# Effects of Binders and Additives on Inkjet Coating Pigment Pore Structures

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## ABSTRACT

This study considers the evidence for pore volume loss, studied by mercury intrusion porosimetry, of inkjet coating structures when using certain binder types and polymer additives. It is shown that starch is particularly disadvantageous as it not only prevents access, when film formed, to the crucially absorbing pores, but is itself non-absorbing. Polyvinyl alcohol (PVOH) on the other hand does absorb up to ~30 % of its own weight of water, but if present in pores acts also to limit the absorption rate by reducing it to the interpolymer matrix diffusivity, and reduces the volume according to the loss of pore space by the presence of the PVOH. It is also shown that latex particulate binder can be used to allow continued access to the nanopore region within the porous pigment particles by choosing the right glass transition temperature, $T_g$, and chemistry of the synthetic polymer. Similarly, the permeability can also be maintained to a large extent when adopting particulate binder. Depending on ink type, pigmented or dye-based, the coating can be dispersed either anionically or cationically for pigmented inks, but the coating must be cationic to enable the development of water fastness when considering anionic ink dyes. This requirement adds another source of pore volume loss, and hence degraded printability, as the added cationic polymer, such as PolyDadmac, used to achieve cationising, itself reduces the available pore volume for absorption by distributing itself on the pigment surfaces and within pores. Linking this pore volume loss to increased feathering and intercolour bleed supports the need to re-consider carefully the use of water soluble polymers and binders, and indicates that coating formulation optimisation for the future, when using cost-effective porous pigments in inkjet coatings, points to the minimising of charge conversion requirements and the development of improved particulate binders.

## INTRODUCTION

In a range of printing methods, including traditional offset and flexography, and the rapidly emerging high-speed digital methods, such as inkjet, liquids are required to wet the print medium surface either differentially, as in offset, or uniformly, as in flexography and inkjet. In the case of pigment coated papers and boards, absorption of liquid is also an integral part of the ink setting and drying process. The rate and volume of liquid absorption is dependent on the porous network structure of the coating layer established via coating pigment particle packing in the presence of binders, for example starch, polyvinyl alcohol (PVOH) or latex. The time scale of absorption falls under the description of network pore structure imbibition theory [1-3] and the chemical nature of the surface encountered by the liquid, together with diffusion effects [4, 5]. The printing process manifests time scales of phenomena from nanoseconds through milliseconds up to minutes and hours depending on ink and coating chemistry. For the absorption of the ink diluent/solvent the coating structure should have enough capacity to hold the fluid and also have rapid absorption speeds to enable fast ink setting.

Inkjet technology is identified as a strong driver for change in the printed paper market. Traditionally, inkjet receiving surfaces, with their need for high volume and rapid liquid absorption capacity, meant that speciality papers arose with these properties as the main design criteria. To achieve the necessary porous structures, coating pigments such as precipitated or fumed silica were used, sometimes together with superabsorbing polymers. The formation of a liquid receiver layer based on such pigments, together with a glossy superabsorbing top layer, lies behind the successful development of photographic quality inkjet papers, for example. The emergence of cost competitive print engines is, however, changing the market perspective toward technologies that challenge the traditional offset production quality, in terms of both speed and, eventually, cost. The ability to reduce inventory is a major factor underpinning these developments. To meet the cost-effectiveness challenge, it is recognized that the cost of coating pigment specialities for such grades needs to be reduced, and silica is seen as being progressively unable to meet this value requirement. Therefore, speciality designed inkjet coatings today increasingly employ the use of alternative highly porous pigments.

The development of calcium carbonate grades for inkjet coatings, either PCC or GCC-based, has seen big progress in recent years. An example of such a porous pigment, developing a discretely bimodal pore structure controlling permeability via the interparticle pores and capillarity via the intraparticle pores, is modified calcium carbonate [1]. Similar structures also exist in respect to precipitated calcium carbonate. These designed structures provide for high absorption volume and fast absorption rate, but depend on the availability

of the pores to perform this action by absorbing the liquid vehicle of the ink. Blockage of pore entries or reduction of pore connectivity can reduce the effectiveness of the potential capillary force and/or the permeability of the coating, respectively. Though primarily with the aim of entering the new cost-effective inkjet printing grades, the technology is advancing at such a pace that it is likely that designs may soon appear to challenge even the highest cost specialities. Clearly, however, the high absorptive performance of silica sets a major technical hurdle to be reached, and the solution lies not only in coating pigment design, but also in formulation design, which requires change from the traditional silica-containing formulation recipes. Principally this change is required to allow calcium carbonate pigments to perform in respect to the demands on pore volume and pore size distribution.

In coating colours, besides the pigments with their particle packing characteristics and internal pore structure, there is also the binder to consider. By changing binder amount or binder type the inkjet ink penetration can be influenced. First of all, the binder amount should be sufficient that the coating colour has an adequate adhesion to the paper surface and cohesion within the coating layer such that dusting problems are minimal. The surface strength is not needed at such high levels as in traditional offset printing, but nonetheless dust generation is critical, as it could lead to blockage or damage of the inkjet nozzles, and so diminish the print quality and reduce the lifetime of expensive print engine components. In coating colours for inkjet papers, polyvinyl alcohol (PVOH) is a very commonly used binder, and it has a high capability to bind pigments. It is also a very hydrophilic binder, and exhibits swelling on contact with water [6-8]. Pinto *et al*. [8] showed in their study that ink diffusion is unrestrained by PVOH, and the colorant concentration profile is uniform in a PVOH layer as shown by time–of-flight secondary ion mass spectrometry (TOF-SIMS) analysis. Recently, the binder type has been shown to have an effect on the inkjet ink print density and bleeding development, Nilsson [9] and Svanholm [10].

Soluble binders, despite their role in some cases of also being absorptive – polyvinyl alcohol (PVOH), for example – nonetheless deplete the available pore volume, as their swelling potential is less than the potential availability of empty pore space. Lamminmaki *et al.* [11] showed that PVOH binder affects both the pore structure and its ability to take up liquid by diffusion. PVOH swells during the diffusion process. Although the volume of liquid imbibition related to PVOH swelling can be small at low binder levels it acts to dominate the ink interaction with the pigment surface and the fine pore structure as binder levels increase. Mercury porosimetry results [11] indicated that PVOH binder can go into or cap (film over the entry) the intra-particle as well as the connecting pores, and exists around the larger inter-particle pores as Boisvert *et al.* [12] and Wedin *et al.* [13] assumed in their studies. At sufficiently high levels, any interaction of the binder with the liquid phase of the ink becomes important, not only in the structural modification of pore volume but in the diffusion of liquid through the polymer network, effecting swelling in the case of PVOH.

The work reported here addresses the loss of pore volume question and illustrates how the future application of inkjet coatings needs a further developed formulating strategy to assist in delivering the required inkjet substrate surface properties. To illustrate the effects, the pore structures of compressed inkjet designed calcium carbonate coating pigments, as well as coatings on aluminium foil, are compared, and their combination with various amounts of soluble polymer and particulate binders, respectively, are studied to determine the impact on pore volume loss and hence print performance in the demanding inkjet field.

## MATERIALS AND METHODS

### Coating Pigments

The pigments used are modified calcium carbonates (MCC) of two different particle size ranges, nMCC and bMCC, with narrow and broad particle size distribution, as might be used in the emerging new generation of inkjet coatings for Transpromo grades and high speed applications, respectively, and a coarse ground calcium carbonate (cGCC) (Hydrocarb 60 ME, Omya AG, CH-4665 Oftringen, Switzerland). The particle size distributions for these pigments can be seen in Figure 1. In addition, a laboratory made MCC, having high pore volume and extremely narrow particle size is used to exemplify more clearly the impact of binder addition (Figure 2).
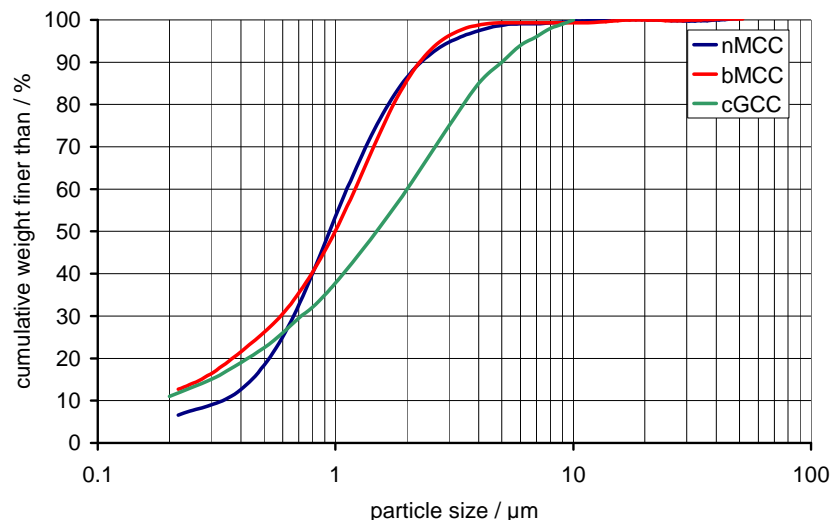
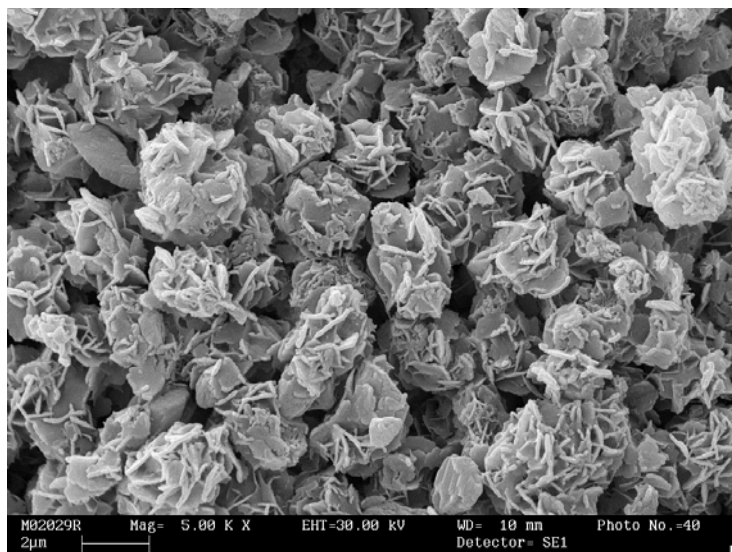**Figure 1.** Particle size distributions of bMCC, nMCC and cGCC



**Figure 2**. An example of a laboratory made high pore volume modified calcium carbonate (MCC).

For illustrative particulate binders, two latices were used: a vinyl acetate (PVAc) (Latexia PVAc, CHP 104, CH Polymers OY, Finland), having $T_g$ 30 $^o$C and styrene acrylic (SA) (Acronal S360D, BASF, Ludwigshafen, Germany), having $T_g$ 5 $^o$C. The effects of soluble binders, starch (Raisamyl 21451, Chemigate OY, Finland) and PVOH (PVOH 88 % (Partly hydrolized) BP-05, CCP, Taiwan) and cationic polymer (PolyDadmac) (Alcofix 169, BASF, Ludwigshafen, Germany) on the pore structure are also investigated.

The coating structures formed using the nMCC and bMCC together with the soluble binders mimic as closely as possible a real world inkjet paper coatings.

## Porous Sample Formation

### Tablet Press

Tablet structures, consolidated from coating colours with cationic polymer or latex, were formed by applying a constant pressure (15 bar) to the suspension/slurry for ~ 3 hours such that water is released by filtration through a fine 0.025 µm filter membrane (Millipore VSWP04700) resulting in a compacted tablet of the pigment, Figure 3. Samples with and without cationic polymer were formed and tablets with and without latex were formed. The tablets have dimensions of ~ 4 cm diameter with a thickness of 1.5 – 2.0 cm, which can be

divided and fashioned into suitable sample configurations for subsequent analysis. The tablets were removed from the apparatus and dried in an oven at 60 $^{\circ}$C for 24 hours [14].
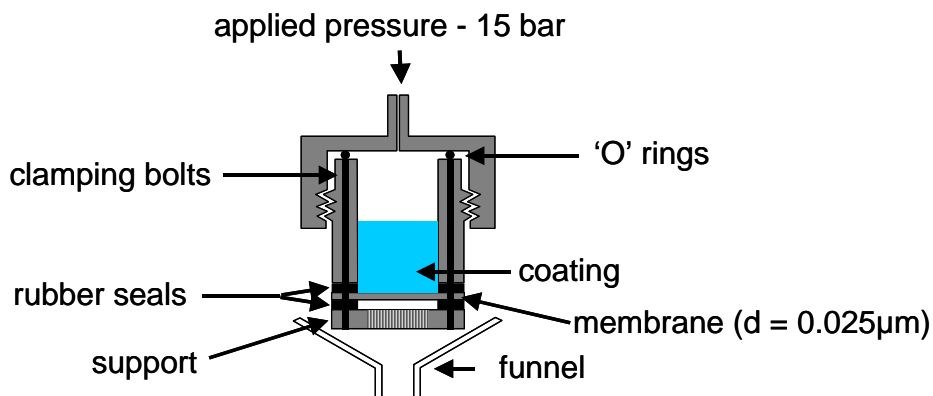


**Figure 3.** Wet tablet press.

**Coatings on Aluminium Foil**

In the case of coating colours containing PVOH and/or starch, the dewatering of tablets becomes extremely long, and so coatings were made on an impermeable foil substrate. The use of the substrate also provides similarity with real coatings due to the unconstrained thin layer shrinkage properties occurring in the presence of soluble binders, but by using foil any basepaper influences on coating holdout, binder migration etc. were excluded.

<u>**Mercury Porosimetry**</u>

A portion of each tablet of approximately 0.7 g (0.3 cm$^3$), or a strip (20 cm x 1.5 cm) of coated foil, was characterised by mercury porosimetry for both porosity and pore size distribution using a Micromeritics Autopore IV mercury porosimeter. The maximum applied pressure of mercury was 414 MPa, equivalent to a Laplace throat diameter of 4 nm.

Mercury porosimetry utilises the intrusion of a non-wetting liquid (mercury) under pressure to reveal a representative pore diameter via the Young-Laplace diameter-pressure relationship. In network structures, frequently large pores are accessed only by a narrower entrance channel or capillary. The volume associated with the larger pore, however, is recorded as volume associated with the finer entry geometry as the mercury is forced first through this smaller dimension at a given pressure associated with that dimension. This effect is known as "pore shielding". By taking the first derivative of the cumulative intrusion curves the pore size distributions based on equivalent Laplace diameter, inevitably including pore-shielding, are revealed. The data were corrected using Pore-Comp for mercury and penetrometer effects and also for sample compression [15].

**RESULTS**

<u>**Modified Calcium Carbonate (MCC) and coarse GCC (cGCC)**</u>

**Effect of Particulate Binder Addition**

The example of a discretely bimodal pore structure, controlling permeability via the interparticle pores and capillarity via the intraparticle pores, is provided by modified calcium carbonate [14]. Similar structures also exist in respect to precipitated calcium carbonate. These designed structures provide for high absorption volume and fast absorption rate, but depend on the availability of the pores to perform this action by absorbing the liquid vehicle of the ink. It was shown previously [16] that within a porous structure it is the smaller voids that supply the necessary driving force for absorption to take place. It was also shown that a structure also needs larger voids to act as local supply reservoirs of fluid if this driving force is to continue unhindered by lack of liquid volume. Furthermore, the interconnectivity of the larger voids define the permeability of the network, i.e. the structure also needs to be connected with a high permeability so that the fluid can flow through to the larger pores (reservoirs) and hence to the smaller pores to promote the faster absorption rate defined by the high capillarity of the discrete finer pores. The interpretation of the separability of the intrusion curves to classify these two parameters, of absorption driving force and liquid delivery limitation, is only possible if the driving force exists

in a network structure discrete from that of the bulk structure determining the permeability, [14]. Tablets were made both with and without latex (12 parts by weight of SA latex based on 100 parts of pigment) using a laboratory made high pore volume example of this type of pigment to illustrate the effects more clearly, Figure 2, and also from the cGCC.

SA latex is used as an example of a virtually inert, liquid-polymer non-interacting, particulate binder. It is not being used here as a recommendation but as an illustration of the beneficial physical role a particulate binder could have in contrast to the limiting effect of soluble binders. The concept is to provide such illustration to encourage the development of more suitable binder systems based on particulates for the inkjet market.

The mercury intrusion curves for the laboratory made MCC with and without latex are shown in Figure 4, and compared with the cGCC. The corresponding pore size distributions of these samples are shown in Figure 5.
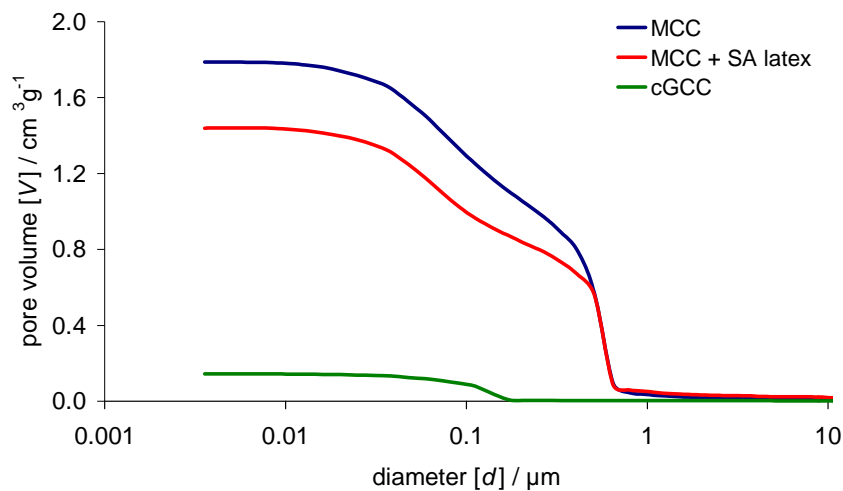


**Figure 4** Mercury intrusion curves of tablets of laboratory made MCC with and without the addition of SA latex (12 parts), compared with cGCC.
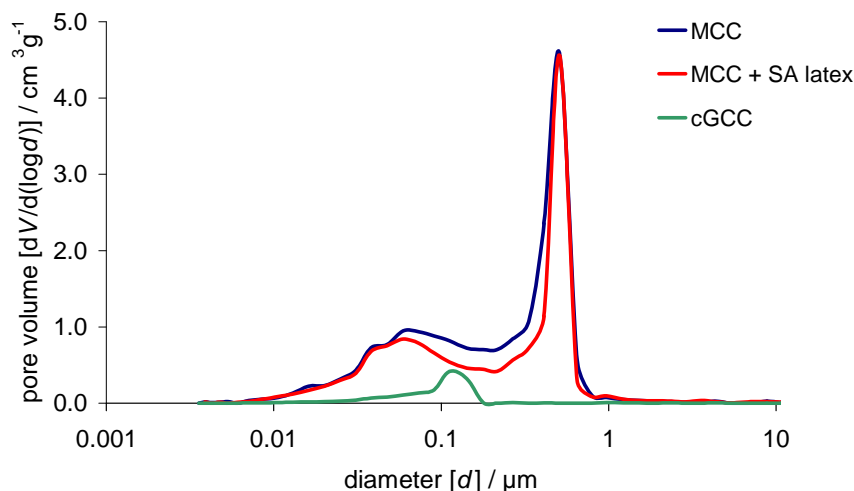


**Figure 5** Pore size distribution of tablets of laboratory made MCC with and without the addition of latex (12 parts), compared with cGCC.

The mercury intrusion curves for the laboratory made MCC samples show how much more pore volume can be achieved using this pigment compared with a standard coarse GCC (cGCC). The addition of latex reduces the total intruded volume but this volume is still much greater than that of the cGCC.

The pore size distribution curve for the standard cGCC shows that in comparison to the MCC there are very much fewer small pores and therefore this structure has a relatively low capillary driving force for absorption. The laboratory made MCC sample, in comparison, has a significantly greater number of fine pores together with a high permeability (larger pore diameter at the point of inflection of the intrusion curve) and therefore a high liquid delivery rate with the higher number of fine pores providing the driving force. These data show that the combination of fine pore size regions and the permeability of the whole are acting as separable parameters in discrete network structures [14].

The clearly defined bimodal distribution of MCC is maintained with the addition of the latex with a more pronounced separation between the two pore size distributions when the latex is present in the structures. The dip in the pore size distribution at 0.1 - 0.2 µm corresponds with the void filling action of the monosize latex. A similar analysis can be made for idealised light scattering, where, in such systems, the differentiation between the two size distributions would be even more pronounced with the separation occurring at 0.2 µm.

### Loss of Pore Volume as a Function Of Additive(s)

### Cationic Polymer Addition

Cationised surfaces are required to provide water fastness when using anionic dye-based inkjet inks. Two different inkjet pigments, nMCC and bMCC, were analysed with the addition of 7 parts per 100 parts by weight of pigment of PolyDadmac, a cationic polymer. Figure 6 shows the mercury intrusion curves for the different tablet samples made from the cationised slurries.
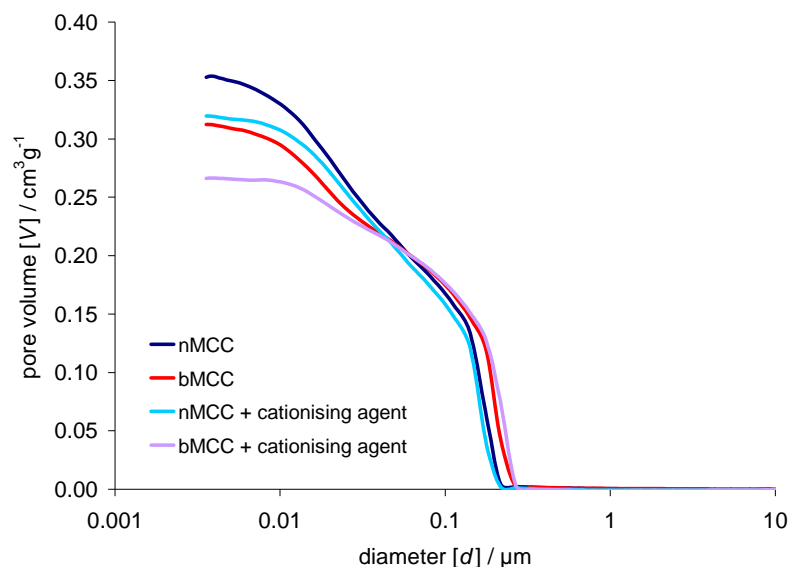


**Figure 6.** Mercury intrusion curves of the tablet samples.

The bMCC is seen to have less pore volume than the nMCC, as would be expected from the difference in breadth of the particle size distributions. Furthermore, and very importantly, the effect of the cationising agent is seen to lower the total intruded volume for both sample types, especially in the important fine pore region, which is needed for capillarity. The porosity values and the intruded volume into the samples are summarised in Table 1, in the case where 7 pph cationising polymer has been added.

| Sample | Total specific intruded volume / $cm^3g^{-1}$ | porosity / % |
|---|---|---|
| nMCC | 0.353 ± 0.004 | 47.5 ± 1 % |
| bMCC | 0.313 ± 0.003 | 44.7 ± 1 % |
| nMCC + cationising agent | 0.320 ± 0.003 | 44.5 ± 1 % |
| bMCC + cationising agent | 0.266 ± 0.003 | 40.0 ± 1 % |

**Table 1**. Total intruded volume into the samples, showing the reduction due to added cationic polymer.

By taking the first derivative of the cumulative intrusion curves the pore size distributions based on equivalent Laplace diameter, inevitably including pore-shielding, are revealed. This is shown in Figure 7.
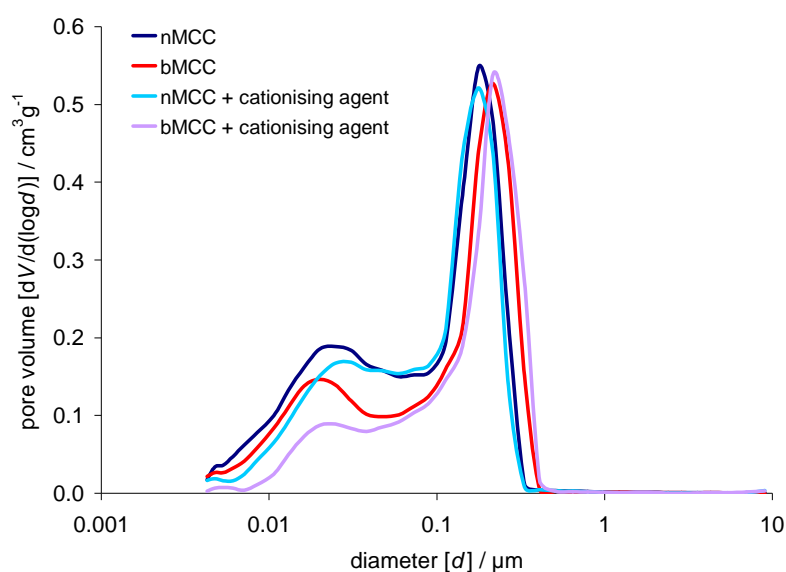


**Figure 7.** Pore size distributions of the tablet samples - effect of cationic polymer addition on pore size distribution

All samples have a large peak in the pore size distribution representing the interparticle pore volume as was shown in general for MCC [14]. This peak falls at 0.18 µm for the nMCC samples and at 0.22 µm for the bMCC samples. The smaller peak at finer diameters represents the intraparticle pore volume. These peaks fall at 0.02 µm for the original samples with more pore volume attributable to these pores for sample nMCC, as seen by the curve lying above that for bMCC. The nMCC also has more pore volume attributable to the pore diameter range between the two peaks, which is related to the connectivity of the packed structure in the case of the discretely bimodal pore size distributions.

Once cationically "flipped" by the addition of the polymer, both samples lose some significant proportion of the high capillarity pore volume. This loss is slightly greater for bMCC. The use of PolyDadamac cationising polymer, therefore, additionally reduces this fine pore-related pore volume. Polymer addition, therefore, to cationise anionic pigments will deteriorate performance in respect to absorption rate and absorption volume. A move to pigmented inks (rather than anionic dye-based inks) should be welcomed, as it would allow more cost-effective coating pigments to be used by retaining more of the original pore volume delivered from the pigment manufacture.

**Effect of PVOH and Starch Addition on Loss of Pore Volume**

PVOH absorbs up to ~30 % of its own weight of water, but if present in pores acts also to limit the absorption rate by reducing it to the interpolymer matrix diffusivity, and reduces the volume according to the loss of pore space by the presence of the swelling PVOH. The role of PVOH in MCC coatings has been studied in more

detail by Lamminmäki *et al.* [11] who studied the action of PVOH as a swelling binder in the coating layer structure, combining these findings with the role of porosity and pore diameters in the inkjet setting process. This work showed how the PVOH coatings operate in defining the print quality formation of dye-based inks in high speed inkjet printing.

In this current study, we combine PVOH and starch as a mixed binder system. The cationic sample was pre-cationised using 5 parts PolyDadmac, as described in the previous section, and is labelled bMCCc. Two coated foil samples were prepared. The coatings were formulated from the inkjet pigment types bMCC and bMCCc plus 2.5 parts PVOH and 2.5 parts starch. To illustrate also the similarity between tablets and coated substrates, Figure 8 shows the mercury intrusion curves for the coated foil samples exemplifying, again, the impact first of all of cationising, but now in the presence of PVOH and starch and as a coating on foil. As can be seen, the effects are similarly displayed as a loss by cationising and an overall greater loss of pore volume induced by the presence of PVOH and starch binder – compare Tables 1 and 2. The comparison is not to be considered in absolute volume terms, due to the different formulations, but rather to illustrate the principle.
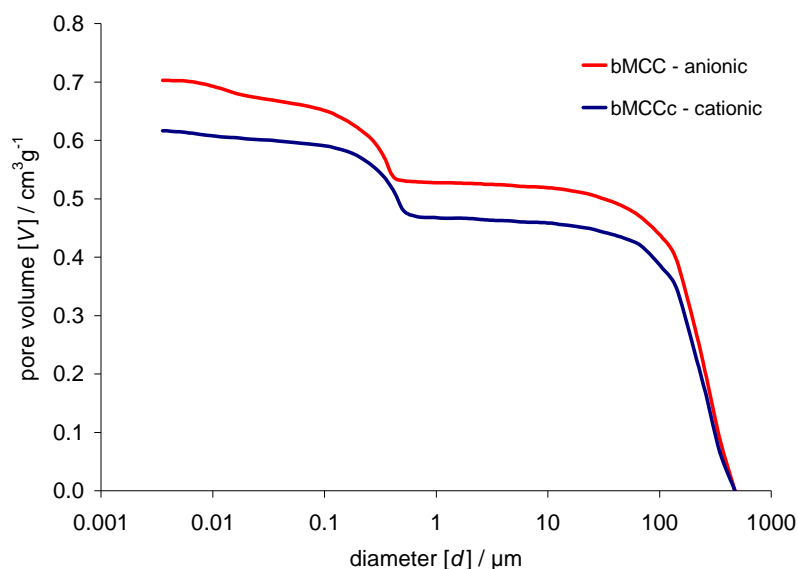


**Figure 8.** Mercury intrusion curves of the coated foil samples, containing both PVOH and starch binders, showing similar pore volume loss due to cationising.

The differences between the coated foil samples at the larger diameters are due to the sample preparation technique, i.e. as the mercury intrudes between the scrolls of the foil, and where the coating may have poor adhesion to the foil. This region of the curve does not contribute any relevant pore structure information in respect to the coating structure and for this reason the data have been truncated at 10 µm. This means that the total porosity cannot be evaluated, rather the relative porosity in those pores with an equivalent Laplace diameter < 10 µm is derivable by direct comparison of the truncated curves. To comment further on the total porosity would require detailed normalisation using oil absorption techniques [17]. The resulting curves are shown in Figure 9.
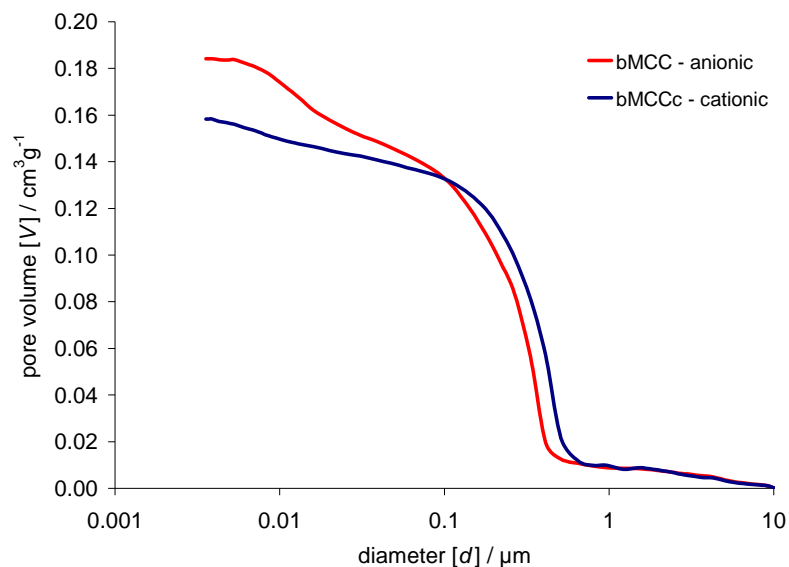
**Figure 9.** Mercury intrusion curves of the coated foil samples, containing both PVOH and starch binders, truncated at 10 µm, showing the impact of cationising.

The total intruded volumes into the samples over the diameter range 0.004 – 10 µm are summarised in Table 2.

| Sample | Total specific intruded specific volume / $cm^3g^{-1}$ |
|---|---|
| bMCC + PVOH + starch | 0.183 |
| bMCCc + PVOH + starch | 0.157 |

**Table 2.** Total intruded specific volume into the coated foil samples, showing the reduction even in thin films when adding cationic polymer to the mix, in this case also in the presence of PVOH and starch.

By taking the first derivative of the cumulative intrusion curve the pore size distributions based on equivalent Laplace diameter, inevitably including pore-shielding, are revealed. This is shown in Figure 10.
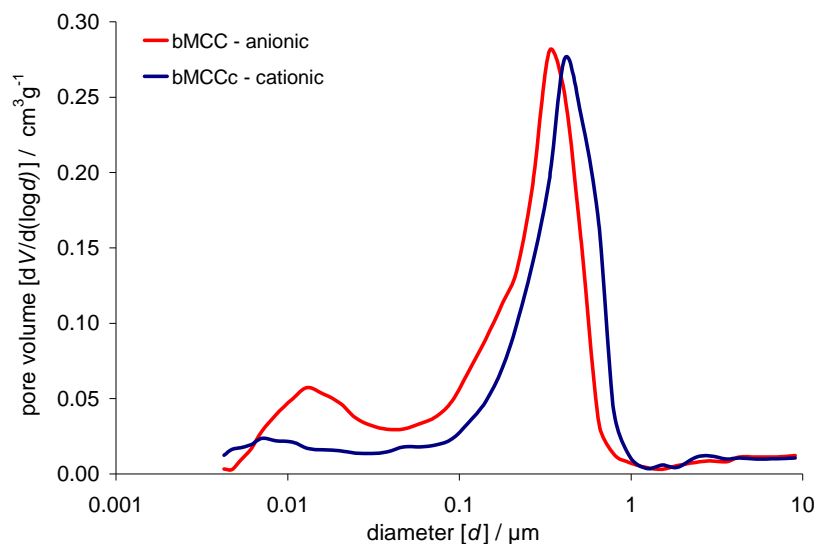
**Figure 10**. Pore size distribution of the coated foil samples, containing both PVOH and starch binders, showing the effect of cationising. The loss of pore volume by the use of PVOH and starch can be seen by comparing with Figure 7.

Both samples show a main peak at larger pore diameters representing the inter particle pore structure. These peaks fall at 0.33 µm and 0.41 µm for anionic and cationic samples, respectively. Both samples show a smaller peak at finer pore diameters representing the intra particle pore structure. The anionic sample has this peak at 0.013 µm, whereas the cationic sample has a similar but much smaller fine pore volume contribution over the diameter range 0.004 – 0.100 µm. There is a slight peak at 0.007 µm.

We can see from these data, that the cationising has two effects when considered in binder containing thin film coatings. First of all the dispersing quality is not as good as the anionic. This can be seen from the slightly larger pore size of the interparticle structure, indicating some agglomerates/flocculation. Additionally, the nanopores needed for high capillarity are reduced in number, and thus volume. This is due to the cationic polymer used to cationise partly filling the pores.

**Latex Addition to Formulations with PVOH and Starch Additives**

Three coated foil samples were prepared. The coatings were formulated from the pigment bMCC plus 2.5 parts PVOH, 2.5 parts starch and 5 parts PolyDadmac. The addition of polyvinyl acetate latex (PVAc) was made at two levels, 5 and 10 parts, and compared to a sample without latex. The truncated mercury intrusion curves are shown in Figure 11.
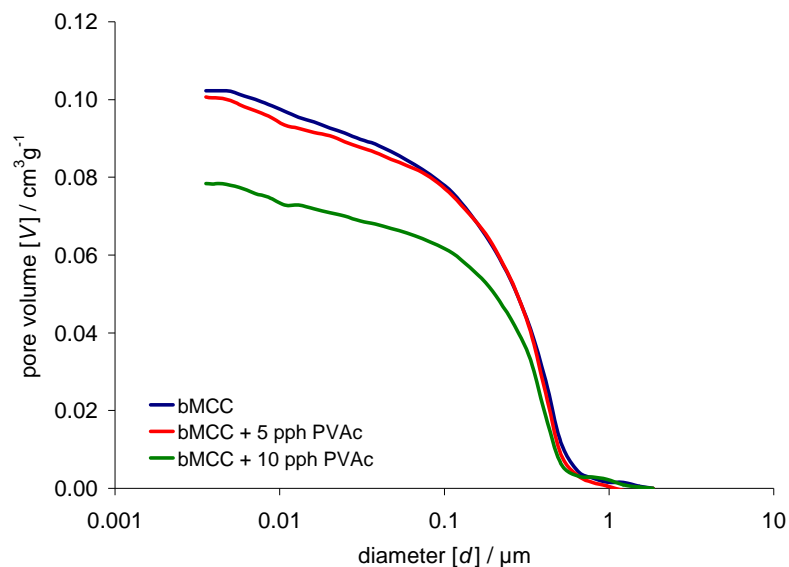
**Figure 11.** Mercury intrusion curves of the coated foil samples truncated at 2 µm, showing the effect of adding particulate PVAc latex to a formulation containing PVOH and starch.

Interestingly, the addition of 5 pph PVAc as a particulate binder has little to no effect on pore volume, whereas 10 pph addition then induces a much lower total intruded volume. The total intruded specific volumes into the samples over the diameter range 0.004 – 2 µm are summarised in Table 3.

| Sample | Total specific intruded volume / $cm^3g^{-1}$ |
|---|---|
| 0 pph PVAc | 0.102 |
| 5 pph PVAc | 0.101 |
| 10 pph PVAc | 0.078 |

**Table 3**. Total intruded volume into the coated foil samples showing the effect of progressive PVAc latex addition into a formulation containing PVOH and starch.

By taking the first derivative of the cumulative intrusion curve the pore size distributions based on equivalent Laplace diameter, inevitably including pore-shielding, are revealed. This is shown in Figure 12.
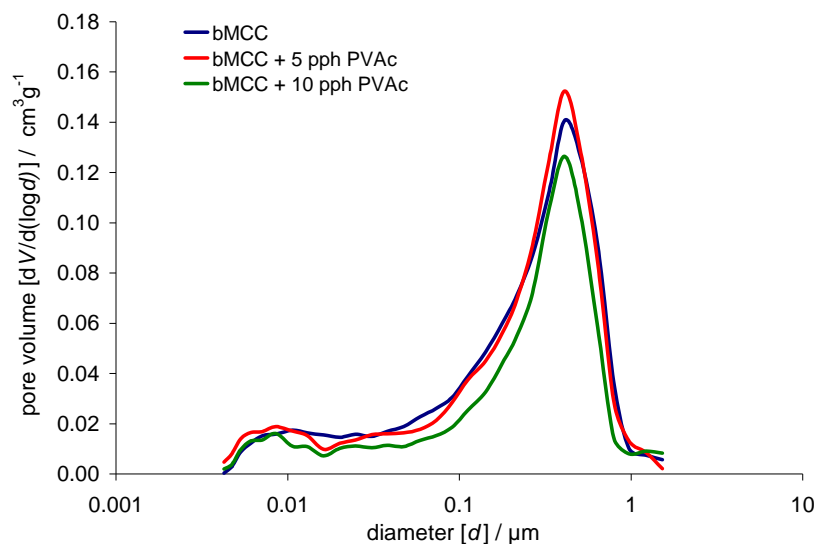
**Figure 12**. Pore size distribution of the coated foil samples, illustrating the loss of mid-range and larger pores when particulate latex is added at higher dose in the presence of PVOH and starch.

All samples in Figure 12 show a main peak in the distribution at 0.41 µm representing the inter particle pore structure. The sample with 5 pph particulate PVAc binder has the highest pore volume attributable to these pores. Thus, we can conclude that the permeability is maintained or even increased a little [14]. This effect of adding a level of latex below ~8 parts has been demonstrated previously by Ridgway *et al*. [18], and is indicative of the disruptive colloidal interference effect when adding latex to a carbonate-based formulation – an effect deriving from depletion flocculation. The next largest peak is shown by the sample containing only the soluble binders without latex addition, and the smallest by the structure with 10 pph particulate PVAc. The sample with 10 pph PVAc has a narrower peak, representing the progressive closure of the interconnecting pores.

In respect to the mid-range (connectivity) pores, the sample without additional latex has the highest pore volume attributable to the pores between pore diameters 0.02 – 0.09 µm, whereas adding latex, especially at the higher dose level, reduces connectivity and so can be expected to reduce permeability.

All samples show a broad peak between pore diameters 0.005 – 0.050 µm representing fine pore volume contributions. It is shown that starch is particularly disadvantageous as it not only prevents access, when film formed, to the crucially absorbing pores, but is itself effectively non-absorbing. It is also shown that latex particulate binder can be used to allow continued access to the nanopore region within the porous pigment particles, and by choosing the right glass transition temperature, $T_g$, and chemistry of the synthetic polymer, the permeability can also be maintained to a large extent, provided the added level is not too high, [14, 18]. Therefore, latex, at least as part of the binder mix has benefits over all-soluble binder formulations as it does not block pores. The disadvantage today, however, is the extremely limited choice of latex binders available that are cationically stable.

**<u>Pore Structure Overview</u>**

Table 4 summarises the pigments and additives used in the sample preparation, and links the combinations with the porosimetry data: displayed are the specific pore volume, and the inter and intra particle pore diameters, to give an overview of the pore structure changes.

| | total specific intruded volume $cm^3g^{-1}$ | interparticle pore diameter peak µm | interparticle specific pore volume $cm^3g^{-1}$ | intraparticle pore diameter peak µm | intraparticle specific pore volume $cm^3g^{-1}$ |
|---|---|---|---|---|---|
| **Figure 4 & 5** | | | | | |
| (tablets)  cGCC | 0.144 | 0.110 | 0.140 | - | - |
| MCC | 1.788 | 0.500 | 1.028 | 0.060 | 0.760 |
| MCC + SA latex | 1.440 | 0.500 | 0.808 | 0.060 | 0.632 |
| **Figure 6 & 7** | | | | | |
| (tablets)  nMCC | 0.353 | 0.180 | 0.201 | 0.025 | 0.152 |
| bMCC | 0.313 | 0.220 | 0.221 | 0.020 | 0.092 |
| nMCC + cationising agent | 0.320 | 0.180 | 0.194 | 0.025 | 0.126 |
| bMCC + cationising agent | 0.266 | 0.220 | 0.219 | 0.020 | 0.047 |
| **Figure 8, 9 & 10** | | | | | |
| bMCC | 0.183 | 0.330 | 0.146 | 0.013 | 0.037 |
| (foil)  bMCCc | 0.157 | 0.410 | 0.139 | 0.007 | 0.018 |
| **Figure 11 & 12** | | | | | |
| (foil)  bMCC | 0.102 | 0.410 | 0.094 | 0.007 | 0.008 |
| bMCC + 5 pph PVAc | 0.101 | 0.410 | 0.091 | 0.007 | 0.010 |
| bMCC + 10 pph PVAc | 0.078 | 0.410 | 0.072 | 0.007 | 0.006 |

**Table 4**. Overview of the pore structure parameters

## Implications For Printability

Changes in the coating formulations will lead to changes in the printing quality. One of the tests used to characterise print quality is the level of colour-to-colour bleed, an example of which is shown below in Figure 13.
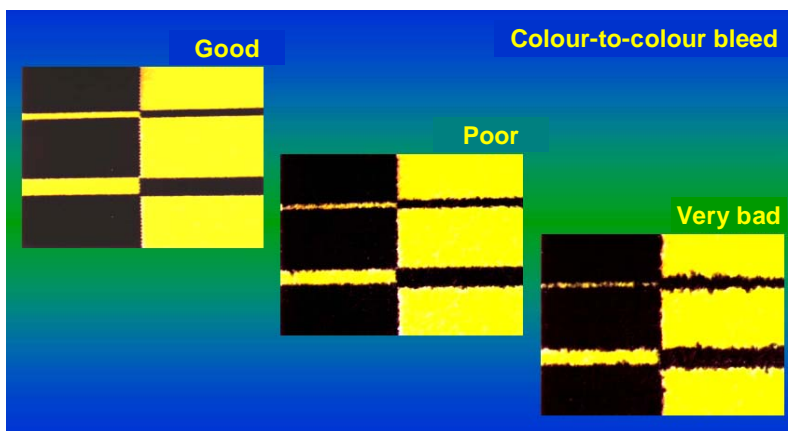


**Figure 13**. Colour-to-colour bleeding example

The changes in the formulations that we have discussed in this study may not lead to effects as large as that illustrated as "very bad" in Figure 13, but reducing the additive amounts by 1-2 parts can already improve the print quality toward that of "good". More notably, if polymer additives for cationising could be eliminated, which is expected as inkjet inks move toward pigmented formulations in the emerging generation of presses, and soluble binders further reduced, being eventually replaced by particulate binder, one would anticipate additional significant cost savings as pore volume could be better retained. As a result, the expensive porous coating pigment component could in turn be reduced whilst maintaining constant pore volume. It is thus seen as a significant step forward to be able to reduce the amount of soluble polymers required in the coating formulation.

## CONCLUSIONS

All polymer additives, especially water soluble ones, in some way reduce the pore volume of speciality calcium carbonate inkjet pigment structures, with particular emphasis on the loss of fine high capillarity pores; especially low molecular weight, water soluble ones.

Because of the requirements of anionic dye-based inks for water fastness, coatings need to be cationised. This is typically achieved by "flipping" anionically dispersed formulations using a cationic polymer, such as PolyDadmac. Even if cationically dispersed pigments are considered, most other coating colour components, if stabilised particulates, also require cationising to become compatible in the dispersion. Inevitably either adsorbed or free cationic polymer will be on the high surface area walls of the fine pores or will migrate to the fine pore regions during the drying process, respectively. This effect impacts on the absorption efficiency due to lost pore volume and lost capillarity.

Soluble binders can be considered either water absorbing, such as PVOH, or relatively insoluble (starch). In both cases, they too act to reduce available pore volume. Even in the case of absorbing/swelling binders, the efficiency of absorption is reduced to that of the interpolymer diffusion in the binder matrix, and the volume is reduced despite its absorbency.

The use of particulate binder, such as PVAc latex, on the other hand preserves to a large extent the total pore volume, and even permeability of the structure can be preserved when used at low to moderate dose levels. Higher dose rates lead to a loss of permeability, but the capillarity is nonetheless retained. A disadvantage of currently available particulate binders nonetheless remains, insofar that, if cationising of the latex or the whole formulation is still required, the stability of the dispersion is compromised, and, once again, the capillarity is reduced.

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