Effects of Binders and Additives on Inkjet Coating Pigment Pore Structures

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Introduction

Aim:

to consider the pore structure change in inkjet coatings when using certain binder types and polymer additives:

- Starch, PVOH, latex particulate, cationic polymer…………..
  - each/all can alter the pore volume and pore structure
    - **Positive?**
    - **Negative?**

Experimental

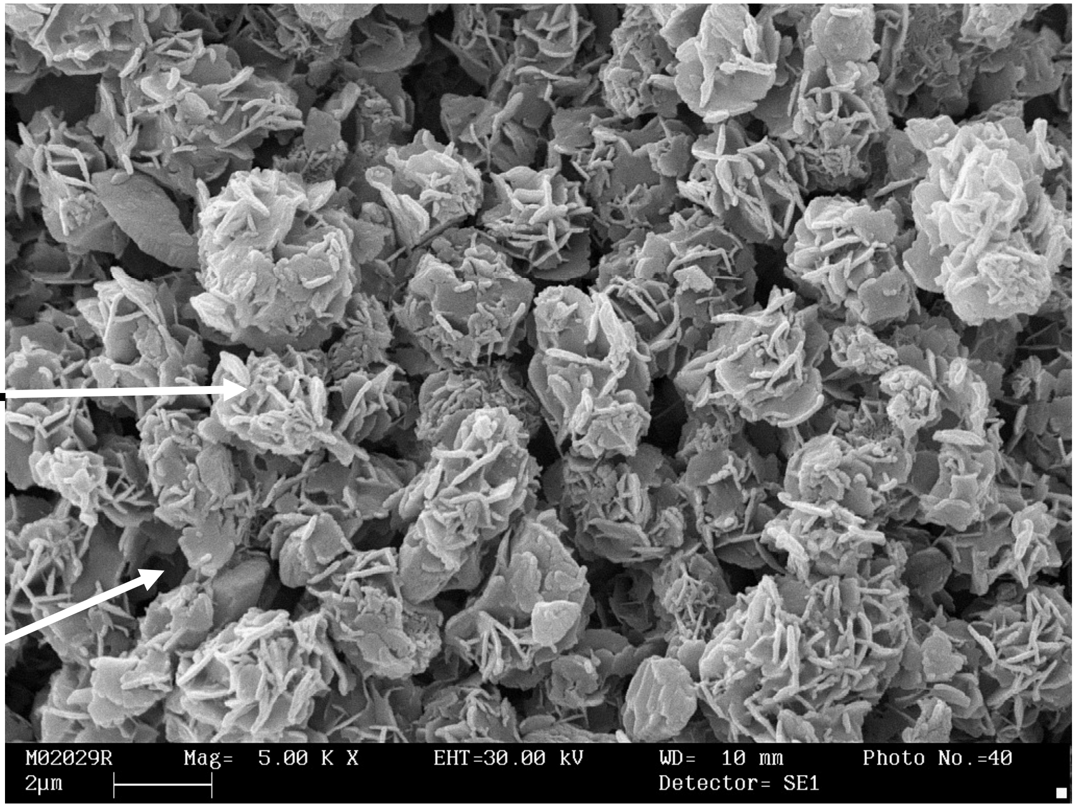
- Effect of particulate binder addition
- Loss of pore volume as function of additives
  - Cationic polymer additive
  - PVOH and starch
  - Latex (plus PVOH and starch)
- Implications for printability

Material used:
Modified Calcium Carbonate – an example

Discretely bimodal pore size distribution

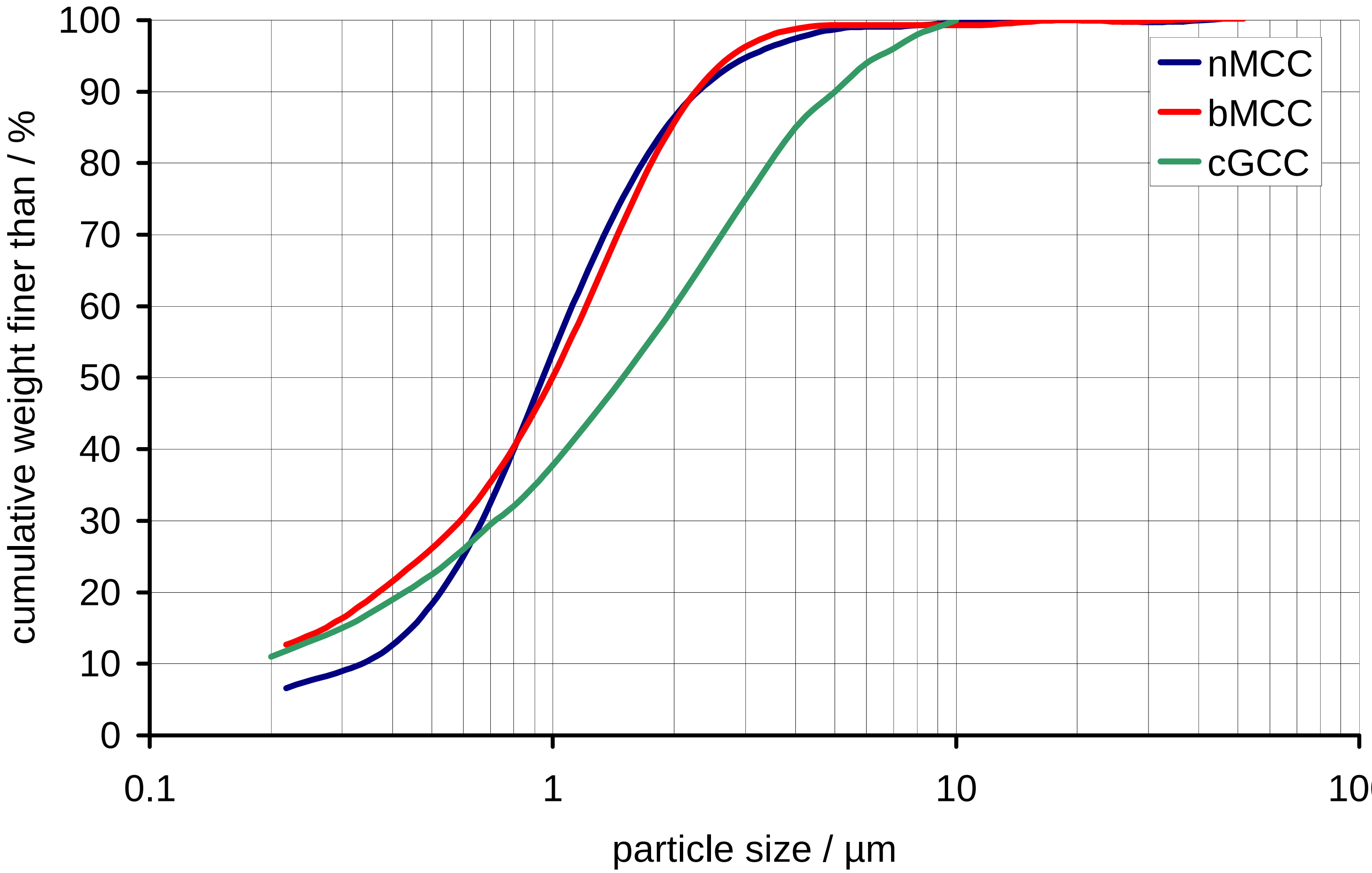
Intraparticle pores

Interparticle pores

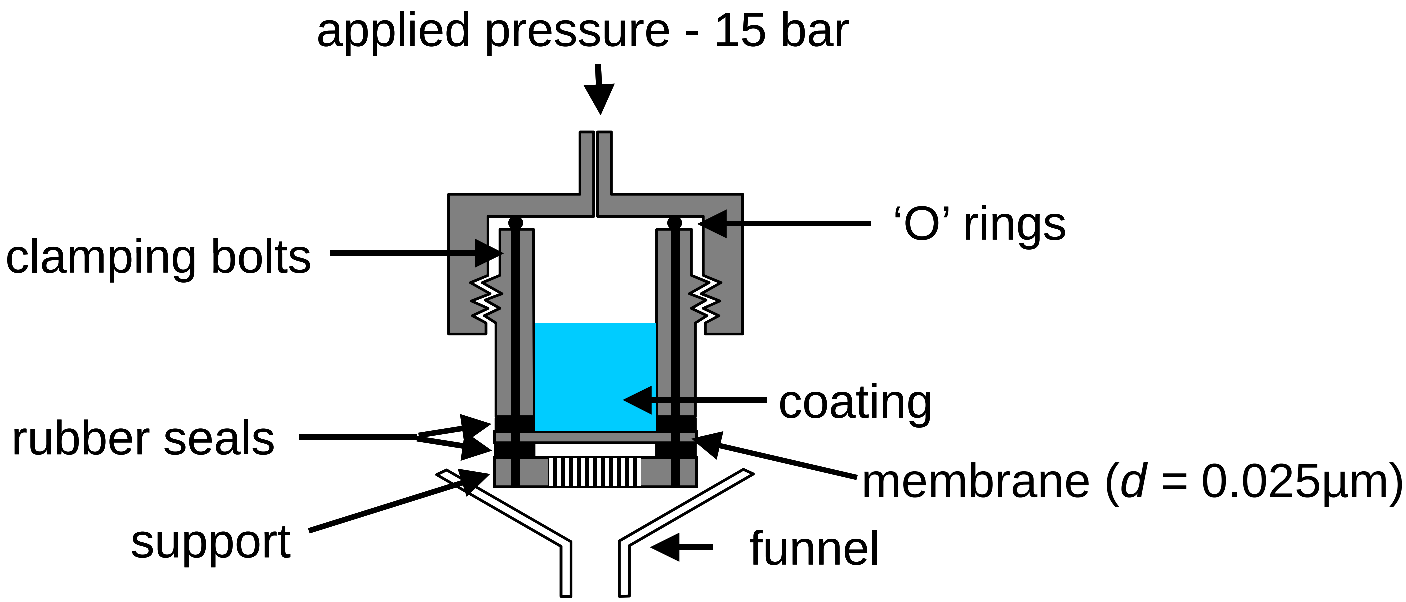


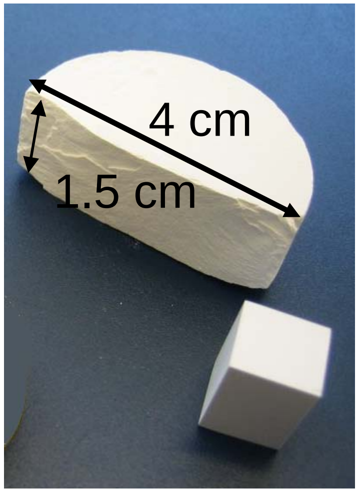
Particle size distribution:

Narrow (nMCC) and broad (bMCC) compared to standard coarse ground calcium carbonate (cGCC)



Forming the porous structures:
Tablet Press





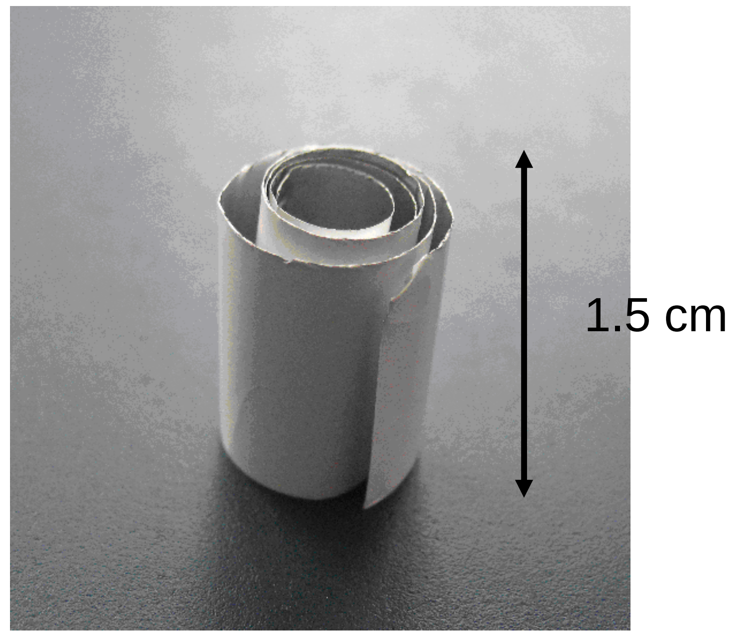
Tablets dried in oven 24 hours at 60 ^{o}C

Coated Layer:
Foil substrate

bench coated foil

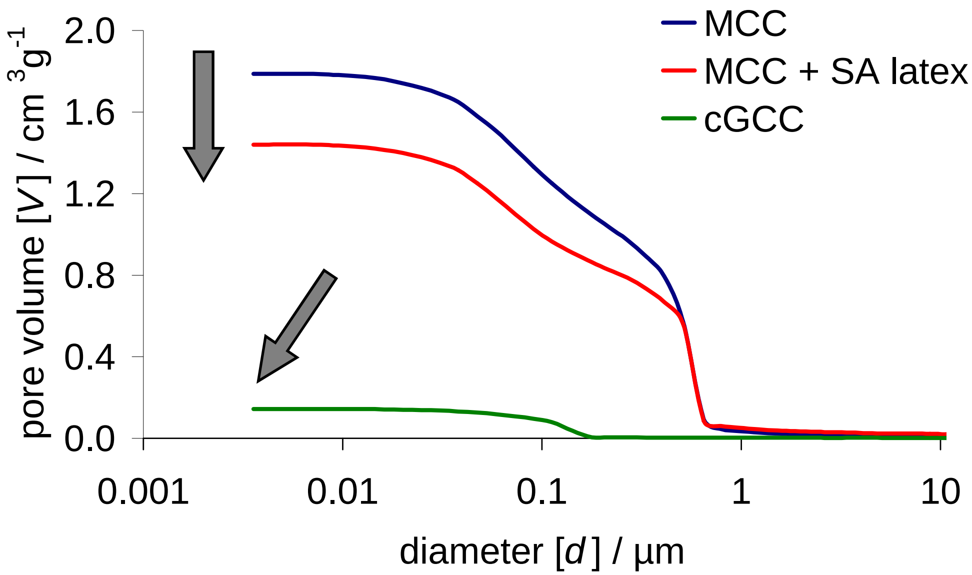
scrolled sample for porosimetry

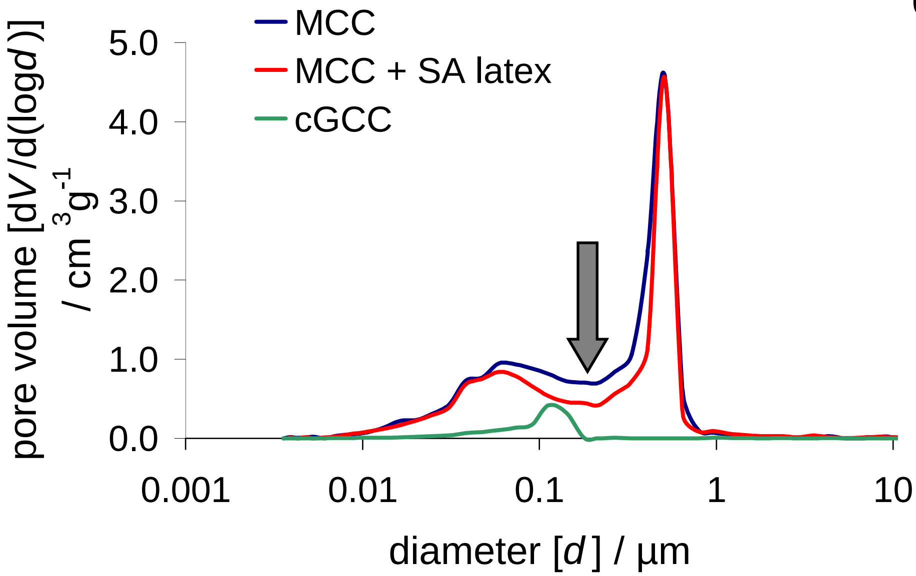
(30 cm x 42 cm)



Effect of Particulate Binder Addition:
Liquid “inert” SA binder containing coating in tablet form

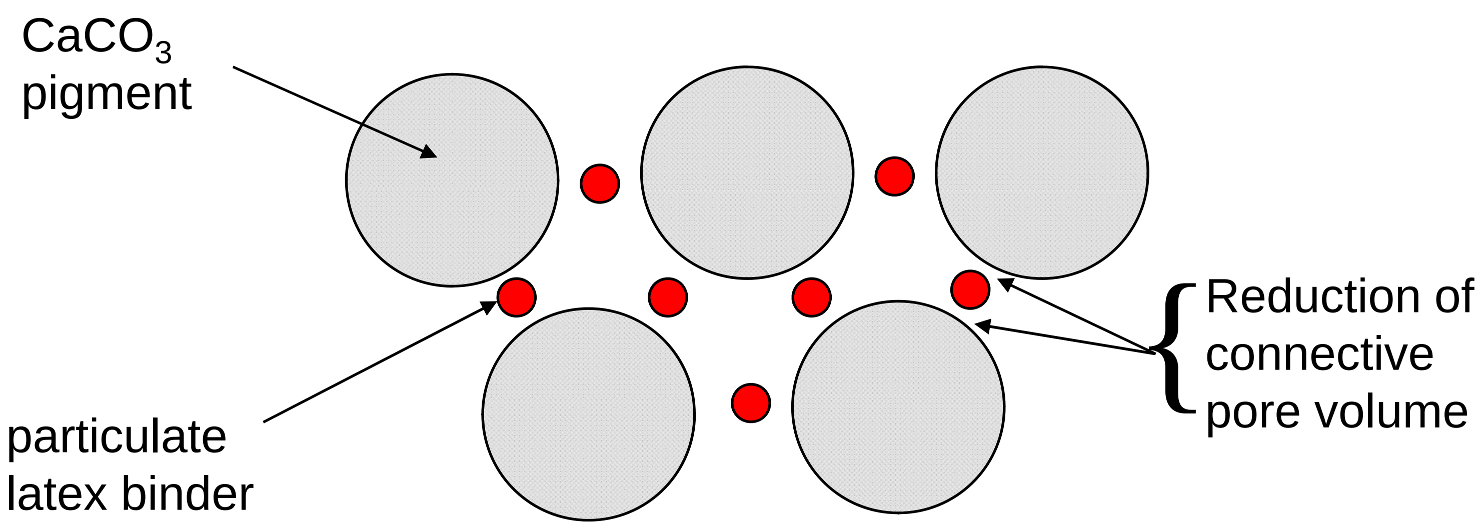
- Volume reduction on addition of SA latex
- cGCC has much lower total specific pore volume





- Discrete bi-modal pore size distribution of MCC
- Reduction of mid-size pore diameter volume contribution due to **latex filling connecting pores**

Latex sites itself interstitially*

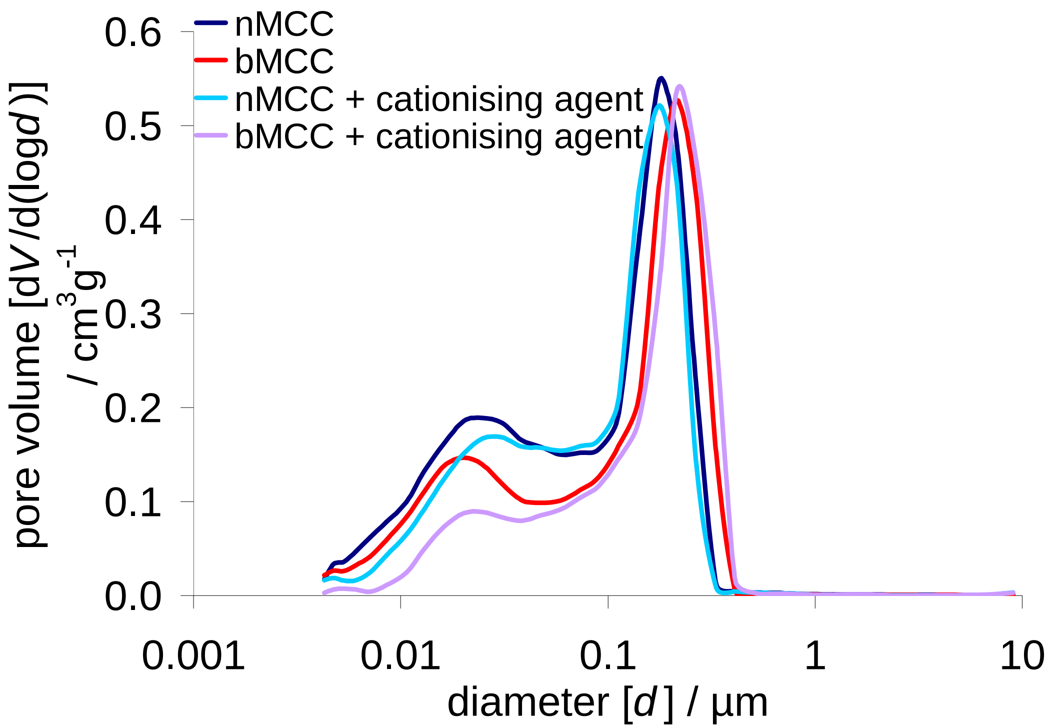


* Ridgway, C.J. and Gane, P.A.C., Journal of Pulp and Paper Science, 33(2), pp. 71-78 (2007)

Cationic Polymer Addition:
Tablet form

Cationisation to provide water fastness when using anionic dye based inkjet inks:

7 pph PolyDadmac



- bMCC has less pore volume than nMCC
  - as expected due to the difference in breadth of particle size distribution
- **Cationising reduces fine pore volume**
  - **reduced capillarity**

Cationic Polymer Addition (tablet form)

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 %

nMCC **volume loss – 8.6 %**
bMCC **volume loss – 16.1 %**

Polymer addition to cationise anionic pigments will

- deteriorate performance in respect to
  - absorption rate
  - absorption volume

Implication:

A move to pigmented inks (rather than anionic dye-based inks)

- 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 (foil preparation)

- PVOH absorbs up to ~ 30 % of its own weight of water

  - creates loss of pore space by the presence of the swelling PVOH

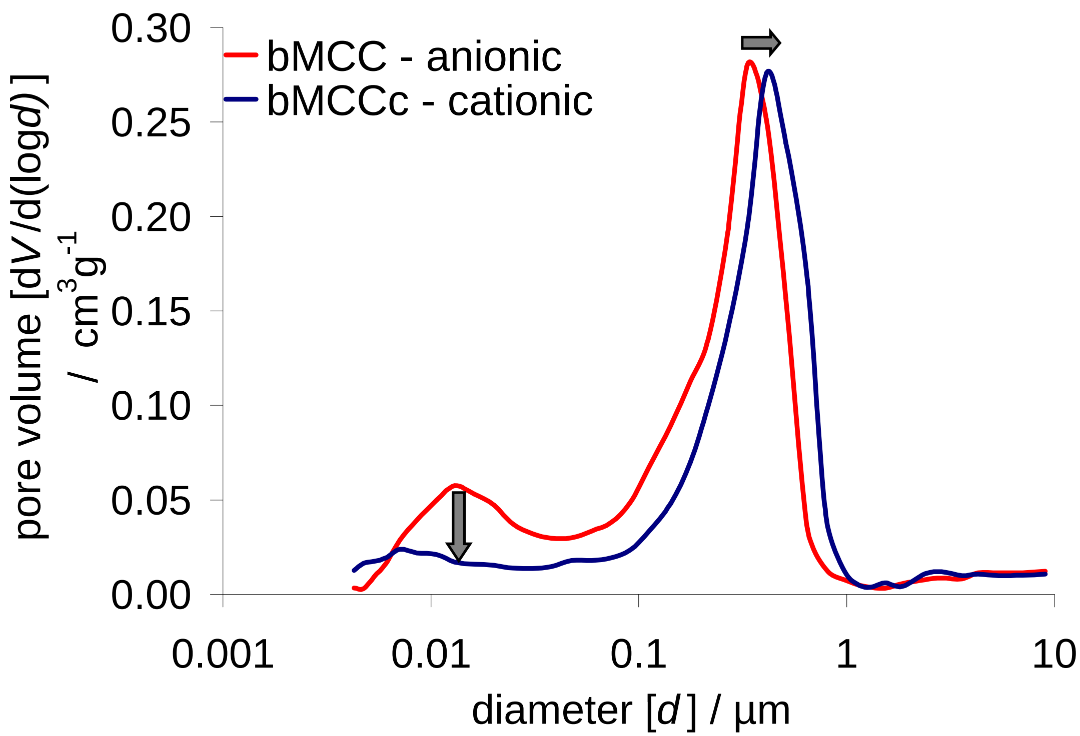
  - limits the absorption rate by reducing it to the interpolymer matrix diffusivity*

  - overall reduced pore volume: 0.18 cm^3g^{-1} compared to 0.31 cm^3g^{-1}

* Lamminmäki, T., Kettle, J.P., Puukko, P., Gane, P.A.C. and Ridgway, C.J., Journal of Pulp and Paper Science, 35(3-4), pp. 137-147 (2009).

Effect of cationising in the presence of PVOH and Starch Addition on Loss of Pore Volume (coating on foil)

100 parts bMCC
5 parts PolyDadmac
plus 2.5 parts PVOH
2.5 parts starch



- Overall **reduced pore volume** on cationising in the presence of PVOH and starch: total pore volume 0.18 to 0.16 cm^3g^{-1}
  intra pore volume 0.04 to 0.02 cm^3g^{-1}

Effect of Cationising on Loss of Pore Volume in presence of PVOH and Starch

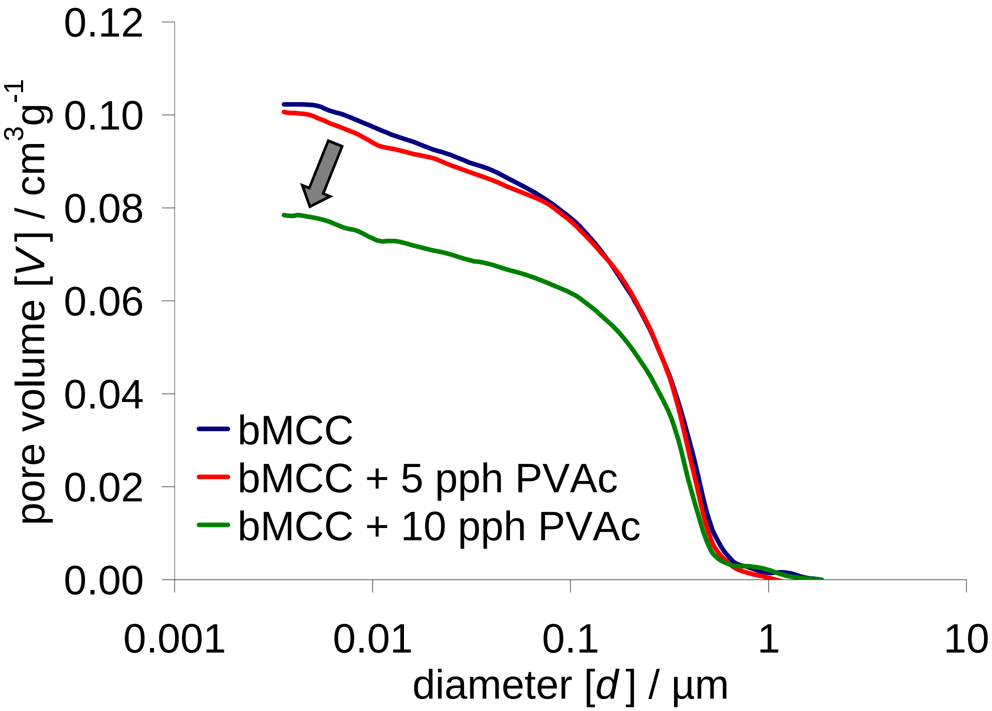
Sample	Total specific intruded specific volume / cm^3g^{-1}
bMCC + PVOH + starch	0.183 ± 0.002
bMCCc + PVOH + starch	0.157 ± 0.002

bMCCc **volume loss – 11.1 %**

- Cationising has two effects when considered in soluble binder containing thin film coatings
  - the dispersing quality is not as good as that of an optimised anionic dispersion
    - the slightly larger pore size of the interparticle structure indicates some **agglomeration/flocculation**
  - the nanopores needed for high **capillarity** are **reduced** in volume
    - the cationic polymer used to cationise the coating is also partly filling the pores

Latex Addition to Formulations with PVOH and Starch Additives: effect on pore volume

100 parts bMCC
5 parts PolyDadmac
2.5 parts PVOH
2.5 parts starch
plus 5 or 10 parts polyvinyl acetate latex (PVAc)



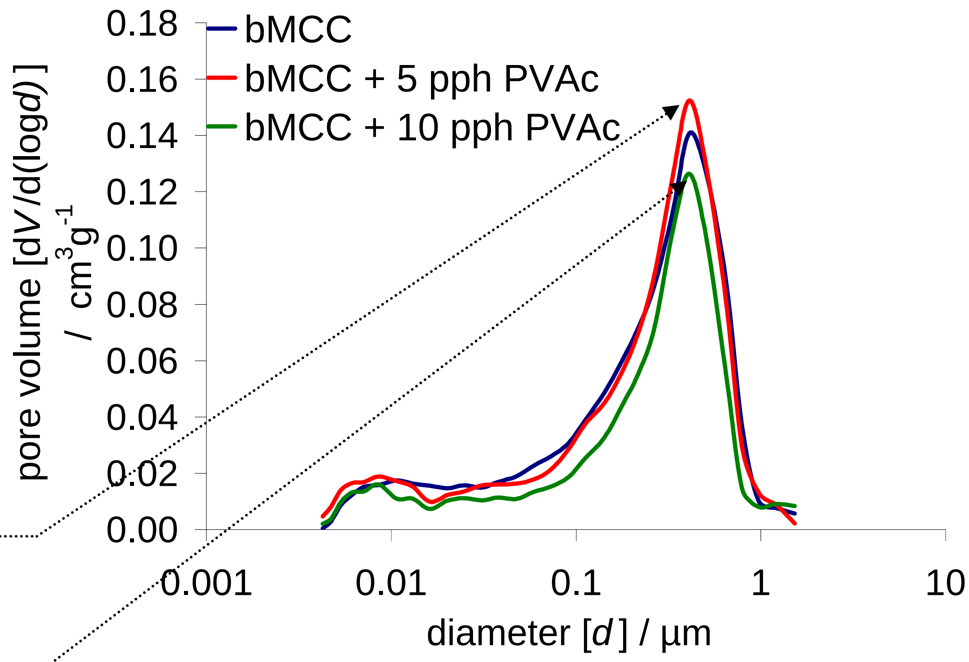
PVAc Addition to Formulations with PVOH and Starch Additives: effect on pore volume

Sample	Total specific intruded volume / cm^3g^{-1}
0 pph PVAc	0.102 ± 0.001
5 pph PVAc	0.101± 0.001
10 pph PVAc	0.078 ± 0.001

- **5 parts** PVAc particulate binder makes **little to no difference in pore volume**
- **10 parts** results in **reduced total pore volume**

Latex Addition to Formulations with PVOH and Starch Additives: effect on pore structure

100 parts bMCC
5 parts PolyDadmac
2.5 parts PVOH
2.5 parts starch
plus 5 or 10 parts
polyvinyl acetate latex (PVAc)



- 5 parts PVAc shows latex depletion flocculation
  - higher peak
- 10 parts shows progressive closure of interconnecting pores
  - lower and narrower peak
- all show fine pores

- **Soluble non-absorbent binder, eg. starch**
  - can be **disadvantageous due to loss of effective pores**
- **Particulate binder allows continued access to the nanopore region**
  - **permeability is maintained**
  - **limited or no choice of cationically stable latex**

Comparison of soluble versus particulate binders

- **Soluble non-absorbent binder**
  - **blocks access**
  - **fills pores**

- **Soluble absorbing binder**
  - **reduces pore volume**
  - **absorbs liquid**
  - **diffusion rate limited**

Particulate binder

  - **allows continued access to the nanopore region**
  - **permeability is maintained**

- **advantageous at low levels**
- But:
  - limited or no choice of cationically stable latex

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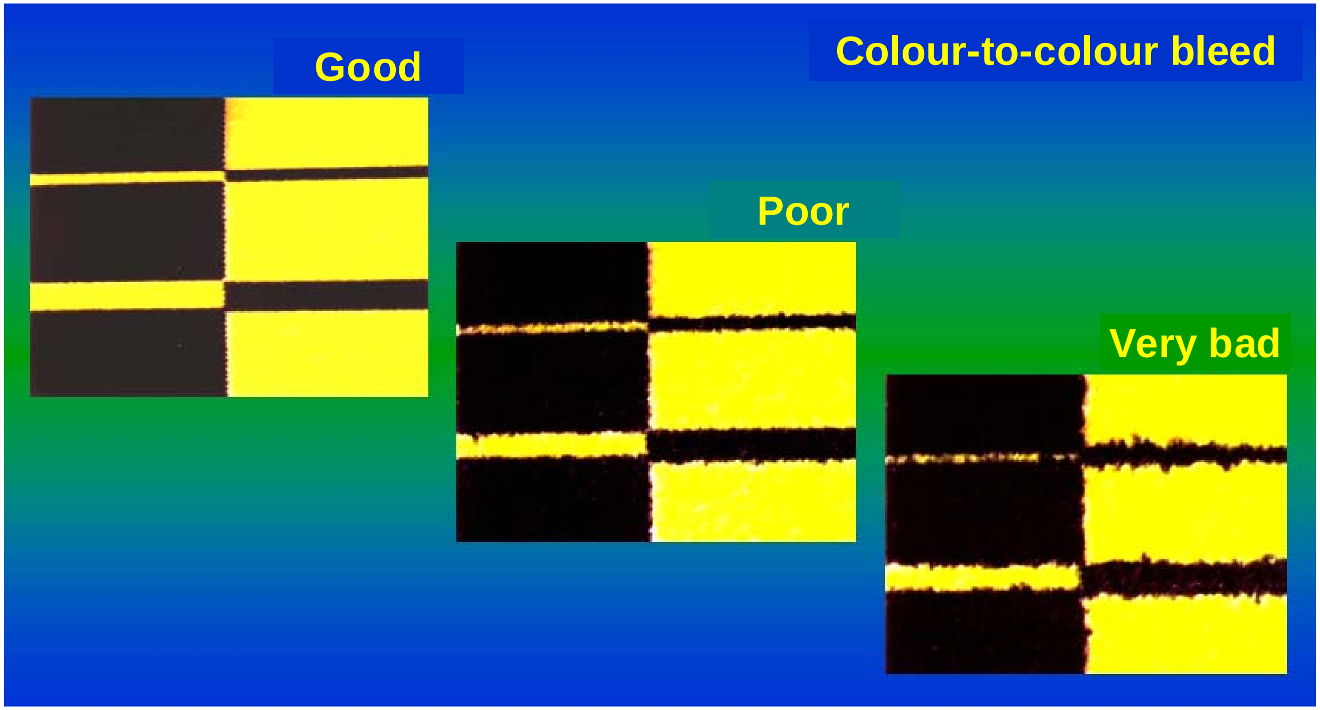
Implications for Printability



Print quality could be improved by:

- reducing additives amounts by 1-2 parts
- eliminating the need for polymer additives for cationising by moving toward pigmented ink formulations
- reducing use of soluble binders by replacing with particulate binders

Conclusions

- All polymer additives reduce the pore volume of speciality calcium carbonate inkjet pigment structures, particularly the fine high capillarity pores

- Coating pigments need to be cationised - requirement for anionic dye water fastness.
  - This affects the fine pore region and therefore the capillarity and the absorption efficiency

- Soluble binders reduce available pore volume
  - Absorbing 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
  - Non-absorbing binders – volume is reduced significantly

- The use of particulate binder when used at low to moderate levels preserves the total pore volume and permeability of the structure
  - Higher levels of particulate binder lead to a loss of permeability but the capillarity is retained.
  - A disadvantage of currently available particulate binders is 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.

Acknowledgements

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