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1. INTRODUCTION
Restoration is an interdisciplinary field that includes art, science and craftsmanship. This article focuses on engineering of the medium-size machinery used in paper restoration. The use of each apparatus is demonstrated in case studies.

2. CALCIUM CARBONATE FLOW BED SOLUBILIZER
Under acidic conditions the acetal link in cellulose is not stable, resulting in degradation of the polymeric structure. Acidic papers are deacidified by washing or spraying them with a solution of an alkaline earth metal salt, usually aqueous solutions of calcium and magnesium hydrogen carbonate or methanol solutions of methyl magnesium carbonate: Special equipment is used to prepare these solutions. Metal ion concentrations of different aqueous solutions are presented in Fig. 1 and discussed later.

2.1 State of the art
The methanol solution of methyl magnesium carbonate has the highest ion concentration of an alkaline earth metal compound. It has approximately 2900 mg Mg ions per liter (119.3 mmol Mg ions per liter). This concentration is never reached in aqueous solutions of alkaline earth metal hydrogen carbonates. The left side of Fig. 1 lists the maximum equilibrium concentrations of magnesium and calcium ions that have been found in water saturated with carbon dioxide at 0.1 and 1 MPa partial pressure and with a sediment of magnesium or calcium carbonate.

Despite the lower ion concentration, we prefer to work with aqueous solutions, as they are more “natural”, or at least closer to traditional methods of paper making and working with paper, in which water is central. In addition, methyl magnesium carbonate solution is strongly alkaline and may harm inks and dyes at a high concentration. Inks and dyes are usually slightly acidic. The pH of an aqueous solution of alkaline earth carbonate is about 5.7 (slightly acidic), if it is saturated with carbon dioxide. After the paper dries and the carbonic acid decomposes into carbon dioxide and water, the paper becomes quite alkaline.
Because water is used in nearly any restoration process, aqueous deacidification can easily be integrated. A methanol bath, in contrast, introduces a new poisonous chemical. In a workshop that restores unique and valuable items, and not merely huge quantities of bound books, the methanol methyl magnesium carbonate solution should only be used when the ink, colour or other elements must not contact water.4

An aqueous deacidification solution can be prepared either by mixing a slurry of hydroxicarbonate powder and water saturated with carbon dioxide in a pressure vessel,5,6 or by pumping carbon dioxide-saturated water through a bed of solid alkaline earth metal carbonate.7,8 The results are presented in the right side of Fig.1.

A magnesium hydroxide carbonate suspension mixed overnight under 0.3 MPa of carbon dioxide produces 1040 mg magnesium ions per liter (42.8 mmol/liter). This is not a thermodynamic equilibrium value. The pH of the fresh solution is about 6.5, but it rises to 8 or 9 as the carbon dioxide evaporates. Passing water saturated with carbon dioxide through solid pieces of calcium carbonate does not produce a saturated solution. The amount of calcium carbonate dissolved depends on the amount of carbon dioxide bubbling through the solution and on time. Fig.2 shows the increase in calcium ion content in relation to time, which is proportional to the number of passes through the bed of marble granulate for the apparatus described in section 2.2.

Magnesium carbonated is preferable to calcium carbonate for paper deacidification.5,6 If granulated minerals such as magnesite or dolomite are available they may be used instead of marble. Higher concentrations of aqueous solution result in a higher alkaline reserve in the paper. The more concentrated solution from the pressure vessel might therefore be preferable to the solution from the flow bed solubilizer, but installing the pressure vessel costs at least six times as much as installing a flow bed solubilizer. Pressure vessels are subject to administrative regulations9; in a small workshop these regulations might be neglected, resulting in danger for the machine and the staff. In a small workshop the flow bed solubilizer is more convenient to install and use than a pressurized mixing vessel.
2.2 Design of the calcium carbonate flow bed solubilizer

The flow bed solubilizer is built from a commercially available kit of glass parts (Fig.3). The core of the apparatus is the flow bed solubilizer, a glass tube 115 cm long and 7 cm wide. The bottom is closed by porous ceramic on which ground marble is poured. The size of the marble particles should be 0.5 to 2 mm. The height of this bed is about 15 cm. The liquid is pumped through the bed; the flow is regulated at 400 l/h. When the pump starts the marble bed begins to float and extends 180 mm high. The gas bubbles from the carbon dioxide intake further improve the floating effect; the result is intensive contact between solid, gas and liquid. The continuous flow of carbon dioxide is between 4.0 and 6.0 normlitres (litres at standard pressure and temperature) per hour (Nl/h). This small amount of carbon dioxide makes an internal carbon dioxide compression ring superfluous. If less carbon dioxide is taken, the saturation process takes much too long (Fig.2). The velocity of the liquid in the glass tube is calculated at 30 mm/s, which is sufficient to prevent marble particles from washing out. Gas and liquid separate at the top of the tube. The gas is exhausted via the storage tank and the liquid goes into the storage tank. After about 3 h, the pump is stopped and the calcium hydrogen carbonate water can be stored for a maximum of one week before use.
The storage tank has a capacity of 35 litres. The liquid content of the whole apparatus is about 40 litres. The entire volume passes over the marble bed every 6 min. Fig. 2 presents the concentration of calcium ions in the water in relation to the number of passes through the marble bed. The content increases proportionally to the number of passes. After 3 hours a concentration of 260 mg Ca ions per liter (6.5 mmol/l) is reached.

Alkaline earth metal concentration is analysed by flame emission spectroscopy.

The apparatus is filled with tap water only at the beginning. If water is taken continuously from the storage tank during the saturation process the calcium ion content is not sufficient.

### 2.3 Components
Magnetic laboratory pump KRP 30 (Labotec, Wiesbaden, FRG)
Glass vessels and tubes (Quickfit, Wiesbaden, FRG)
Braided tubing
Frame made from Dexion steel parts (Dexion, Hemel – Hempstead, UK)

### 2.4 Case Study
A case study of this apparatus does not seem to be necessary. Paper is quite often deacidified using an aqueous solution of alkaline earth metal carbonate. The solution prepared in the apparatus can be used in the same way as solutions prepared otherwise. On days when such aqueous treatments as washing or bleaching are planned, the apparatus must be turned on early in the morning. About 3 h later the solution is finished and ready for use. Further, if a new batch is made whenever the storage tank is nearly empty, solution is then always available. It is better to make unnecessary batches of solution than to fail to make one when necessary.

### 3. Steam Chamber
Sometimes artwork on paper can not tolerate aqueous treatment. If water causes damage, the artwork can be treated with an air-water aerosol or with steam. Steam is rejected by most restorers because its high temperature may harm colours and even paper. Nevertheless, hot steam can have positive effects:
Like the vacuum table described later, the steam chamber is built with V2A steel (Fig. 4). Its volume is about 0.6 m$^3$, and the working area is about 1.2m x 1.6m = 1.9m$^2$.

The chamber consists of a lid and a base. The steam from the generator passed through metal tubes into the base. Just after starting, the cold tubes are heated by condensing steam, so several taps allow the drainage of water. The steam passes through several plates of sintered metal at the bottom of the base and is evenly distributed over the working area, a perforated plate. The plate is covered with a filter and the artwork is placed on top.

The whole chamber is thoroughly insulated by 10cm of glass wool shielded by steel to prevent penetration of moisture and dirt. The lid is hinged to the base, so that the lid can be elevated above the base, which stands on the ground. Because the lid is heavy, the lifting is supported by two shock absorbers and is done by small pulley. After lifting, the position of the lid is fixed by a steel bar. This is important to prevent serious injury and damage in case the pulley fails.

After the artwork is positioned on the plate, the lid is lowered and steaming is started. There is no rubber seal between the metal edges of the base and the lid, and the small gap is closed by water droplets from condensing steam. The lid is heated electrically to 110°C to prevent steam from condensing and dripping onto the artwork. The heating elements are inside the glass wool, and must reach operating temperature before the steam generator is turned on. One must be careful opening the chamber during or after steaming: hot steam streaming out may scald. Again, the large inner metal parts must not be touched.

It has been demonstrated that the steam generator can be stopped after 20 min, because the good insulation maintains the hot steam atmosphere inside the chamber for several hours. If several objects are to be treated successively it is advisable to reheat the chamber for several minutes between runs.

### 3.2 Components

- Steam generator BM 1060 (Bekermesser, Bergheim, Erft, FRG)
- Sinter metal plates (Krebsöge, Radevormwald, FRG)
- Shock absorber (Getolift/Gebr. Titgemeyer, Osnabrück, FRG)
- Frame: V2A steel chamber (prototype)

### 3.3 Case Studies
All restorers encounter adhesion that cannot be resolved in any way. The steam chamber is not a panacea for this, but can help. For example, we had a seventeenth-century European drawing that adhered fast to a wooden board with animal glue. It could not be loosened easily and seemed hopeless. After this drawing was treated in the steam chamber for about 6 min, the glue became soft enough that a folder could be inserted between wood and paper. This had to be repeated twice, but finally the drawing was free and could be treated as usual. The backing glue was not really soluble in water, but it could be removed.

A series of paper rolls from inside a Tibetan wooden statue of Buddha, called Fo-Zang (Buddha’s soul); were red woodcut prints using cinnabar for pigment. They presented two problems that were both solved by applying hot steam. The rolls f stuck together, could not be unrolled, and could not be cleaned. Treatment in the steam chamber loosened the dirt and softened the paper, so the rolls were prepared for further restoration. Later the steam chamber was used to fix the colours, which run in aqueous treatments. Because the red colour began to run less than 1 min after contact with water, aqueous treatment seemed to be ruled out. The red colour stopped running after the sheets sat in the steam chamber for about 10 min. The binding agent seemed to be partially cross-linked by the steam. After deacidification the woodprints were further restored on the vacuum table.

European water colours with thick paint layers can also be fixed in the steam chamber and thus prepared for further treatment, such as on the vacuum table. We discovered this while restoring painting by Emil Nolde.

Thick layers of book painting can also be fixed by steam treatment, in the same way as cold moisture, but much quicker. We put these objects in the steam chamber for several minutes and immediately afterward in a press using as little pressure as possible. The objects were positioned between adhesive paper. The paint layers were then fixed again on the paper, solidly enough to move the paper and to exhibit it.

We also succeeded in cleaning and washing dirty and/or discoloured paper. The steam chamber very effectively washes out solid dirt, yellowing and even stains caused by fatty substances, probably because of several chemophysical reactions. The fibre in the felt that forms the paper is loosened, so that water can penetrate better and remove dirt particles; the material that is perceived by the human eye as dirt and discoloration may also be dissolved. These substances are also somewhat chemically decomposed by the hot steam in the chamber and the end products of this decomposition are washed out more easily than the substance itself.

4. Vacuum Table

A vacuum table is used for localized treatment of paper with water or other solvents to prevent chromatographic effects and also for leafcasting. Vacuum tables have been used to restore paintings for a long time. Since 1983 they have been widely accepted in paper restoration. Vacuum tables can be bought commerciall.
Nevertheless, some improvements seem to be necessary to meet the demands of delicate restoration of paper and, for paintings from sia, of silk mounted on paper. The grid system, the vacuum system and the mechanical stability of the table are the main areas to be improved. We therefore, decided to design a vacuum table connected to circulating (water ring) pump that has the following advantages:

- Large amounts of water can drain through the table into the pump.
- Large amounts of dirt and paper pulp can drain because the pump has a self-cleaning effect.
- Water-soluble organic liquids that form volatile mixtures can drain because they are made inert by the water in the pump. If the table is used for organic liquids, the runoff must be treated as hazardous waster.

4.1 Design
The vacuum table is illustrated in Fig.5. The grid area is 1.1m x 1.5m = 1.65 m², which is necessary for large artwork such as posters. The artwork is not put directly on the grid, but a screen, thin felt or a suitable nonwoven material is always used as an intermediate material. The metal grid used has a conical shape, so that water, solvent and pulp are easily drawn into the vacuum from the artwork lying on the table. The volume of the table below the metal grid is about 0.15m³. The table is connected to a vacuum pump by 2m of 50-mm-diameter tube. The vacuum pump has a capacity of 100m³/h. This means an average air velocity through the grid of 17mm/s, which is not enough to maintain a sufficient vacuum over the whole grid area. Most of the artwork on the grid thus has to be covered by plastic. The best material is 0.2-mm-thick silicone foil. The vacuum pump is a commercially available circulating pump¹⁵ that needs to be supplied with electricity and with water for cooling and for sealing. It operates very robustly. The air is drawn from the table into the pump together with water and solvents, which are made inert in the pump even if they are inflammable. Dirt is continuously washed out by the permanent stream of water through the pump.

4.2 Components
Conically shaped sieve plate (Trislot/N. V. Bekaert, Zwevegem, Belgium)
Circulating (water ring) pump (Sihi, Itzehoe, FRG)
4.3 Case study
The vacuum table is mainly used to clean artwork on paper and on textiles, to remove old and damaged backings and to fill in missing part. These three steps are demonstrated by the restoration of a Chinese silk painting by Tsai Tzer (1694).

The painting was 140 cm high and 69 cm wide. This silk was backed on three different layers of paper. The silk was extremely brittle, and the fibres were separated. The first layer, called the core, was not removed despite it brittleness, as some of the colour had penetrated into it and removing it would risk losing originality. The artist backed the silk before painting but the silk was already partly separated from its core over large areas.

The first step was washing (Fig. 6A). We put a screen (the type used in paper making) directly on the grid. We put the painting (face up) on this screen and brushed it with a very thin solution of methyl cellulose. Then several pieces of nonwoven material were put on the wet silk painting. Its fibres were partly cellulose, so that the material can retain some water, and partly synthetic fibre so that the material does not expand and shrink (as pure cellulose paper would) when it gains and loses moisture. The material had to be thin so that it would loosely follow the painting and prevent the painting positioned on it from sliding during the whole process. We placed thick cotton (extra soft Turkish towels) on the nonwoven material. Warm water was poured on these towels several times and sucked through the nonwoven material, artwork and screen into the vacuum table.

Even warm water (up to 60°C) or an aerosol can be used. Because the water is removed immediately by the vacuum pump, the colours are not harmed, but the dirt is adequately washed away.

The old and brittle paste became soft enough by this repeated wet and warm treatment that the damaged backings could be removed. The painting had to be turned upside down (Fig. 6B). The towels were removed; then the three layers (screen, painting and nonwoven material) could be turned and, after the screen was removed, we could begin to remove the two layers of the old backings. As mentioned above, the core was preserved. The utmost care was necessary to prevent any movement between the painting and the nonwoven material. For damaged silk this would mean irretrievable damage and loss.
First the core had to be reattached to the silk (Fig. 6C). The core was composed of six layers of thin paper. Each layer was separated from the silk, thin paste was brushed on each part of the core and the core was carefully brushed onto the silk. This was done successively for all six parts of the core. Liquid was drained from the painting with a vacuum. The painting was turned around carefully and the nonwoven material was removed. A new backing of very strong thin paper was positioned to support the old core. All subsequent treatments, including drying on the board, new silk for the frame, new edgings and all the other details of correct Chinese mounting were performed according to traditional Asian methods.\textsuperscript{12}

The vacuum table can also be used to fill in holes and missing parts (mending). For paper we prefer to do this by leafcasting after checking carefully the amount and the colours of the fibre. This can be successfully accomplished directly on the vacuum table using a small box or frame as described previously\textsuperscript{16} immediately after removing the backings. For mending using sheet-shaped materials instead of fibre it is even possible, presuming utmost care, to move the artwork to the light table. Before doing this, the vacuum must operate for several minutes with full power to guarantee that the artwork quite solidly adheres to the nonwoven material. As mentioned above, sliding must be prevented.

5. \textbf{Stirring Vessel}

Wheat starch paste is used in this workshop to mount and to repair artwork on paper. The preparation of fine, soft and sticky starch paste depends on a lot of different treatments and additives. Chinese and Japanese books have quite complicated recipes for preparing paste. One of these treatments includes steady long-term mixing of the starch and water mixture.\textsuperscript{17} A stirring vessel can be bought\textsuperscript{18} or designed for maximum flexibility.

We coupled a laboratory thermostat with a 5-litre steel vessel and placed another steel vessel inside it containing the starch and water mixture (Fig. 7). We usually use water a heating medium, so that the starch and water mixture is not burned. The speed of the mixer can be regulated. The form of the mixer is important to optimize mixing of this non-Newtonian system. There are three rows of blades, and the blades in each row are bent at a different angle.

The stirring vessel can also be used to prepare alkaline earth metal salt solutions for deacidification. A sediment of magnesium hydroxicarbonate in water is mixed at
full speed and carbon dioxide is introduced on the surface of this system. By the water funnel that is formed by the stirring the carbon dioxide is intensively mixed with the suspension. Very little carbon dioxide is needed for this. After 1 h the solid is allowed to settle and the solution can be used for deacidification in the same way as the solution prepared in the calcium carbonate flow bed solubilizer (Fig.1).

The components include:
Thermostat 2 kW (Lauda, Lauda, FRG)
Stirrer engine 150 W 10-1000 l/min (Janke + Kunkel, Staufen, FRG)
V2A frame and pots (prototype).

6. Conclusion
We use well tested substances whenever possible in paper restoration: water (liquid or steam), aqueous solutions of alkaline earth metal salts and starch. The compatibility of these chemicals with paper has been tested and confirmed for centuries in different cultures. Different sophisticated machines are required to apply these basic chemicals in a wide range of different areas. Interdisciplinary cooperation is thus essential between the engineer, the scientist and the restorer, who is part craftsperson and part artist.

Appendix Fig. 1
The equilibrium values (left part of Fig.1) are taken from: Gmelins Handbuch der Anorganischen Chemie (Weinheim: Verlag Chemie 1956); and Freier, R. K.: Aqueous solutions (Berlin: de Gruyter, 1978)
- Ca/1: 10.8 mmol Ca ions per liter aqueous solution in equilibrium with solid CaCO3 and pressure of 0.1 Mpa CO2.
- Ca/10: 25.6 mmol Ca ions per liter aqueous solution in equilibrium with solid CaCO3 and pressure of 1 Mpa CO2.
- Mg/a: 15.0 mmol Mg ions per liter aqueous solution in equilibrium with solid MgCO3 and pressure of 0.1 Mpa CO2.
- Zn/1: 0.6mmol Zn ions per liter aqueous solution in equilibrium with solid ZnCO3 and pressure of 0.1 MPa CO2.

The following values are measured values discussed in the text (right part of Fig.1). They are not equilibrium values. The left bar shows the pH value of the solution, the right bar the corresponding concentration of the metal ion in mmol per litre.
- Ca/F: 6/5mmol/l Ca ions, pH 5.7. Flow bed solubilizer. See Fig.2.
- Mg/3: 42.8 mmol/l Mg ions, pH 6.5, Mg hydroxicarbonate under treatment of 0.3 Mpa CO2. Pressure vessel.6
- Mg/T: 3.5 mmol/l Mg ions, pH6.9 Mg hydroxicarbonate. Stirring vessel. See section 5.
- Zn/T: 0.5 mmol/l Zn ions, Ph8.0 Zn hydroxicarbonate. Stirring vessel. See section 5.

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SUMMARIES

Machinery for Paper Restoration

Four machines designed and constructed by the authors are presented in detail: an apparatus to produce saturated solutions of calcium carbonate, a steam chamber to dissolve stubborn adhesives, to fix running colours and for other purposes, an improved suction table for work on extremely delicate art works, and a mixer to prepare pastes and deacidification solutions. Components of the machines and their manufacturers are listed. Examples of practical use of the machinery are described.

Machines pour la Restauration du Papier
Quatre machines conçues et construites par les auteurs sont présentées en détails: un appareil pour la production de liquides saturés de carbonate de calcium, une chambre à vapeur pour la dissolution d’adhésifs difficiles, pour la fixation de couleurs qui fondent et à d’autres fins, une table de succion améliorée pour les travaux sur des objets d’art très délicats, un malaxeur pour la preparation de pâtes et de liquides de désacidification. Les détails concernant les machines et les fabricants sont également indiqués et des exemples de l’emploi pratique des machines sont décrits.

Geräte für die Papierrestaurierung

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