Freeze-Drying Wet Digital Prints: An Option for Salvage?

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Abstract. On the occasion of the collapse of the Historical Archive of the City of Cologne in March 2009 and the ensuing salvage effort, questions were raised about the use of freeze-drying for soaked digital prints, a technique that has not yet been evaluated for these materials. This study examines the effects of immersion, air-drying, drying in a blotter stack, freezing and freeze-drying on 35 samples of major digital printing processes. The samples were examined visually before, during and after testing; evaluation of the results was qualitative. Results show that some prints were already damaged by immersion alone (e.g. bleeding inks and soluble coatings) to the extent that the subsequent choice of drying method made no significant difference any more. For those samples that did survive immersion, air-drying proved to be crucial for water-sensitive prints, since any contact with the wet surface caused serious damage. Less water-sensitive prints showed no damage throughout the entire procedure, regardless of drying method. Some prints on coated media suffered from minor surface disruption up to total delamination of the surface coating due to the formation of ice crystals during shock-freezing. With few exceptions, freeze-drying did not cause additional damage to any of the prints that hadn’t already been damaged by freezing. It became clear that an understanding of the process and materials is important for choosing an appropriate drying method.

1. Introduction

On March 3, 2009, the six-story building of the Historical Archive of the City of Cologne collapsed within minutes into a large crater created by the faulty construction of a subway line beneath the street. During the ensuing six-month initial salvage effort of physically damaged, humid or soaked photographs, documents, maps, illuminated manuscripts and books, the question was raised whether wet digitally printed matter could be vacuum freeze-dried along with other archival materials or if it needed to be sorted out and treated separately. An investigation was initiated to determine the effects of freeze-drying on samples of the most common digital printing processes.

When facing large numbers of moist or wet archival materials, speed is an essential factor. In order to avoid excessive bleeding of inks, dissolution of water-sensitive coatings and mould growth, prints must either be dried quickly and safely, or, if this is not possible, frozen. Freezing instantly stops deterioration that occurs in wet materials and it gives the salvage team time to consider a variety of drying methods. While much is known about salvage methods for traditionally printed documents and photographic materials, only few studies have been published so far on the sensitivities of digital prints to liquid water and on methods of drying wet prints. These studies indicate that prints of
different processes show different sensitivities to water: while dye diffusion thermal transfer prints survive flooding quite well, for example, since they do not tend to wet at all, inkjet prints with swellable (polymer) coatings absorb large amounts of water and become tacky to the touch or even suffer from total dissolution of the ink receptor layer. It has been shown that microporous inkjet prints, on the other hand, are generally less sensitive to water damage [1].

However, available investigations have not examined the option of freeze-drying, a method that is common for drying large numbers of documents or books within a short period of time in order to avoid ink bleeding, physical distortion, blocking and microbial activity. In vacuum freeze-drying, water is removed from the documents while these remain frozen. Within a vacuum, the frozen water held in the documents sublimates, leaves the document and is reformed as a solid on a condensing surface in a separate chamber. As drying progresses, the temperature within the vacuum chamber is incrementally increased in order to promote the release of residual water bound in the documents.

This study examines the effects of vacuum freeze-drying on a wide variety of digital prints that were chosen because they broadly represent those often found in homes, offices or archival environments. In order to determine whether freeze-drying itself caused damage or whether changes that incurred in the prints were simply due to their preliminary wetting or subsequent freezing, the simpler methods of air-drying and drying in a blotter stack were also included in this study for the purpose of comparison.

2. Materials and Experimental

The samples consisted of prints made with nine different digital printing processes; within some of the processes, prints showing variations of inks and papers were selected. The 35 samples included inkjet (dye- and pigment-based inks on various coated and uncoated media), direct thermal (D1T1, monochrome and Polaroid ZINK), direct thermal transfer (D1T2), dye diffusion thermal transfer (D2T2), electrophotography (dry toner prints and liquid toner HP Indigo print), photothermographic transfer (Fuji Pictrography), thermal autochrome (Fuji Printpix) and digital exposure to photographic paper (gelatine silver and chromogenic). The processes and print materials have been described in detail elsewhere [2]. The prints were not made specifically for this experiment; instead they were taken from a larger collection of prints collected over the past ten years. They thus reflect a variety of dates and applications such as one might find in the holdings of a typical archive. Examples include printed office documents and scientific graphs, faxes, medical imaging prints, photocopies, reproductions and snapshots or documentary photographs. The samples were treated in four experiments that reflect common practice in water damage salvage efforts:

1. immersion and air drying
2. immersion and drying in a blotter stack
   2a. directly between blotters
   2b. between blotters but with a sheet of Bondina on the image side
3. immersion, freezing and air drying
4. immersion, freezing and freeze-drying in a vacuum chamber

In all procedures, samples were immersed in a bath of 18°C tap water for 10 minutes without movement, then removed from the water, held vertically and allowed to drip briefly. Care was taken not to touch the wet print surfaces. In experiment 1, samples were air-dried face up on blotters without first blotting off the surface. While air-drying avoids any potential interaction with the printed surface, which may be sensitive to the touch and/or tacky when wet, it has the disadvantage of taking up large amounts of table space – a factor that is critical when many objects need to be dried quickly in a restricted space. In addition, prints may cockle and curl while drying.

In experiment 2, samples were dried in a stack of blotters that was weighted with moderate weight, a method that allows for the drying of more samples on a smaller table space with the added advantage of resulting in flattened prints. In 2a, the wet print was in direct contact with the blotters on both recto
and verso, but in 2b an interleaving sheet of Bondina (a thin, smooth, heat-bonded, non-woven 100% polyester fabric similar to Hollytex) was placed on the print surface to protect it from potentially becoming stuck to the blotter.

For experiments 3 and 4, the wet samples were placed individually on a rack, not stacked, and shock-frozen to -19°C in a freezer. In experiment 3, samples were then allowed to thaw and air-dry face up on blotters. In experiment 4, the frozen samples were freeze-dried in a vacuum chamber with a pressure of 1.6-1.8 mbar and without incremental heating.

The samples were examined visually before and after testing with the naked eye and under 10-40x magnification with the use of normal, raking, and specular light. Some samples were examined with ultraviolet (UV) radiation as well. Comparisons with untreated control strips were made. Evaluation of the results was qualitative, since no instrumental analysis was carried out.

3. Results and Discussion
The wide variety of processes and materials in this study produced results that vary greatly in type and extent. Within each process and each combination of materials (the latter being mainly relevant for inkjet printing, in which different inks can be used on different media), however, similar results were observed, so they have been summarised in table 1 and are discussed in the following.

3.1. Inkjet prints
The 15 inkjet prints reacted very differently to the experiments. Bleeding of the dye-based inks upon immersion into water was expected, since the inks were aqueous. Dyes can be quite waterfast on matte and microporous coated media, however. The pigment-based inks were waterfast regardless of media. The difference in water sensitivity between swellable and microporous coatings was very obvious: while the former were seriously damaged by immersion alone, with deterioration ranging from partial separation of two different layers to complete dissolution, the microporous coatings in general and that on a plastic film in particular withstood immersion and subsequent drying with hardly any physical changes. Following immersion, the matte and microporous coatings tended to yellow to varying degrees, the former more than the latter. This change was especially noticeable at the print edges. The cause of the yellowing is not clear – it may be the result of either the loss or migration of optical brightening agents, oxidative reactions of the coating’s organic components, or both.

When examined under a microscope, the subsequent matte surface of the formerly glossy prints with swellable coatings that were frozen was found to be a result of the formation of minute craters in the coating; these may have been caused by the formation of ice crystals in the waterlogged layers. Freezing also caused two of the three swellable coatings to become opaque and flaky, leading to a white veil over the image and partial delamination.

The prints made with solvent-based inks on poly(vinyl chloride) banner media were not sensitive to any of the experiments; this is due to the non-solubility of the colorants in water and the lack of an ink receptor coating on the PVC. While inkjet prints made with solid inks were not tested, it may be assumed that the results would be similar to those of the direct thermal transfer prints, since they are similar in materials (colourant in waxy binder) and structure (ink on surface of paper or plastic).

3.2. Electrophotographic prints
In areas of high density it was found that the thick toner layer of the colour laser prints cracked when the prints were immersed into the water bath. Toner contains as a binder a blend of thermoplastic resins and is therefore hydrophobic. The paper support to which the toner is fused, on the other hand, expands when it becomes wet as a result of the uptake of water; this expansion is greatest across the grain, or fibre direction, of the sheet. Since the toner does not expand in the water bath, it relieves the accumulating stress caused by the expanding paper by cracking parallel to the grain direction. The difference in tension between the paper and the toner layer may also be the reason for the substantial concave curling of the wet prints; this curl remained, if to a lesser degree, in the dried prints, regardless of drying method.
### Table 1. Summarised results of the experiments. “N/C” indicates: no significant changes observed.

| Process and materials | Immersion | 1. Air-drying | 2. Blotter-drying | 3. Freezing and air-drying | 4. Freezing and freeze-drying |
|-----------------------|-----------|---------------|-------------------|---------------------------|-----------------------------|
| Inkjet (dye ink on uncoated paper) | Profuse ink bleeding. | Moderate cockling and curl. | Bleeding into blotter. | Ice crystal marks in areas of bled ink. | Ice crystal marks in areas of bled ink. |
| Inkjet (pigment ink on uncoated paper) | N/C | Moderate cockling and curl. | N/C | N/C | N/C |
| Inkjet (2 dye and 1 pigment ink on matte coated papers) | Dye: minor ink bleeding. Pigment: N/C | Slight to serious yellowing of coating. | Slight to serious yellowing of coating. | Slight to serious yellowing of coating. | Slight to serious yellowing of coating. |
| Inkjet (4 dye and 1 pigment ink on microporous media: 2 papers, 1 fibre-based paper, 1 plastic, 2 RC-papers) | Dye: occasional minor ink bleeding. Pigment: N/C | Occasional moderate yellowing of coating. Fibre-based paper: moderate curl. | Occasional moderate yellowing of coating. Fibre-based paper: surface is matted. | Occasional moderate yellowing of coating. Fibre-based paper: surface is matted. |
| Inkjet (2 dye and 1 pigment ink on swellable RC-papers) | Dye: profuse ink bleeding. Pigment: N/C Coating separates into 2 layers and partially disintegrates. | Minor curl. | Surface sticks to blotters and is matted by Bondina. Verso can also stick to blotters. | Upper and/or lower coating layer is matted, can become opaque and show ice crystal marks. | Delamination of opaque upper layer possible. |
| Inkjet (solvent ink on PVC banner) | N/C | N/C | N/C | N/C | N/C |
| Electrophotography (3 dry toner colour laser prints) | Printed areas do not wet, and thick toner cracks parallel to fibre direction. | Cockling and curl can be serious. | Minor curl. | Minor curl. | Minor curl. |
| Electrophotography (liquid toner HP Indigo print) | Printed areas do not wet, and strong curl. | Minor curl. | N/C | Minor curl. | Minor curl. |
| Digital Exposure (3 chromogenic, 1 silver gelatine fibre-based print) | N/C | Fibre-based print: moderate curl. Chromogenic RC papers: minor curl. | Surface sticks to blotters and is matted by Bondina. | Fibre-based print: moderate curl. Chromogenic RC papers: minor curl. | Fibre-based print: moderate curl. Chromogenic RC papers: minor curl. |
| Direct thermal (1 fax, 1 ticket, 1 bank statement) | Strong curl possible. | Moderate cockling and curl and slight yellowing of coating. | Slight yellowing of coating. | Slight yellowing of coating. | Slight yellowing of coating. |
| Direct thermal (Polaroid ZINK print) | Topcoat becomes opaque. | Topcoat clears, reticulation of topcoat where water pools on glossy surface. | Topcoat clears, surface is matted by both blotters and Bondina. | Topcoat clears, reticulation of topcoat where water pools on glossy surface. | Formation of opaque crystals in topcoat. |
| Direct thermal transfer (1 colour, 1 black-and-white print on paper) | Printed areas do not wet. | Moderate cockling and curl. | N/C | N/C | N/C |
| Dye diffusion thermal transfer (2 prints with, 2 prints without wax topcoat) | Print does not wet, but edges may swell where water enters into support. | Matte deposits where water pools on glossy surface. | N/C | N/C | N/C |
| Photothermographic transfer (Fuji Pictrography) | N/C | N/C | Surface sticks to blotter, not to Bondina. | Surface is matted. | Surface is matted. |
| Thermal autochrome (Fuji Printpix) | Topcoat becomes opaque. | Topcoat clears, surface is matted. | Topcoat clears, surface is matted and sticks to blotter, not to Bondina. | Opaque topcoat with ice crystal marks. | Opaque topcoat with ice crystal marks, local delamination of topcoat. |
3.3. Digital exposure to photographic materials
While photographic materials are not necessarily considered to be digital prints, the fact that today they are almost always exposed by digital means and are often present in archives along with the other types of prints was sufficient to include them in this study. The samples tested withstood short-term immersion well. Due to the increased surface tack of the swollen gelatine emulsion, the prints did stick to the blotters in experiment 2. They could be removed easily, but some paper fibres remained adhered to the surface. While this problem was avoided with the use of Bondina as a non-sticking, water permeable layer, the wet emulsion took on the surface texture of the Bondina and became matte when dry. The samples that were not physically restrained during drying (experiments 1, 3, 4) tended to curl due to tension between the emulsion and the support.

3.4. Direct thermal
Two of the direct thermal prints that were on a very thin paper support curled strongly during immersion. The prints retained their curl to a lesser degree when air-dried. Blotter-drying, freezing and freeze-drying did not appear to have negative effect on the prints except for an overall slightly irregular surface. All of the prints showed slight yellowing, and examination under a UV light source revealed that immersion caused a great loss or at least migration of optical brightening agents.

Polaroid ZINK (stands for ‘Zero Ink’) is a direct thermal process which uses a special media that has three thermally sensitive layers, one each for yellow, magenta and cyan dyes. It is used for small-format amateur snapshots and may be regarded as a digital sequel of the earlier instant prints that were based on photographic technology [3]. Although the protective topcoat became opaque when wet, it cleared again upon drying. It did form a reticulation pattern where water pooled on the surface during air-drying, however, so contact with water beyond the immersion period of ten minutes may be damaging. The prints seemed to withstand immersion, freezing and air-drying well, but the freeze-dried samples suffered from opaque crystalline enclosures in the protective topcoat.

3.5. Direct thermal transfer
The binder used to hold the colourants in this process is a blend of waxes and resins and is therefore hydrophobic. The prints were not damaged by immersion and only suffered from moderate cockling and curl when air-dried. The blotter-dried, frozen and freeze-dried prints dried flat and without apparent changes.

3.6. Dye diffusion thermal transfer
Also known as dye sublimation prints, these samples did not wet in the water bath. This is due to the hydrophobicity of the materials on both sides of the prints: the image layer is a blend of synthetic, organic polymers such as polyester and polycarbonate, which can be further coated with a protective layer of wax following printing, and the support is usually a complex laminate of layers of synthetic fibres and plastic films. Some media may have a paper core; this may be the explanation for the swelling of the edges in two of the four different samples during immersion. Apart from the swollen edges, which did not regain their original form during drying, no changes were observed in the prints except for some superficial matte deposits where water had pooled on the prints that were air-dried.

3.7. Photothermographic transfer
While the Fuji Pictrography sample showed no changes in the water bath or after air-drying, it did slightly adhere to the blotters in experiment 2a. This is likely a result of the fact that the receptor layer contains gelatine and therefore swells and becomes slightly tacky when wet. Freezing the wet samples resulted in a overall change of the surface from glossy to matte. The original surface gloss was not regained during both experiments 3 and 4.
3.8. Thermal autochrome
The Fuji Printpix samples suffered changes in all of the experiments. The prints reacted similarly to the ZINK prints in that the protective topcoat became opaque when wet but cleared again upon drying. However, the originally glossy surface air-dried matte and adhered to the blotters, indicating that the wet topcoat was tacky. Freezing left the topcoat opaque and freeze-drying then caused it to flake off, revealing the intact image below.

4. Conclusions
Although this study set out to determine whether freeze-drying could be an option for drying wet digital prints, it turned out that the key factors that determined whether a print would survive water damage were first its resistance to becoming wet and secondly its sensitivity to freezing, this being a preliminary step before freeze-drying. With the few exceptions of some swellable inkjet media, thermal autochrome and ZINK, freeze-drying did not cause any further damage than immersion and freezing had not already caused. Thermal autochrome and ZINK are relatively rare processes, and only one of the three examined swellable inkjet media suffered from delamination of the ink receptor layer when freeze-dried.

Freezing damaged more of the prints than had been expected. The frozen inkjet prints on fibre-based paper, a popular microporous media for aqueous inkjet that imitates traditional silver gelatine fibre-based photographic paper, suffered from matting. One of the swellable inkjet media turned opaque and showed marks left by ice crystals within the areas of ink bleeding, as did the simple dye-based ink on uncoated paper. Finally, the originally glossy photothermographic transfer print turned matte, and the topcoat on the thermal autochrome print became opaque, thereby obscuring the image.

For inkjet, results show that pigmented inks and microporous coatings have a clear advantage over dye-based inks and swellable coatings when wet. Dye-based inks generally bled into any material in contact with them, although on microporous coatings bleeding was only minimal. The overall best results were found with pigmented inkjet on uncoated paper and also with solvent-based inkjet on PVC banner, dye diffusion thermal transfer, direct thermal transfer and electrophotography, processes in which some or all of the involved materials are hydrophobic.

Although some prints suffered from image disruption by damaged coatings, the majority of the tested digital prints generally remained structurally undamaged in this study; it can therefore be concluded that most digital prints can be frozen and freeze-dried following water damage. Since they are simpler and therefore less likely to cause unexpected damage, however, the methods of air-drying and blotter-drying are preferred when possible. Individual recommendations for drying prints of different processes should be always be taken into consideration; these are given in table 2.

As a result of this study and information from earlier publications, the following general recommendations can be formulated for best practice for drying wet digital prints:

- Identify the processes as best possible before water damage occurs or at least before selecting a drying method once the prints have become wet. If the process is unknown, choose air-drying as the potentially least damaging method. Although most air-dried prints will show curl and/or cockling, they can usually be flattened later by a conservator.
- Any wet prints that feel slightly tacky to the touch should be air-dried rather than dried in a blotter stack. This is especially important for inkjet prints on swellable media.
- Physical contact with wet surfaces should be avoided if possible.
- Drying in a blotter stack will reduce curl, however prints with sensitive surfaces may stick to the rough and fibrous blotter surface. In these cases, Bondina or a similar material can reduce this blocking; however some print surfaces may then become matted.
- Dye-based inkjet prints should be air-dried individually to avoid bleeding into other materials.
- Inkjet prints on fibre-based paper and on swellable media, as well as thermal autochrome and photothermographic transfer prints should not be frozen.
- In addition, thermal autochrome and ZINK prints should not be freeze-dried.
Table 2. Recommendations for drying wet digital prints.

| Process                          | Air-drying | Blotter-drying | Freezing and air-drying | Freezing and freeze-drying |
|----------------------------------|------------|----------------|-------------------------|----------------------------|
| **Inkjet (dye ink on uncoated paper)** | ++         | –              | –                       | –                          |
| **Inkjet (pigment inks, matte and microporous coatings)** | +          | ++             | o                       | o                          |
| **Inkjet (swellable coatings)**   | ++         | –              | –                       | –                          |
| **Inkjet (solvent ink on PVC banner)** | 0          | 0              | 0                       | 0                          |
| **Electrophotography**           | +          | ++             | o                       | o                          |
| **Digital Exposure**             | ++         | –              | o                       | o                          |
| **Direct thermal (monochrome)**   | +          | ++             | o                       | o                          |
| **Direct thermal (Polaroid ZINK)** | ++, blot surface first | +          | o                       | –                          |
| **Direct thermal transfer**       | +          | ++             | o                       | o                          |
| **Dye diffusion thermal transfer** | +, blot surface first | ++          | o                       | o                          |
| **Photothermographic transfer**   | ++         | +, only with Bondina | –                     | –                          |
| **Thermal autochrome**           | ++         | +, only with Bondina | –                     | –                          |

a ++ : best method  
+ : second best method  
o : possible method but no preference  
– : method not recommended

Continued research in this area could include the systematic study of cross-sections of the prints in relation to these experiments; this would result in a better understanding of the problems found with the reactions of some of the supports and coatings to wetting and freezing. In addition, chemical analysis of some of the coatings, for example of that of photothermographic transfer prints, for which technical literature is scarce, would be useful. It would furthermore be interesting to determine whether the method of drying has a long term influence on the mechanical properties of the supports and coatings. The application of a brittleness test to the samples treated in this experiment would be one example [4]. Finally, it would be interesting to compare the results of this study, in which the samples were frozen and freeze-dried individually, to samples freeze-dried within stacks of wet documents, which is perhaps a more likely scenario for archival materials.

Appendix
Materials and equipment:
- Blotters: Type 040, Klug Conservation, Walter Klug GmbH & Co. KG, Badeweg 9, 87509 Immenstadt, Germany, www.klug-conservation.com
- Bondina: Type H3228, Conservation Resources International LLC, 5532 Port Royal Road, Springfield, Virginia 22151, USA, www.conservationresources.com
- Freezer: Rivacold, Cool Italia GmbH, Schmidener Weg 13, 70736 Fellbach, Germany
- Freeze-drying equipment (condensation device I-20 and vacuum chamber): Martin Christ Gefriertrocknungsanlagen GmbH, Postfach 1713, 37507 Osterode am Harz
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