the sides of the stack and the top sheet. The cumulated "stress" of this water migration weighs on the top-most sheet of paper and the sides of the stack. This is the reason why documents and books stored without protective enclosures display significantly greater signs of ageing which manifest themselves as discolorations and brittleness along the edges and in case of documents with iron gall ink inscriptions in the migration of inks (Fig. 11a and 11b). In the case of individual sheets of paper, absorption and desorption occurs quickly. Equilibrium with the surrounding atmosphere is attained within a matter of minutes, because the area exposed to the atmosphere is large in comparison to the paper volume and slow diffusion processes are limited. External humidity fluctuations and/or changes in temperature therefore lead to a rapid uptake or release of water and the equilibrium of the paper’s humidity content with the surrounding atmosphere is reached within few minutes.

Fig. 11a: Page 1 of the symphonic poem “Festklaenge” by Franz Liszt, c. 1854, 363 x 271 mm, recto. The manuscript was stored for a long time without any protective covering. The first page of the manuscript was exposed directly to the atmosphere. It displays extensive browning, deterioration at the edges, and the iron gall ink has migrated from the verso side of the page (red box). Klassik Stiftung Weimar, Goethe- und Schiller-Archive, Inv. Nr. GSA 60/A 7a. © Klassik Stiftung Weimar

Fig. 11b: Verso side of the page shown in Figure 11a; the browning cannot be discerned, the migration of the iron gall ink to the recto page is caused by the musical notation surrounded by the red box. Klassik Stiftung Weimar, Goethe- und Schiller-Archive, Inv. Nr. GSA 60/A 7a. © Klassik Stiftung Weimar
Results – filled boxes:

Fig. 12: Paper stack in a corrugated cardboard two-piece box during a rise in external temperature. The box barely minimizes the temperature rise, and the heat is transferred to the interior of the box almost without delay. During temperature increase, the paper releases the water it had absorbed. This evaporates through the top sheet and the sides of the stack into the air inside the box (large arrows), but remains trapped inside the box. The relative humidity in the air space inside the box therefore increases. The migration of water out from the centre of the stack to the surfaces occurs by diffusion and is slow (small arrows).

Fig. 13: Temperature transfer influenced by the cyclical temperature fluctuations between 23°C and 58°C in four-hour cycles:

1 (rot) temperature in test room
2 (dotted red) filled boxes, sensor positioned at the side of the stack
3 (dashed red) filled boxes, sensor positioned in the centre of the stack

The data are comparable for the various kinds of box materials; therefore only one line is represented for each.

A protective enclosure separates a stack of paper and the space that immediately surrounds it from its environment. Thus, a microclimate is created in the box which can differ significantly from the surrounding macroclimate. If the temperature increases, the paper must release a part of the absorbed water into its immediate environment, firstly because water can no longer be retained in the same quantity in the paper matrix; secondly, because the relative humidity content of the air in the box is lowered by a temperature increase which causes perturbations in the relative humidity equilibrium between the air and the paper. Water evaporates through the cover sheet and the sides of the paper stack, but remains trapped in the air inside the box (Fig. 12). In the paper stack, water evaporates into the very small air space between the pages, so that the relative humidity in these areas can increase significantly. The equilibrium inside the stack is established by diffusion processes and is therefore slow. The interpretation of the climate measurements taken inside the box filled with paper is made more complex by the fact that desorption of water from the paper requires heat, whereas absorption of water releases heat.

This is inverse to the temperature cycle impinging on the stack from the outside – water is desorbed from the paper with an increase in temperature, and is absorbed again by a temperature decrease, which counteracts the effects of temperature fluctuations of the surrounding.

Figure 13 represents the temperature transfer to a stack of paper, which was exposed to temperature fluctuations between 23°C and 58°C in four-hour cycles, enclosed in a box made from E-flute. The temperature transfer to the interior of the stack is temporally delayed due to the above explained effect. The temperature in the box is an average of 5°C lower than the outside temperature which is never reached inside (curve 3). Only at the sides of the stack (curve 2) is the temperature transfer significantly faster and comparable to the data taken in empty containers. Clearly, the box and the stack stored inside it must be interpreted as a closed system in this context.
The temperature insulation is also evident if one considers the changes in the relative humidity in the centre of the paper stack with and without a protective container, which is significantly lower if the stack is contained in a box (Fig. 14). The changes in relative humidity induced by temperature changes in the centre of a stack of paper enclosed by a protective cover are shown in Fig. 15. Boxes made of E-flute and Twinwall Polypropylene were subjected to temperature fluctuations between 23 °C and 58 °C in a cycle of four hours. For technical reasons, the relative humidity in the climate chamber could not be kept constant. The relative humidity therefore sinks when the temperature rises and rises again when the temperature drops, as the dotted black line indicates. The development of the relative humidity in the centre of the enclosed stack of paper is inverse, because the paper releases moisture when the temperature rises and absorbs it again from the atmosphere when the temperature falls.

The resulting humidity curves allow conclusions about the humidity-moderating effects of various materials. In particular, curve 5 (yellow), representing humidity levels in a box made of Twinwall Polypropylene, rises during the cooling phase, thus suggesting that this material provides no humidity-moderating effects with respect to the surrounding atmosphere in the climate chamber; the significant increase of relative humidity in the interior of the box during the cooling phase cannot be explained otherwise.

Fig. 14: Changes of the relative humidity (RH) in an empty (2) and a filled box (3), influenced by cyclical temperature fluctuations between 23 °C and 58 °C in four-hour cycles:
1 (red) temperature
2 (dark blue) empty box, E-flute
3 (light blue) filled box, E-flute
Sensor position: empty box: middle of the box, filled box: centre of the stack.

Fig. 15: Changes of relative humidity caused by external cyclic temperature fluctuations between 23 °C and 58 °C in four-hour cycles:
1 (red line) temperature
2 (dotted black line) climate chamber
3 (light blue line) E-flute/English Buckram box, empty
4 (dark blue line) E-flute/English Buckram, filled
5 (yellow line) Twinwall Polypropylene material box, filled
Sensor position: empty box: middle of the box filled box: between box wall and side of stack.
Summary:
To summarize the outcome of this study it can be stated that boxes made of corrugated cardboard or cardboard moderate external fluctuations in relative humidity. However, protective enclosures made of Twinwall Polypropylene material do not counteract humidity fluctuations of the surrounding atmosphere and changes are transferred to the interior of the box without delay. Adaptations of climatic conditions inside protective containers to cyclic temperature fluctuations between 23 °C and 58 °C in the surrounding atmosphere are not influenced significantly by the material of the box. In the case of boxes filled with paper, the enclosed stack of paper delays the temperature transfer. Constructing protective boxes from cellulose-based materials rather than Twinwall Polypropylene material thus appears to be the better choice in respect to climatic stability. As for climate systems in collection depots, it can be concluded that maintaining a constant temperature is of greater importance than the stability of the relative humidity in the ambient air.

References:


Acknowledgement:

This project was generously supported by the Landesstiftung Baden-Württemberg. The authors wish to express their gratitude to Alana King and Sigrid Eyb-Green for the substantial help in translating and editing the manuscript.

Materials and suppliers:

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